

AN INVESTIGATION INTO THE REDUCTION KINETICS OF NANOPARTICULATE MANGANESE OXIDES VIA DISSOLVED ORGANIC CARBON SOURCES



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Introduction

- The sequestration of carbon in soils is among the most important processes in the carbon cycle with respect to the influence of global climate change.
- Manganese oxides (e.g., MnO_2) is one of the most effective naturally occurring oxidizing agents of carbon compounds found in terrestrial and aquatic systems.
- The kinetics of carbon oxidation via manganese oxides is a relevant reaction for soil and marine sediments.
- Analyzing reactions such as carbon reduction by manganese species will allow for informed decision making on how to counteract the harmful impacts of a changing climate on carbon.
- Measuring the redox reaction rate between MnO_2 and dissolved organic matter (DOM) will improve our ability to model global carbon cycling.

Objectives

- Measure the reduction rate of MnO_2 via oxalic acid as a benchmark to DOM.
- Determine if the reduction capacity of DOM is greater than that of oxalic acid.
- Modify experimental conditions with respect to carbon and manganese concentration and pH to measure changes in the rate constant

Materials and Methods

- Ultraviolet-visible spectrophotometer measured absorbance versus time to allow for a derived concentration and a building of kinetics data to determine best fit and rate constants. Instrument: Olis computerized HP8452 UV-VIS
- Scanning electronic microscope (SEM) visualized the lattice topography and environment of the stock MnO_2 solution. Instrument: Hitachi S-4300SE/N (FESEM) (CASM)
- Transmission electron microscope (TEM) visualized the lattice morphology of the stock MnO_2 . Instrument: Hitachi 1200EX
- Carbon/Nitrogen Analyzer used for extraction and quantification of leaf litter DOC. Instrument: Shimadzu Total Carbon/Nitrogen Analyzer



Figure 9: Leaf litter collected at Lubbock Mae Simmons park for DOC extraction



Figure 10: DOC collected from leaf litter materials; post 48 hour shaking of raw greenery

