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Degradation of wood veneers by Fenton reagents: Effects of 2,3-dihydroxybenzoic acid on mineralization of wood

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ABSTRACT

Pine sapwood veneer strips were subjected to Fenton's reagent (hydrogen peroxide and iron ions) without and in the presence of the iron chelator 2,3-dihydroxybenzoic acid (DHBA). Incubation was carried out in water (unbuffered) and in acetate buffer in order to assess the effect of the oxidising systems on the weight loss and tensile strength loss as well as on the mineralisation of wood. A great amount of carbon dioxide was produced during the incubation and revealed that organic substances (wood, DHBA, and acetate buffer) were mineralized due to Fenton's reaction. The degree of oxidative wood degradation by Fenton's reagent was greater in the buffered solutions than in the aqueous solutions. DHBA accelerated the decomposition of H_2O_2 in the solution but reduced the loss in weight and tensile strength and the degrees of mineralization of wood as compared to the system without DHBA.

1. Introduction

Brown-rot is the main degradation type of wood in service and drives the carbon cycle in nature [1]. Brown rot fungi mineralize the polysaccharides in wood leaving lignin undigested. Polysaccharide-degrading enzymes, however, normally exhibit a size larger than the diameter of the cell wall micropores [2,3]. As a result, initial degradation of cell wall polysaccharides cannot be brought about by direct enzymatic attack. Fenton's reagent [4] is a diffusible low molecular weight agent which is known to play a key role in brown rot decay of wood [5–9]. The reagent is able to penetrate the non-crystalline regions of cellulose and cleave the glucan chains, thereby causing strength loss prior to any apparent weight loss [10–12].

Ferrous iron-catalysed Fenton reaction preferentially proceeds under acidic conditions generating highly oxidative hydroxyl radicals and/or other reduced oxygen species such as hydroperoxy or superoxide radicals (Eqs. (1)–(2); the reactions of the hydroperoxyl radical with a ferric ion, a hydroxyl radical or another hydroperoxyl radical (disproportionation) results in the formation of molecular oxygen (Eqs. (3)–(5)) [13–16]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad (2)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+ \quad (3)$$

$${}^{\cdot}OH + HO_2^{\cdot} + \rightarrow H_2O + O_2 \quad (4)$$

$$HO_2^{\cdot} + HO_2^{\cdot} + \rightarrow H_2O_2 + O_2 \quad (5)$$

$$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^- \quad (6)$$

$${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2 \quad (7)$$

In Fenton's reaction, ferrous iron is oxidized to trivalent ferric iron (Eq. (1)). To promote a continuous generation of hydroxyl radicals, ferric iron must be reduced to the bivalent state. Although hydrogen peroxide or the formed hydroperoxyl radicals can reduce the Fe(III) to Fe(II) (Eqs. (2)–(3)), the reaction rate is considerably slower than that of Fenton's reaction [17].

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The redox reaction of iron taking place during brown-rot decay has been assumed to occur in presence of extracellular low molecule weight substances such as oxalic acid, 4,5-dimethoxycatechol, 2,5-dimethoxyhydroquinone, and 2,3-dihydroxybenzoic acid. These low molecular weight substances secreted by the brown-rot fungi can form an Fe(III)-chelator complexes, within which the Fe(III) can be reduced to Fe(II) [18–22].

In a previous paper we investigated the effects of wood constituents and 2,3-dihydroxybenzoic acid on wood decay by Fenton's reagent in order to mimic the initial oxidation process during brown rot of wood [23]. An increasing redox turnover of ferric iron was observed with increasing amounts of wood material in the solution, suggesting that wood constituents participate in the Fenton reaction. The degree of wood degradation was greater at a higher concentration of ferric iron or hydrogen peroxide; however, addition of the low molecular weight, metal-binding, phenolic compound (2,3-dihydroxybenzoic acid) and of a non-chelating hydroquinone to the reaction mixtures increased the decomposition of hydrogen peroxide but restrained the strength loss of wood. Evolution of gas was also observed during the incubation [23].

The evolution kinetics of O_2 has previously been examined in the solution of H_2O_2 and Fe(III) sulphate using a pressure gauge [24], but to date few systematic studies exist on the dynamics of gas evolution during wood degradation by Fenton's reagent. This study was devised to investigate the effects of wood and of the low molecular weight compound 2,3-dihydroxybenzoic acid (DHBA) on the gas production in water and in acetate buffer by Fenton's reagent.

