Chemical mediated depolymerization of cotton cellulose for the understanding of non-enzymatic fungal decay

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Overview

- Brown-rot fungal decay is characterized by rapid & extensive depolymerization of hemicellulose and cellulose
- Pore size in wood is too small for known brown-rot enzymes to penetrate however, poly-saccharides in the S2 layer are degraded at a distance from the hyphae of brown-rot
- Small, low molecular weight non-enzymatic compounds capable of diffusing through the wood cell wall and are thought to be linked to early stages of brown-rot decay

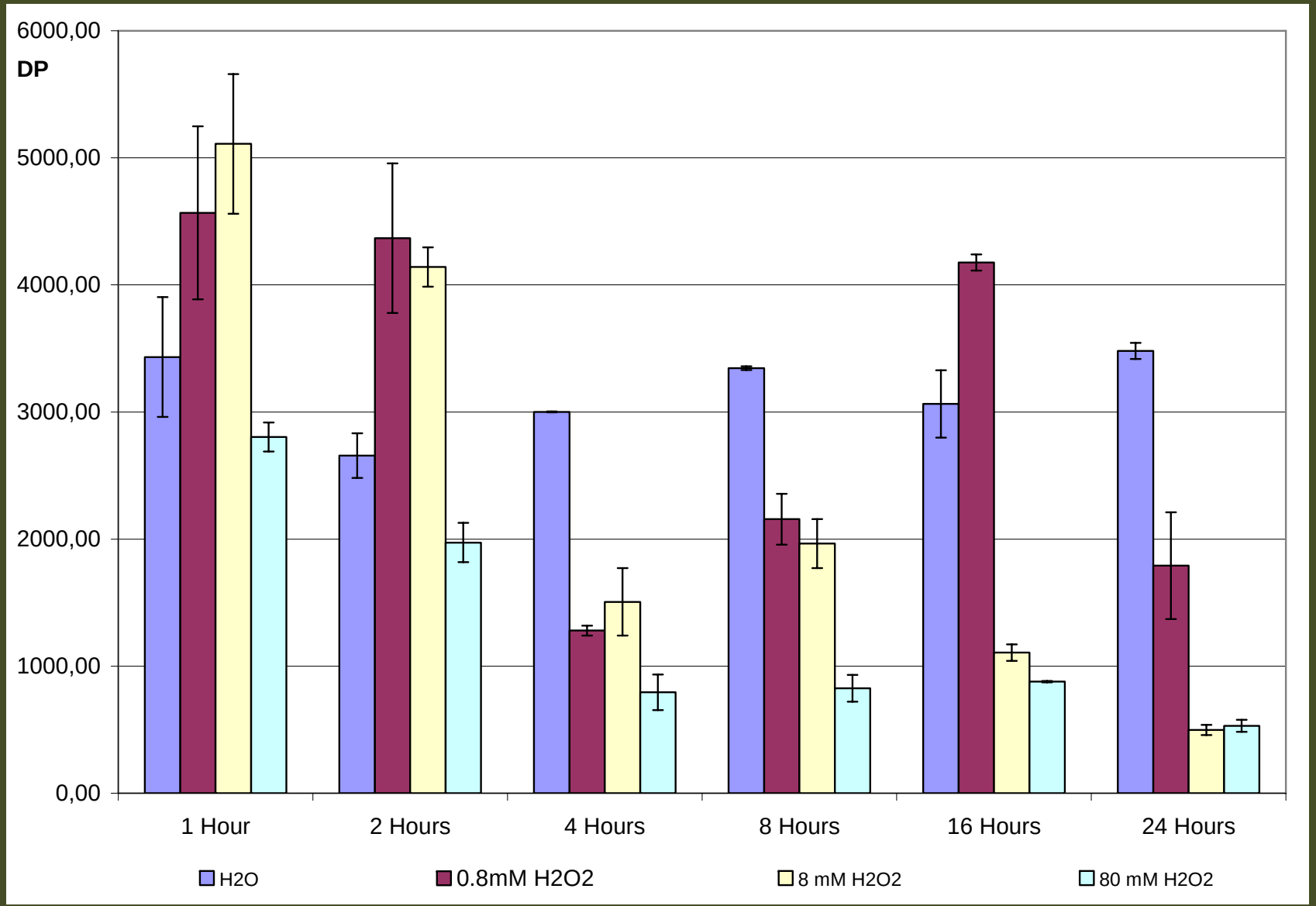
Fenton Reaction

- H.J.H. Fenton 1893 and the oxidation of tartaric acid:
  - (1) $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^-$
  - (2) $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH\cdot + H^+$
- Does Fenton chemistry depolymerize cotton at low pH in presence of OA?
- Can Mn^{3+} be substituted for $Fe^{2/3}$?
- How does acetate buffer effect Fenton chemistry at pH 4.2?