Results

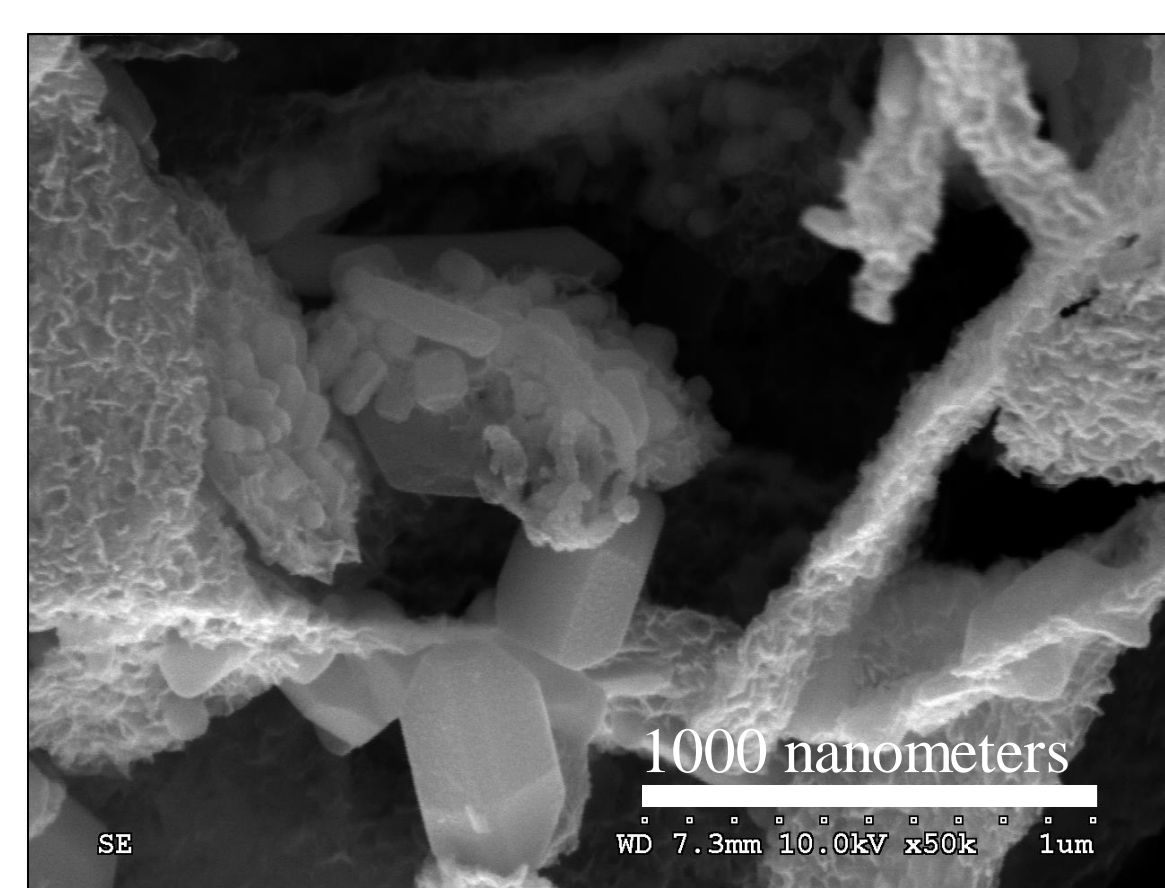


Figure 1: SEM detailing crystal structure in 10mM MnO_2

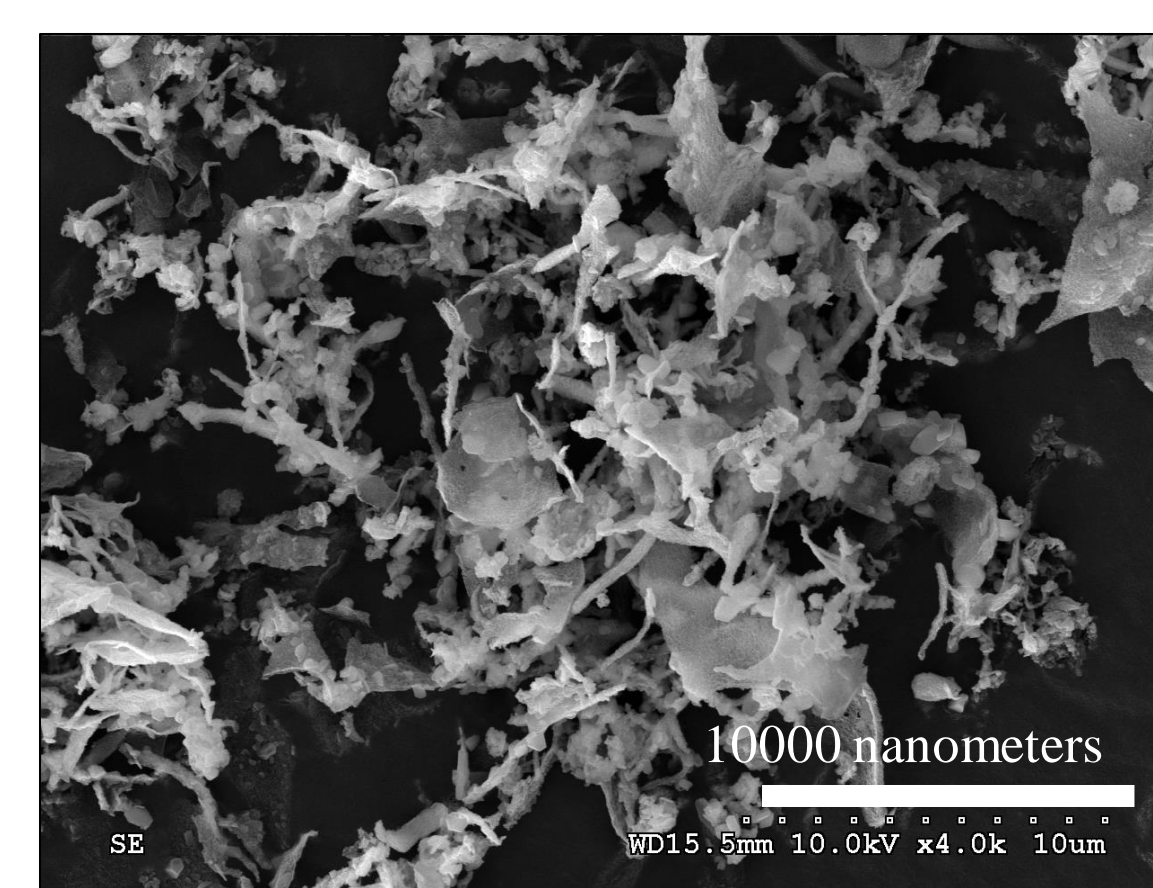


Figure 2: SEM of flake-like constitution in 10mM MnO_2

