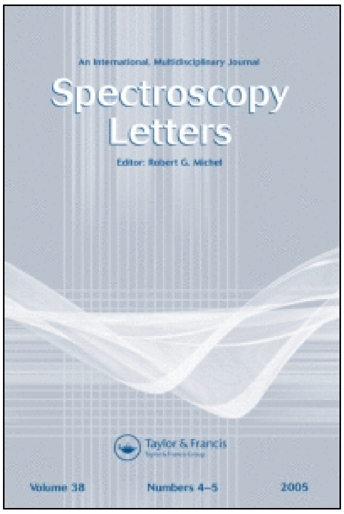

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SPECTROPHOTOMETRIC EVIDENCE FOR THE FORMATION OF SHORT-LIVED Mn(VI) AS TRANSIENT SPECIES INTERMEDIATE DURING THE PERMANGANATE OXIDATION OF CHITIN AND CHITOSAN POLYSACCHARIDES IN ALKALINE SOLUTIONS

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ABSTRACT

The formation of short-lived manganate (VI) intermediate has been confirmed during the oxidation of chitin and chitosan polysaccharides by permanganate ion at pH's ≥ 12, spectrophotometrically. The Mn(VI) transient species intermediate was characterized by a band at a wavelength of 610 nm, an absorption maximum, with a molar extinction coefficient of $1250 \pm 75\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$.

Key Words: Mn(VI); Permanganate oxidation; Chitan; Chitosan; Polysaccharides

INTRODUCTION

Although, permanganate ion has been widely used as a powerful oxidizing agent for oxidation of most organic[1–5] and inorganic[6–10] substrates; the oxidation of polyelectrolytes has not received much attention[11–13].

In Alkaline solutions, the reduction of permanganate ion proceeds via formation of detectable short-lived intermediates such as Mn(III)[14], Mn(IV)[15,17], Mn(V)[18,19] and Mn(VI)[1,3,20,21]. However, the stopped-flow technique is usually utilized for detection of such intermediates, the conventional spectrophotometric methods have received a little attention[22,23].

In view of the above aspects and the current interest in redox reactions involving permanganate ion as an oxidant of polysaccharides[24] in alkaline solutions, the present reaction seems to merit further investigation with a view to gaining unequivocal information on short-lived manganate(VI) intermediate using the conventional spectrophotometric techniques.

EXPERIMENTAL

Chemicals and Reagents

All materials used were of Analar (BDH) grade. Doubly-distilled water was used in all preparations.

Stock solutions of reagents were prepared and standerdized as described elsewhere[22,23].

Instruments and Spectrophotometric Measurements

The spectral change during the reduction of permanganate ion by chitin or chitosan in alkaline solutions ($pH \geq 12$) was monitored in a thermostated cell compartment at ± 0.1°C on a Shimadzu UV double-beam spectrophotometer using cells of path length 1 cm.

RESULTS AND DISCUSSION

A wealth of information revealing the formation of manganate (VI) and/or hypomanganate (V) are presented in Fig. 1 through 3. A gradual