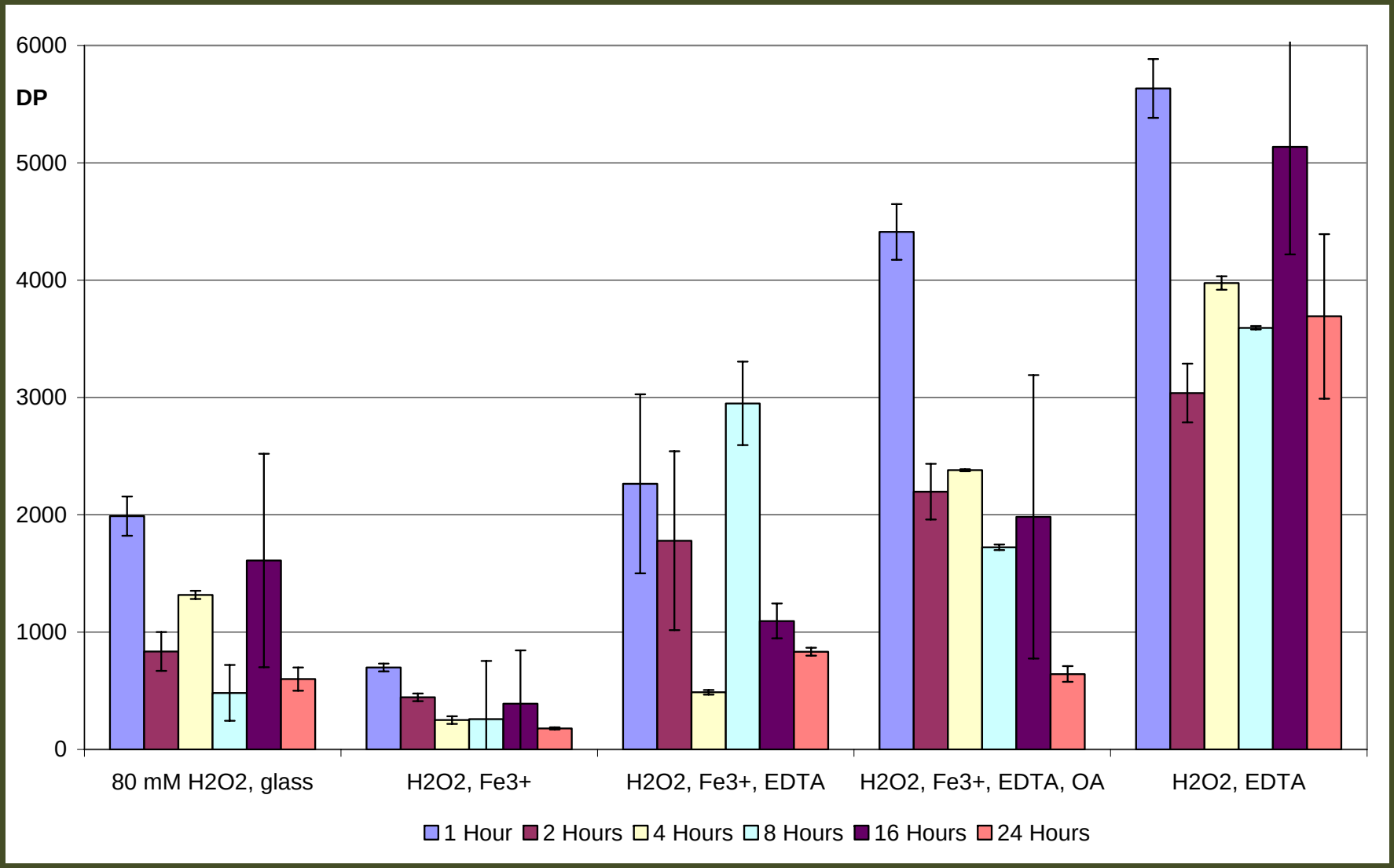
Materials and Methods

- Biomemetic reactions were performed *in vitro* on cotton cellulose using combinations of Iron, hydrogen peroxide and oxalic acid
- Cotton samples were incubated in a 30mL test tube for 24 hrs and rinsed twice with DI water to stop further reactions
- 0.05g of cotton cellulose was placed in 5mL of 1M cupriethylenediamine
- Samples were tested in a #300 Cannon-Fenske viscometer tube to measure DOP