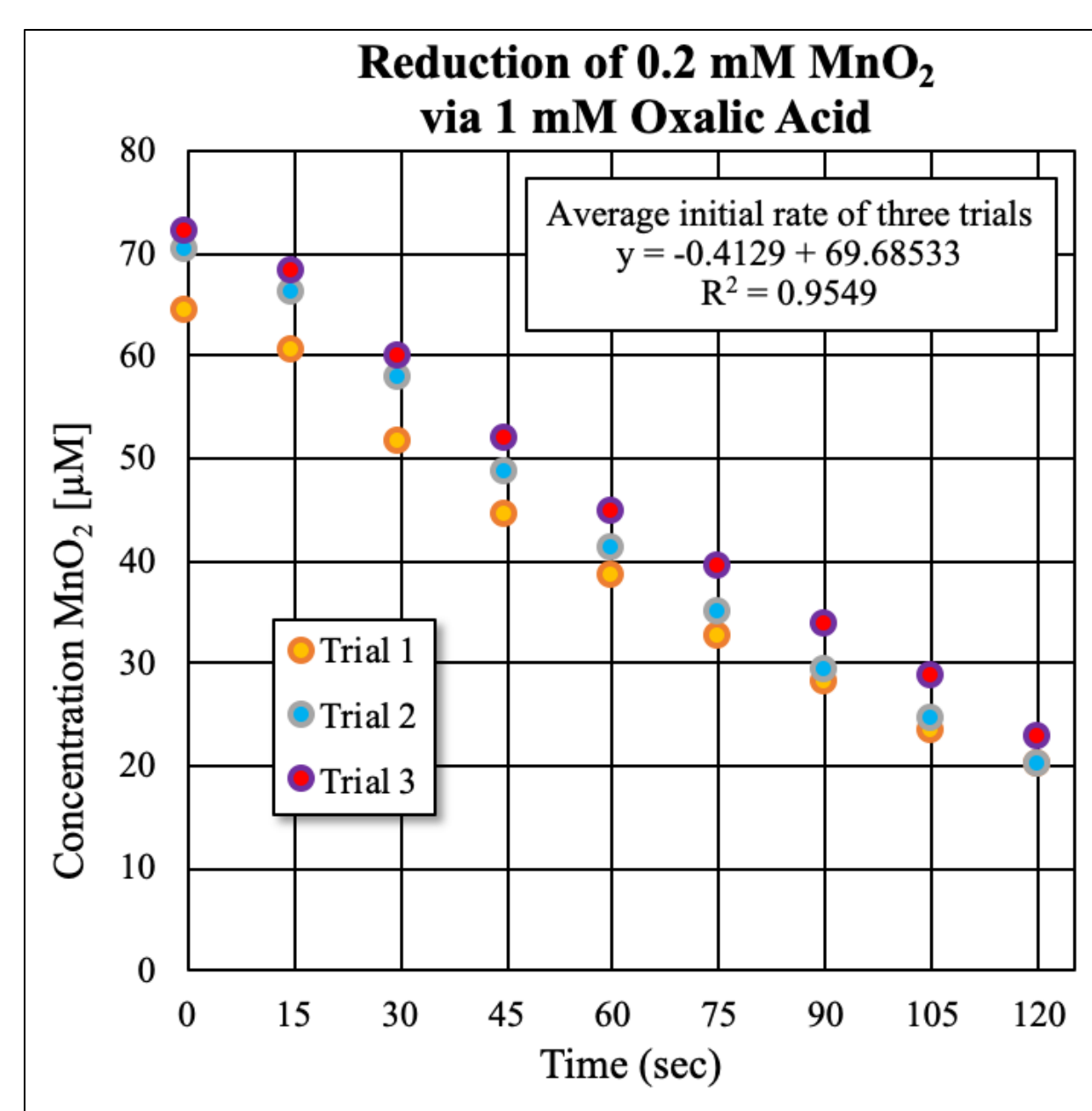


Figure 5: Reduction of polymeric (colloidal) manganese oxide (MnO_2) via oxalic acid. Initial concentrations were 1 mM oxalic acid and 0.2 MnO_2 . Thus, in this reaction there is a 5:1 ratio of excess oxalic acid to MnO_2 . The rate equation and R^2 value shown on the plot represent the initial rates of the reaction base on the first 30 seconds.