2. Materials and methods

2.1. Wood micro-veneer strips

Micro-veneer strips measuring 100 mm (longitudinal) × 15 mm (radial) × 80 μm (tangential) were prepared as described previously [23].

2.2. Chemicals

Hydrogen peroxide (35 wt.%), Iron(III) sulphate hydrate, and 2,3-dihydroxybenzoic acid (2,3-DHBA) were purchased from Sigma–Aldrich Chemie GmbH (Munich, Germany). Sodium thiosulfate and potassium iodide were obtained from AppliChem GmbH (Darmstadt, Germany) and KMF Laborchemie Handels GmbH (Lohmar, Germany), respectively. Starch was obtained from Merck KGaA (Darmstadt, Germany). All chemicals were used as received.

2.3. Micro-veneer strip treatment

Each micro-veneer strip was halved: one half was treated with Fenton's reagent in deionized water or 0.1 mol l^{-1} acetate buffer (pH 3.0) and the other half used as control stored only in the respective solvent (Table 1). Before treatment, all veneer strips were oven dried at 105 °C for 6 h and their weight determined. The treatment was carried out in 100 ml serum bottles accommodating 50 ml of solution. Three halves of wood strips (ca. 1.5 mg ml^{-1}) were firstly put into the bottle and water or buffer solution was added; the iron solution was afterwards added into the bottle following with DHBA solution. Hydrogen peroxide was finally added to initiate the redox reaction. In addition, solutions without wood were also prepared to study H_2O_2 decomposition and gas production. The serum bottle was immediately sealed with a rubber capsule and an aluminium cover once the solution was prepared.

Table 1
Treatment solutions and compounds used in this study.

Treatment	H_2O_2 [mmol l^{-1}]	Fe(III) [mmol l^{-1}]	DHBA [mmol l^{-1}]	Wood [mg ml^{-1}]
Control	–	–	–	1.5
Fenton	50	0.2	–	–
Fenton + DHBA	50	0.2	0.1	–
Fenton + DHBA	50	0.2	0.2	–
Fenton + DHBA	50	0.2	1.0	–
Fenton + Wood	50	0.2	–	1.5
Fenton + DHBA + wood	50	0.2	0.1	1.5
Fenton + DHBA + wood	50	0.2	0.2	1.5
Fenton + DHBA + wood	50	0.2	1.0	1.5

The serum bottle was then gently shaken in a closed, dark water bath at a temperature of 30 °C for the desired period, after which the gas in the serum bottle was sampled using a syringe for chromatographic analysis. Following that, 1 ml treating solution was withdrawn to measure the concentration of H_2O_2. The veneer strips (if any) were gently taken out and washed several times with deionised water. In total, 12 replicates of serum bottles were used per treatment and three of them were used after 1, 6, 24, and 48 h, respectively, to determine gas production, tensile strength and weight of the veneers. At the beginning and end of the treatment the pH of the treating solution was measured using a pH meter (pH 526, Wissenschaftlich-Technische Werkstätten, Weilheim, Germany).

2.4. Determination of hydrogen peroxide concentration

The concentration of H_2O_2 in the treating solution was determined iodometrically as described previously [23,25].

2.5. Gas chromatography

The gas pressure in the serum bottle was determined using a tensiometer which is a pressure transducer equipped with a hypodermic needle (Thies Klima, Göttingen, Germany). To determine the mass change of CO_2 and O_2, a volume of 10 ml gas was sampled from the serum bottle using a syringe and then transferred into an evacuated tube (10 ml) for gas chromatography (GC) analysis. Oxygen analysis (O_2) was carried out using a gas chromatograph (Fractovap 400, Carlo Erba, Milan, Italy) equipped with a thermal conductivity detector and a packed column (1.8 m in length, 4 mm ID, molecular sieve 5Å) using helium as carrier gas; for CO_2 measurement, it was a gas chromatograph (Fisons GC 8000, Milan, Italy) equipped with a split-injector, an electronic capture detector, and a HP-PLOT Q column (30 m in length, 0.32 mm ID; Agilent Technologies, Santa Clara, USA) with a working temperature of 30 °C. The split ratio was 1:8 and an argon-methane mixture (95/5) was used as carrier and make-up gas. The control gas was sampled from the serum bottle without Fenton's reagent. The amounts in the controls were subtracted from those of bottles containing Fenton's reagent. The gas produced and dissolved in the solutions was calculated based on Henry's law as described previously [26].

2.6. Zero-span tensile strength and weight loss of veneer strips

Zero-span tensile strength was determined as described previously [23]. The fragments of each veneer strip were oven dried and weighed to determine the mass loss.