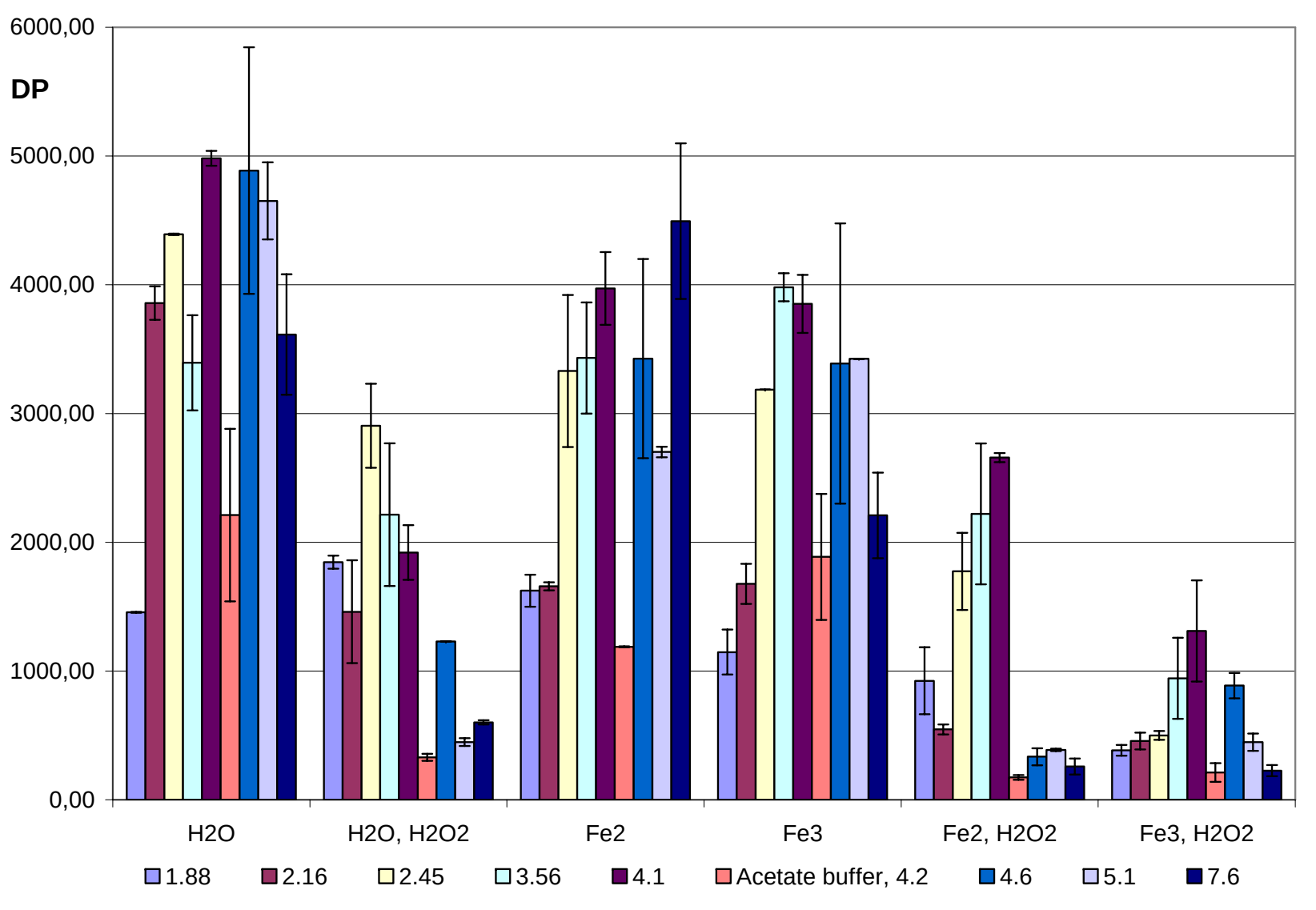
The influence of different concentrations of H_2O_2 on the depolymerization of cotton cellulose