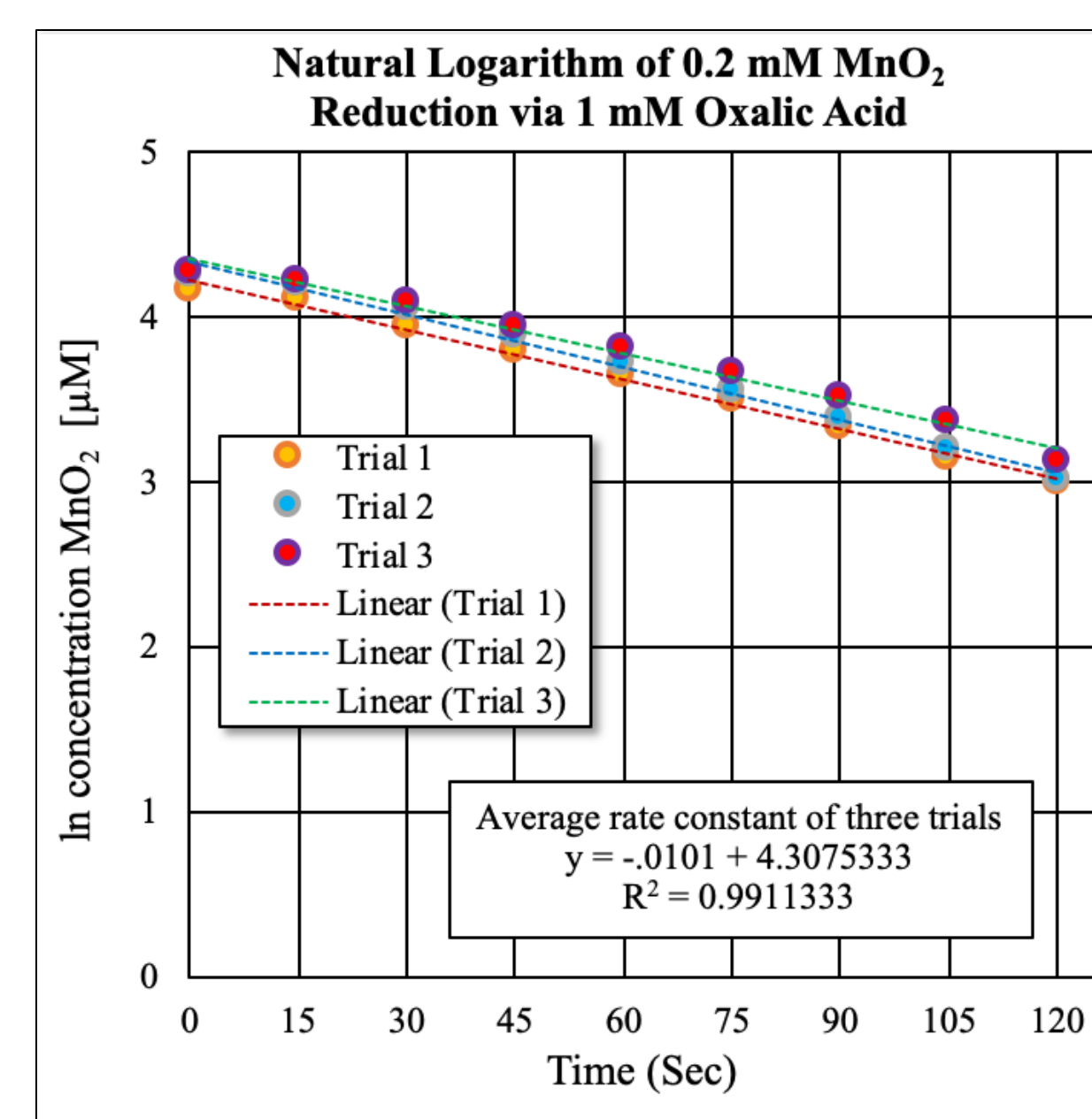


Figure 6: Natural logarithm of the reduction of polymeric (colloidal) manganese oxide (MnO_2) via oxalic acid. Initial concentrations were 1 mM oxalic acid and 0.2 MnO_2 . Thus, in this reaction there is a 5:1 ratio of excess oxalic acid to MnO_2 . The rate equation and R^2 value shown on the plot represent the average reaction rate over the entire 120 second interval.