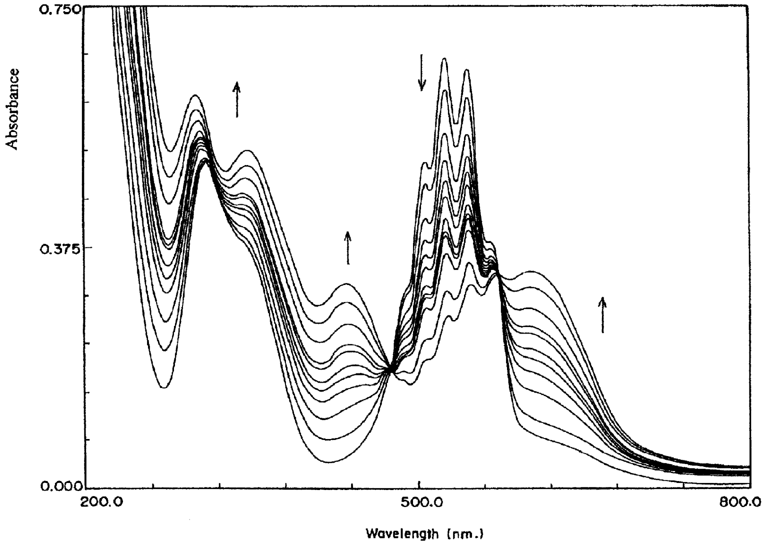


Figure 1. Successive UV-visible spectra for disappearance of permanganate ion and formation of manganate (VI) during the permanganate oxidation of chitin substrate at $[MnO_4^-] = 3 \times 10^{-4}$, $[\text{chitin}] = 3 \times 10^{-4}$, $[OH^-] = 3 \times 10^{-2}$ mol dm^{-3} and 25°C (scanning time intervals between successive curves=2 min.).

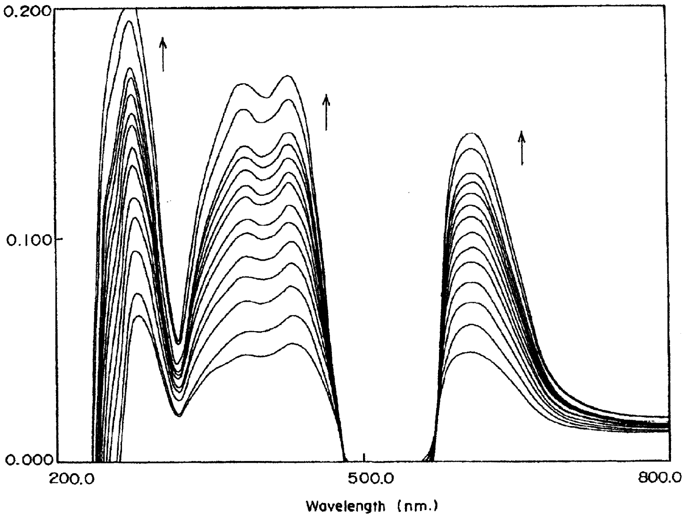


Figure 2. Spectral changes during the formation of the intermediates during the permanganate oxidation of chitin substrate at $[MnO_4^-] = 3 \times 10^{-4}$, $[OH^-] = 3 \times 10^{-2}$ mol dm^{-3} and 25°C (Reference cell: MnO_4^- and OH^- of the same reaction mixture concentration and scanning time intervals = 2 min.).