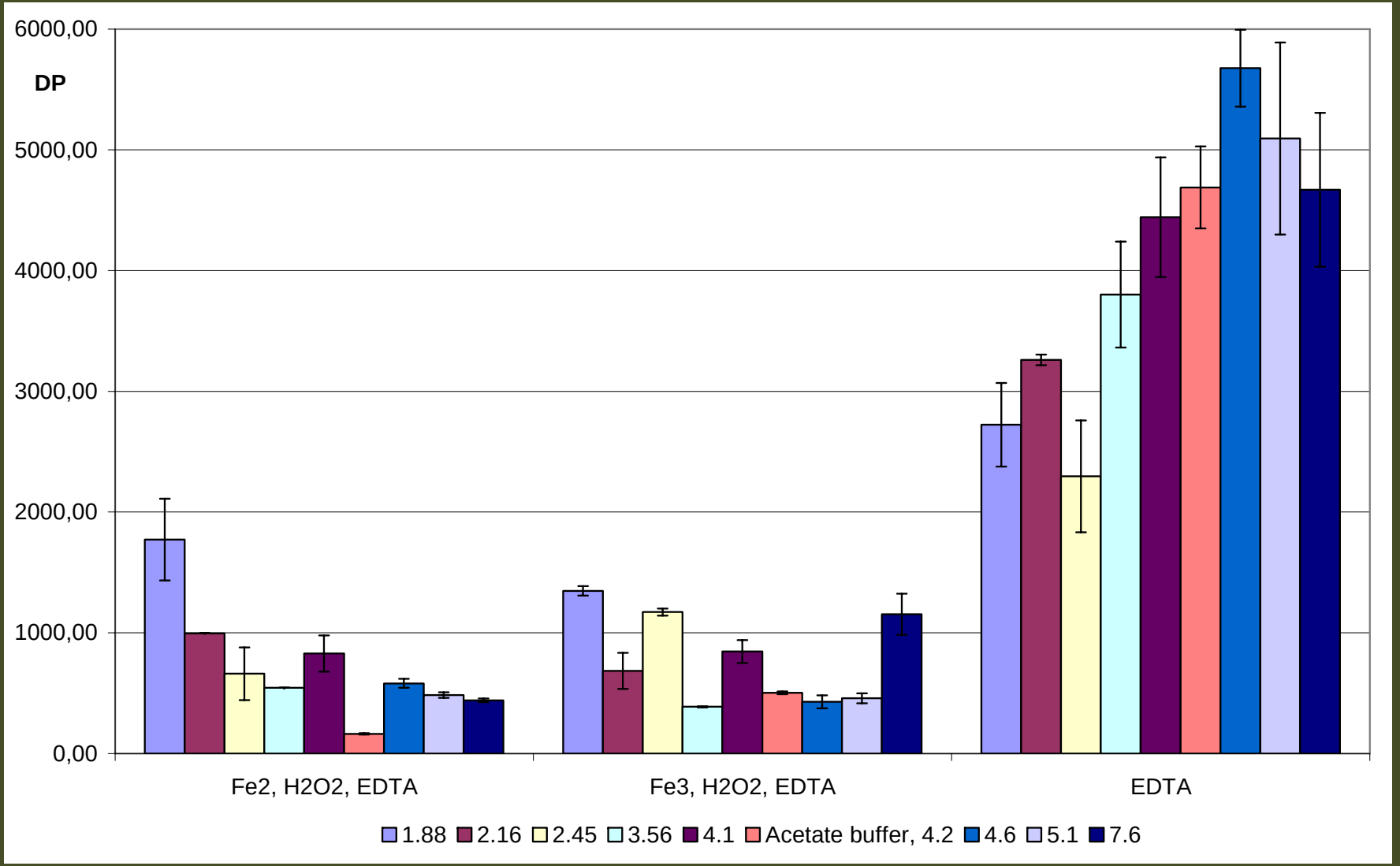
Treatment of cotton with a combination of H_2O_2, iron, EDTA, and OA over numerous time periods