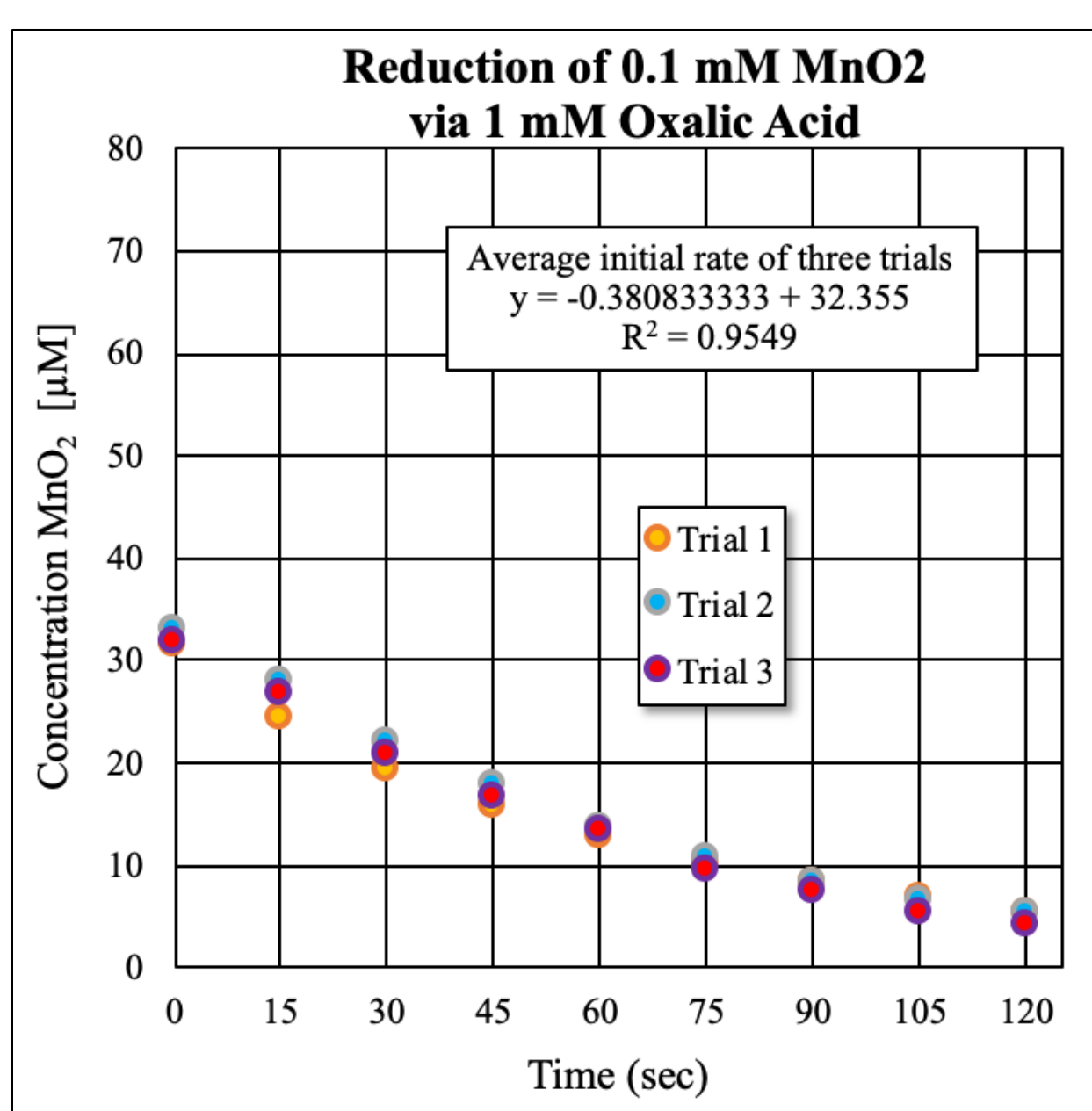


Figure 7: Reduction of polymeric (colloidal) manganese oxide (MnO_2) via oxalic acid. Initial concentrations were 1 mM oxalic acid and 0.1 MnO_2 . Thus, in this reaction there is a 10:1 ratio of excess oxalic acid to MnO_2 . The rate equation and R^2 value shown on the plot represent the initial rates of the reaction base on the first 30 seconds.

