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Further mechanistic orientation for the oxidation reaction between alkaline permanganate and poly galacturonate methyl ester. Novel spectrophotometric tracer of intrahypomanganate(V) – Intermediate

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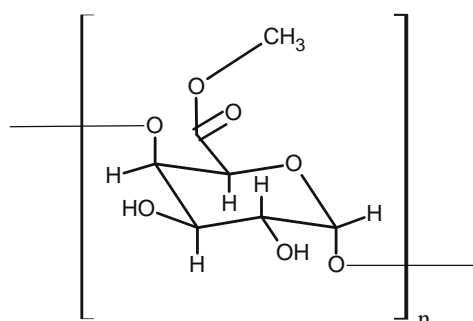
ABSTRACT

The kinetics of formation of the green manganate(VI) intermediate complex formed during the oxidation of pectin polysaccharide (poly galacturonate methyl ester) (PGME) by MnO₄⁻ in alkaline solution at pH ≥ 12 have been studied. The rate law was suggested to be: rate = *k*_{obs}[MnO₄⁻]. The reaction was found to be base – catalyzed and fractional second – order in [PGME]. The activation parameters have been evaluated and discussed. A reaction mechanism was suggested according to the experimental data. A new blue hypomanganate(V) coordination polymer intermediate sol was spectrophotometrically detected for the first time for pectin (poly galacturonate methyl ester) oxidation reaction. A further mechanistic presentation was proposed.

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1. Introduction

Pectin is the methyl ester of pectic acid and is composed of long chains of galacturonic acid (Whistler & Smart, 1953). Pectin is a polysaccharide derived from the cell wall of higher terrestrial plants. Chemically, pectin is a linear polysaccharide containing from about 300 to 1000 monosaccharide units. D-Galacturonic acid is the principal monosaccharide unit of pectin. The D-galacturonic acid residues are linked together by alpha-1, 4 glycosidic linkages.



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The kinetic oxidation of polysaccharides containing secondary alcoholic OH groups by KMnO₄ in basic medium were found to occur via the formation of an intermediate complex involving manganate(VI) (Mn^(VI)O₄²⁻) as a transient species in the first stage of oxidation followed by a slow decomposition of the intermediate at the last stage of reaction to give soluble manganese(IV) and keto-derivatives as final product of the oxidation for the oxidant and substrate, respectively (El-Khatib, 2002; Hassan, 1993a,b; Khairou, 2001; Shaker, 2001a,b; Shaker, El-Khatib, & Makran, 2007).

The oxidation of sodium pectate polysaccharide was studied previously in alkaline solutions at [OH⁻] from 2.55 × 10⁻³ to 7.65 × 10⁻³ mol dm⁻³. The reaction was found to be complicated which proceeded by the formation of Mn(VI)-pectate spectrophotometrically observed intermediate (Khairou, 2003; Khairou & Hassan, 2000). The rate of formation followed a first – order dependence in [MnO₄⁻] and fractional – order in sodium pectate concentration (Khairou & Hassan, 2000). Therefore, this complexity in the reaction pathway would deserve further investigation in order to throw more light on the reactive species, as well as, more details in the reaction mechanism.

In view of this and current interest of redox reactions involving polysaccharides as reducing substrates (El-Khatib, 2002; Hassan, 1993a,b; Khairou, 2001; Shaker, 2001a,b; Shaker et al., 2007), the oxidation of poly galacturonate methyl ester (pectin) (PGME) by KMnO₄ has been undertaken employing wide range of [OH⁻] (from 8 × 10⁻³ to 2 × 10⁻² mol dm⁻³) and substrate (from 2 × 10⁻³ to 6 × 10⁻³ mol dm⁻³) concentrations. As an attempt to reach a more