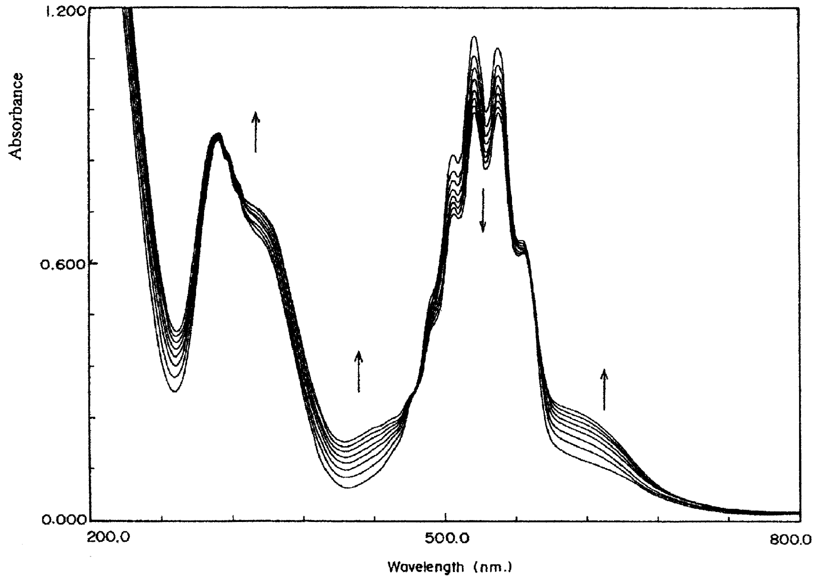
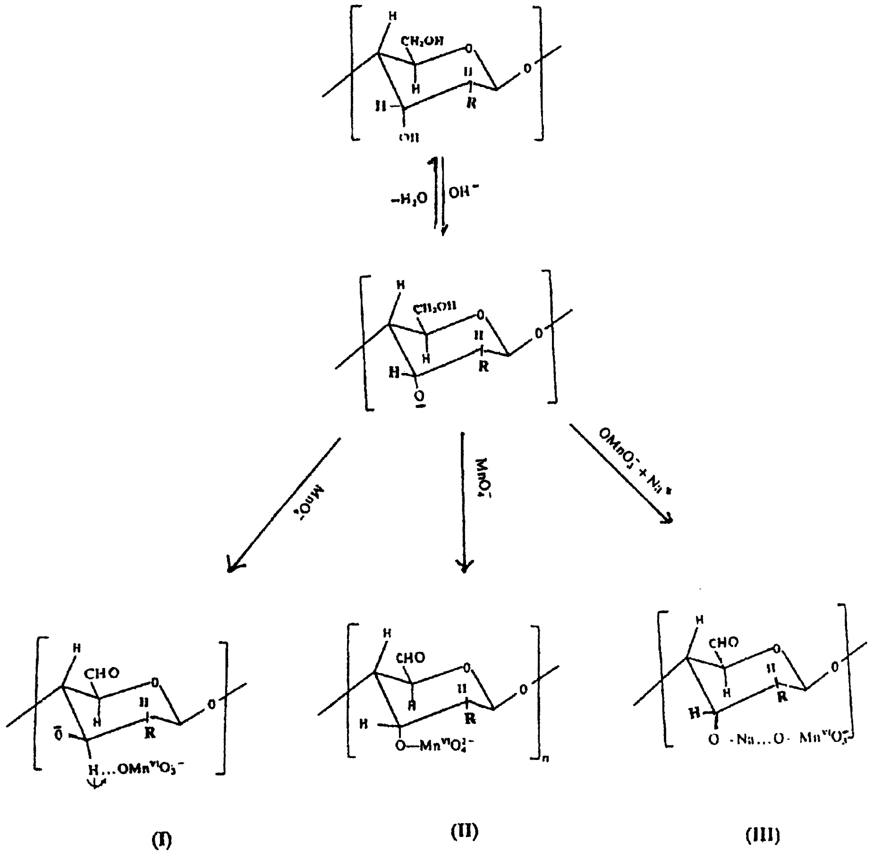


Figure 3. Successive UV-visible spectra for disappearance of permanganate ion and formation of manganate (VI) during the permanganate oxidation of chitosan substrate at $[MnO_4^-] = 4 \times 10^{-4}$, $[\text{chitosan}] = 3 \times 10^{-4}$, $[OH^-] = 3 \times 10^{-2}\,\text{mol}\,\text{dm}^{-3}$ and 25°C (scanning time intervals between successive curves = 1 min.).

decrease in the height of the 525 nm peak with a simultaneous increase in the height of the 610 nm peak is observed. These spectral changes of the reaction mixtures were provided by repetitive spectral scans of the redox reaction at suitable intervals. To our knowledge, the 525 nm band corresponds to the absorption maximum of MnO_4^- ion, whereas that of 610 nm band is corresponding to manganate (VI)[14]. At this later band, the absorption of MnO_4^- is much weaker, thus the detection of MnO_4^{2-} may has no difficulty. The isobestic point, which is seen at 575 nm during the course of reaction indicates the conversion of MnO_4^- to MnO_4^{2-}, whereas that of ~475 nm reveals that both Mn(VII) and Mn(IV) formed do not necessarily exclude the detectable Mn(VI) intermediate[11–13]. Furthermore, the change in the intensity of the bands observed at wavelengths of 435 and 350 nm is due to the increase of the formed soluble Mn(IV) concentration which does not absorb above 540 nm[22,23].