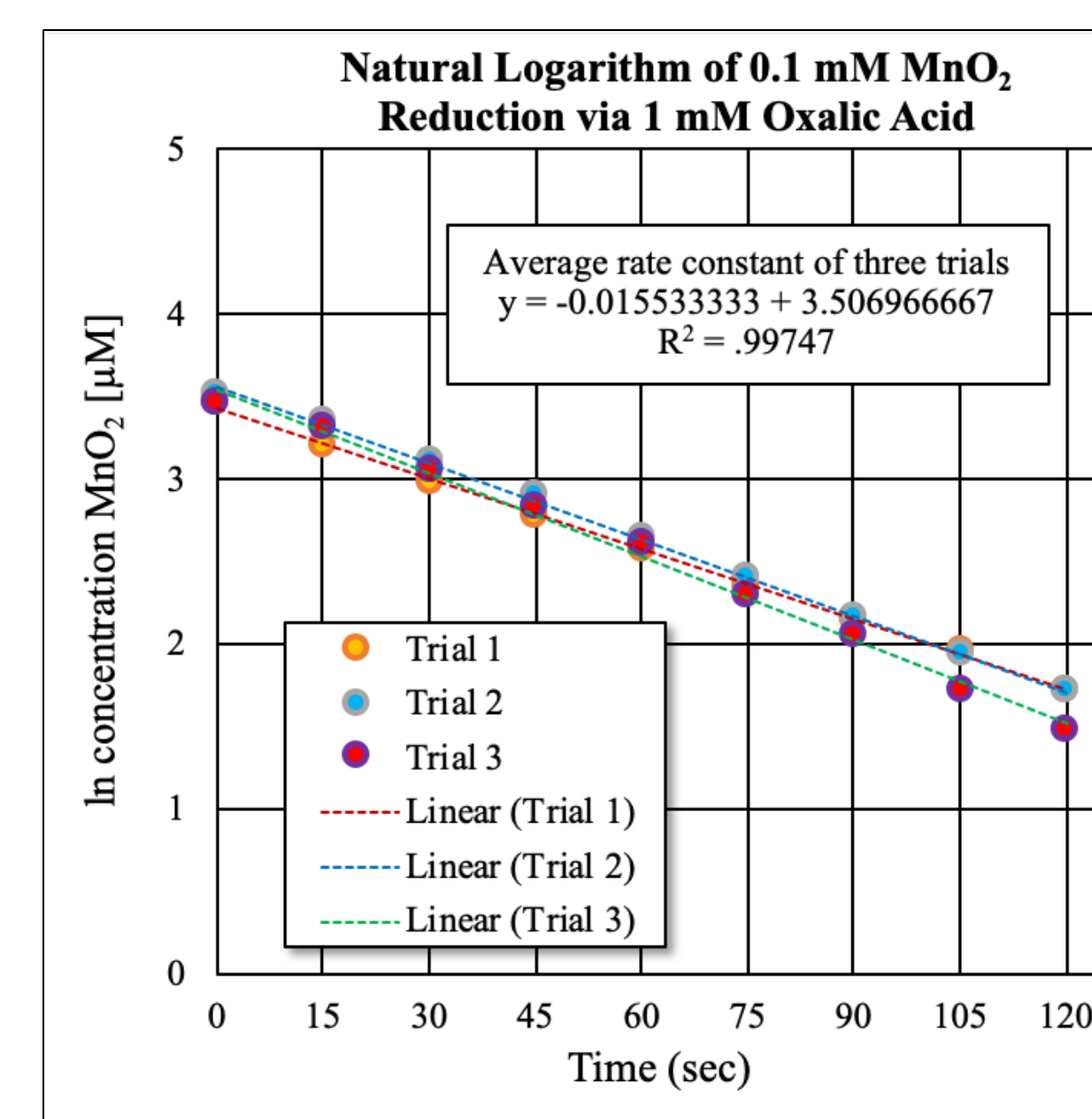


Figure 8: Natural logarithm of the reduction of polymeric (colloidal) manganese oxide (MnO_2) via oxalic acid. Initial concentrations were 1 mM oxalic acid and 0.1 MnO_2 . Thus, in this reaction there is a 10:1 ratio of excess oxalic acid to MnO_2 . The rate equation and R^2 value shown on the plot represent the average reaction rate over the entire 120 second interval.