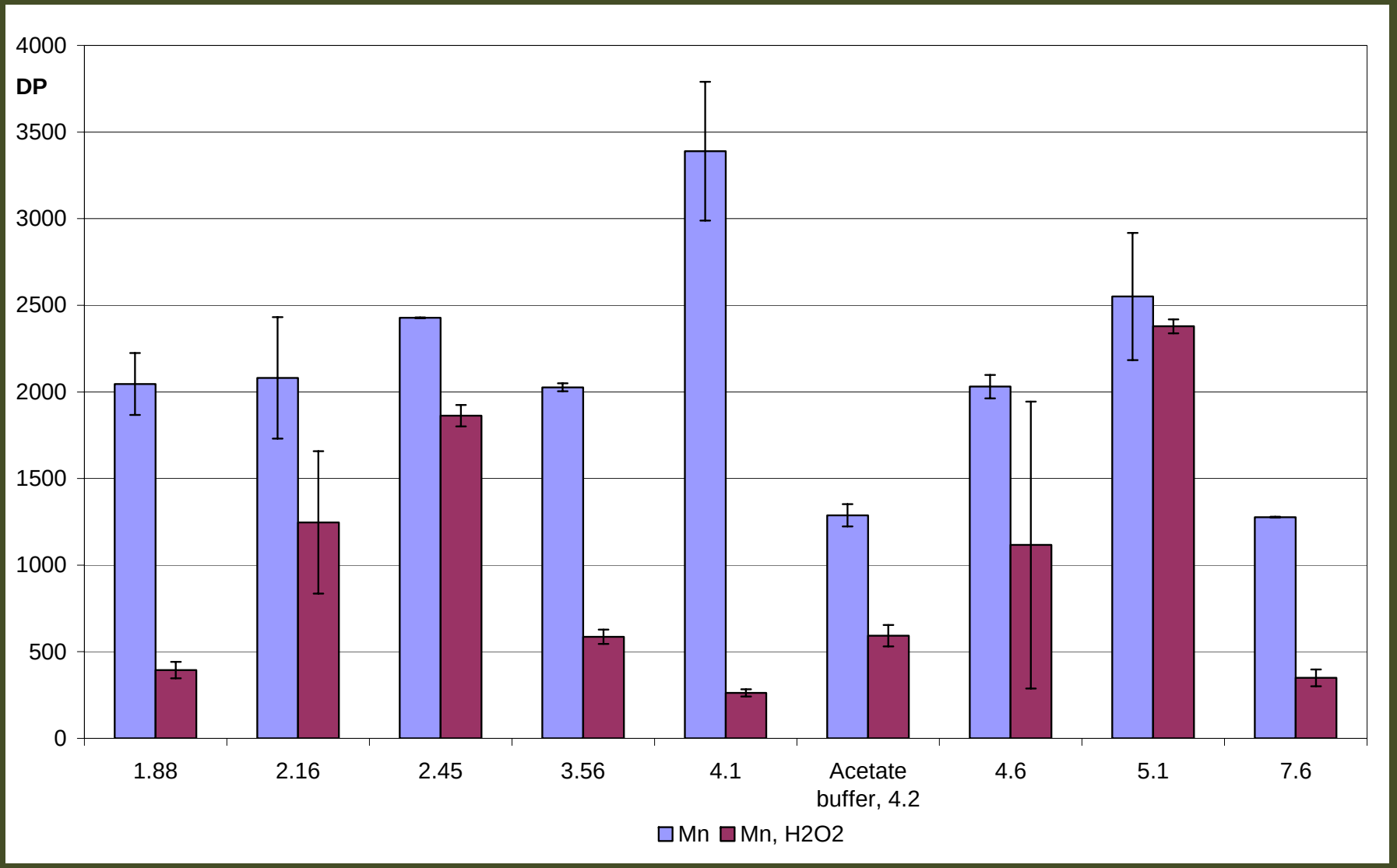
Treatments with a combination of H_2O_2, Fe^{2+}, Fe^{3+} in oxalate/sodium oxalate or acetate buffered media



Treatments with a combination of H_2O_2, Fe^{2+}, Fe^{3+}, and EDTA in sodium oxalate or acetate buffered media



Manganese treatment of cotton with and without H_2O_2 in an oxalate buffer solution at different pH values (n = 3)



Conclusions

- Low molecular weight metabolites:
  - Hydrogen peroxide, iron and oxalic acid are shown to be effective for DP of cellulose *in vitro*
- Fenton reaction can still occur at a low pH (1.88) in the presence of OA produced by brown-rot fungi
- Manganese was found to be an effective substitute for iron in combination with H_2O_2
- Acetate buffer at pH 4.2 with H_2O_2 in solution effectively depolymerized cotton, which may help explain how low oxalic acid producers (e.g. *G. trabeum*) can effectively degrade cellulose

Thanks!