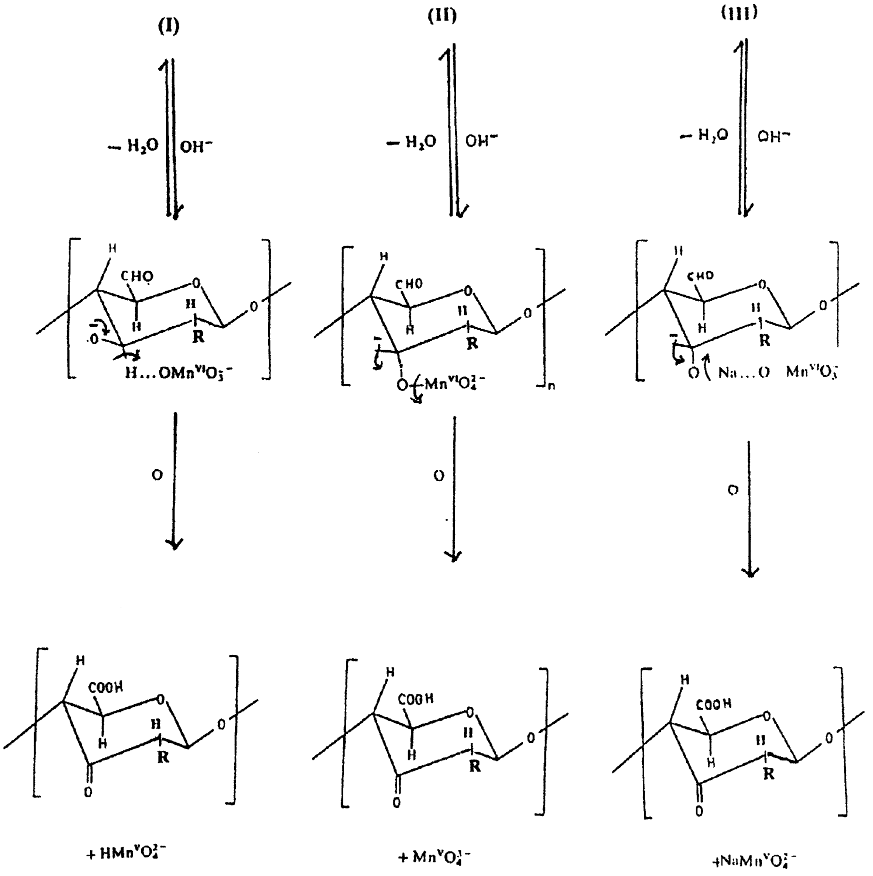
Evidence against the formation of hypomanganate(V) intermediate is provided by the absence of an absorption maximum around 700 nm unless at very low temperatures[3,19]. The failure of detection of Mn(V) may be explained by its extreme short lifetime[3,25], which undergoes a rapid disproportionation, which is autocatalytic in the presence of manganese(IV).

Furthermore, the change in color of the solution mixture as the reaction proceeded, from purple-pink to blue to green may confirm these suggestions for the intermediate. The yellow colour which persists after the disappearance of all the MnO_4^- ions may suggest the formation of stable soluble manganese (IV) as a final product rather than a colloidal suspension of MnO_2[2,16,23,28]. Many investigators have postulated the formation of Mn(VI) and/or Mn(V) as short lived intermediates during the oxidation of organic substrates by permanganate ion in alkaline solutions[14,19].



Scheme I.

Preliminary experiment indicated the formation of ketoderivatives as reaction products of the oxidation of chitin and chitosan by alkaline permanganate. These products could be separated from the reaction mixtures and its presence confirmed by IR and elemental analyses[19]. Hence, mechanisms consistent with the experimental observations may be suggested as in Schemes I and II. The first step corresponds to the removal of H^+ ion from the substrate by the alkali to give an alkoxide form, followed by the attack of MnO_4^- ion to form intermediate complexes involving manganate (VI) transient species in the rate-determining steps as shown in Scheme (I).



Scheme II.

Again, these formed intermediates are slowly decayed to give rise to the products. The decay takes place by fast protonation of the intermediates by the alkali, followed by the transfer of either an electron or an hydride ion from the substrates to the manganate (VI) in the rate-determining steps as shown in Scheme (II).

The kinetics and mechanisms of these redox reactions have been discussed in more details and presented elsewhere[29].

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