Results

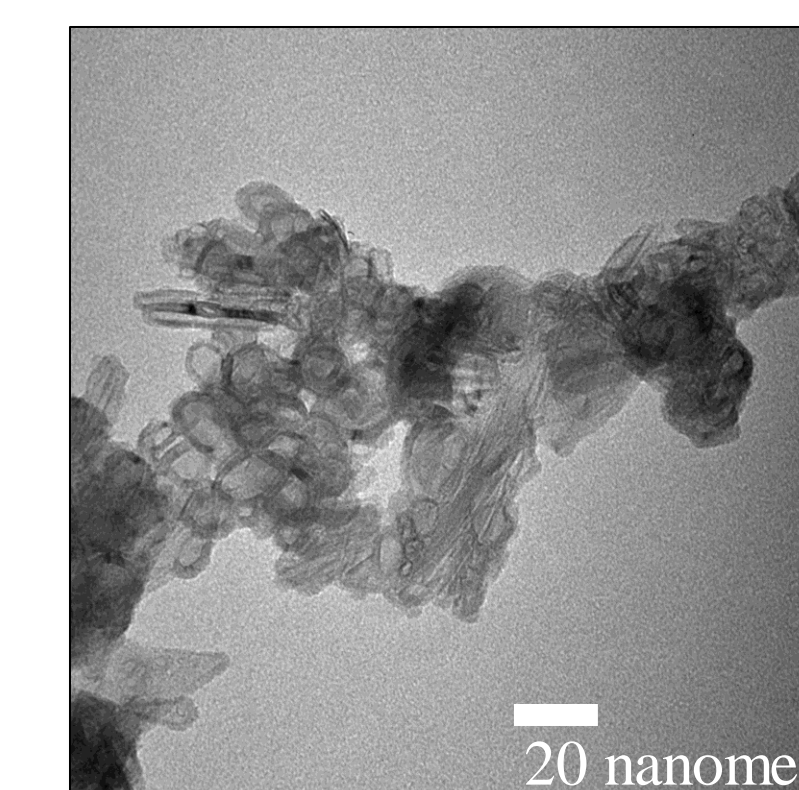


Figure 3: TEM capture cell of lattice constitutions, depths in 10mM MnO_2

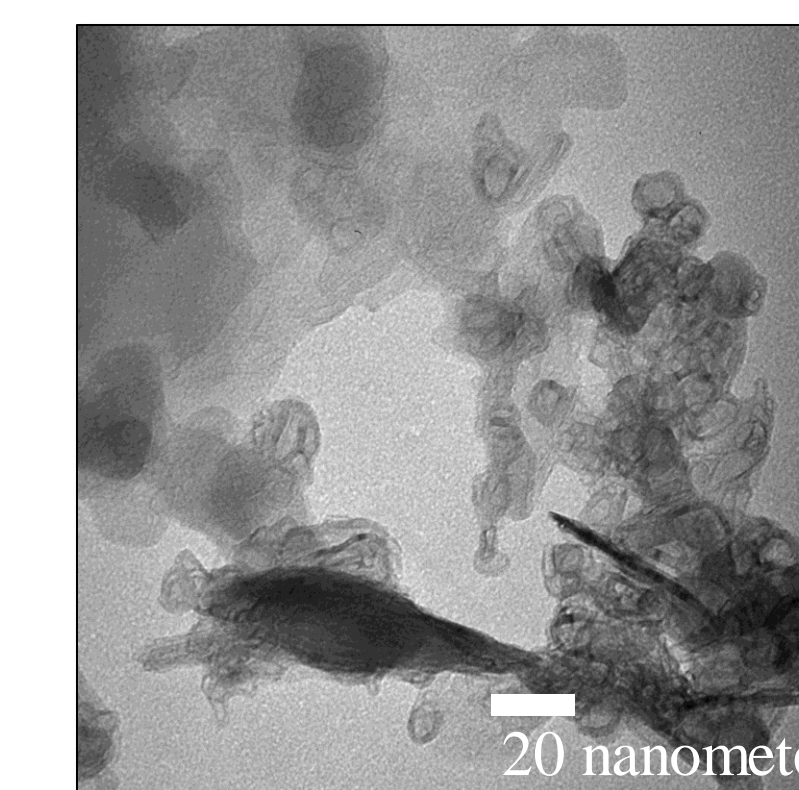


Figure 4: TEM capture cell of lattice conglomerate in 10mM MnO_2

Discussion

- The UV-Vis absorbance runs yielded the rate constant values of
 - 0.0101 s^{-1} (0.2 mM MnO_2 , 1.0mM oxalic acid),
 - 0.0155 s^{-1} (0.1mM MnO_2 , 1.0mM oxalic acid), and
 - 0.0248 (0.2mM MnO_2 , 2.0mM oxalic acid).
- The initial rates of reaction were found to be
 - $0.4129 \mu\text{M } MnO_2 \text{ s}^{-1}$ (0.2mM MnO_2 , 1.0mM oxalic acid),
 - $0.3808 \mu\text{M } MnO_2 \text{ s}^{-1}$ (0.1mM MnO_2 , 1.0mM oxalic acid), and
 - $0.8434 \mu\text{M } MnO_2 \text{ s}^{-1}$ (0.2mM MnO_2 , 2.0mM oxalic acid).
- The rate of the reaction doubled with the concentration of oxalic acid was doubled
- The high R^2 values indicate that the reaction kinetics are first order with respect to the loss of MnO_2
- The values of these rate constants and initial rates indicate that their relative ratios influence the reaction rate of MnO_2 as an oxidizing agent of oxalic acid.
- It is important to note the possibility of a surface passivation incident with the manganese(IV) oxide. Contact of the lattice with other substances or gaseous compounds in ambient air may leave the metal complex inactive to chemical processes.

Future Work

- A decreased amount of MnO_2 in terms of the adequate ration of reaction will impair the reaction in terms of rate and length; thus, lower ratios will be tested.
- Future work will observe the kinetic differences between the rates of a dissolved organic carbon (DOC) source to compare to pure-phase oxalic acid.
- Pursuits will also continue to observe the oxalic acid and DOC reactions' response to environmental stresses such as pH and ratio adjustments.

Acknowledgments

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