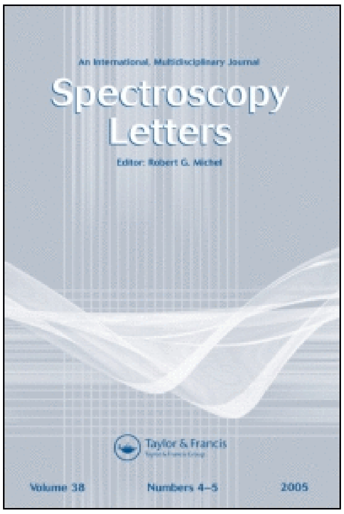

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Spectrophotometry Detection of Short-Lived Manganate (VI) Intermediate Through Oxidation of Some Natural and Synthetic Polymers by Alkaline Permanganate

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Spectrophotometric Detection of Short-lived Manganate (VI) Intermediate Through Oxidation of Some Natural and Synthetic Polymers by Alkaline Permanganate

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Summary :

Spectrophotometric evidence for the formation of a short-lived Mn(VI) intermediate has been confirmed during the oxidation of pectin polysaccharide, a natural polymer, as well as poly (vinyl alcohol) [PVA], a synthetic polymer, by potassium permanganate in alkaline medium at pH's > 12. This Mn(VI) intermediate was characterized by a band at a wavelength of 606 nm an absorption maximum, with a molar extinction coefficient of 1200 ± 50 $dm^3 mol^{-1} cm^{-1}$.

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Introduction :

The nature of detectable short-lived intermediates is of great importance in studies of the mechanisms of oxidation of organic and inorganic compounds by permanganate ion.(1-4)

Although there are many reports on the stopped – flow detection of Mn(III)(1,5), Mn(IV)(6,7), Mn(V)(8-16), and Mn(VI)(16-20), short-lived intermediates in the permanganate oxidation of organic and inorganic substrates, a little attention has been focused on the conventional spectrophotometric detection of these transient species.(21-23) Therefore, we now report a direct evidence for the detection of manganate ion, MnO_4^{2-}, using a Shimadzu UV double beam spectrophotometer during the oxidation of poly (vinyl alcohol)(24,25) and pectin(26) polymers by alkaline permanganate.

Experimental :

Chemicals and Reagents :

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

Sodium pectate and poly (vinyl alcohol) sols of known concentrations were prepared by dissolving the requisite amounts of the reagent salts in bidistilled water. This process was performed by the stepwise addition of the powdered reagents whilst rapidly stirring the water to avoid the formation of a lumpy solution which swells with difficulty.

Stock solution of potassium permanganate was prepared by dissolving reagent grade $KMnO_4$ in doubly distilled water, boiling the solution and standardizing it against As_2O_3(27) after filtration through a fine glass filter to remove MnO_2.

All other reagents were of analytical grade and their solutions were prepared by dissolving the appropriate amounts of the samples in bidistilled water.

Instruments and Spectrophotometric Measurements :

The spectral change during the oxidation of either pectin or poly (vinyl alcohol) by alkaline permanganate ($pH > 12$) was monitored in a thermostated cell compartment at (5–22) ± 0.1°C on a Shimadzu UV double – beam spectrophotometer using cells of path length 1 cm.

Results and Discussion :

As shown in Figures 1 and 2, most of the spectral changes of MnO_4^- ion are displayed, but superposition of other species is apparent. (A wealth of information revealing the formation of manganate (VI) and/or hypomanganate(V) short-lived intermediates.) There is a gradual disappearance of MnO_4^- ion at a wavelength of 525 nm, its absorption maximum, with the formation of new absorbance intermediates at

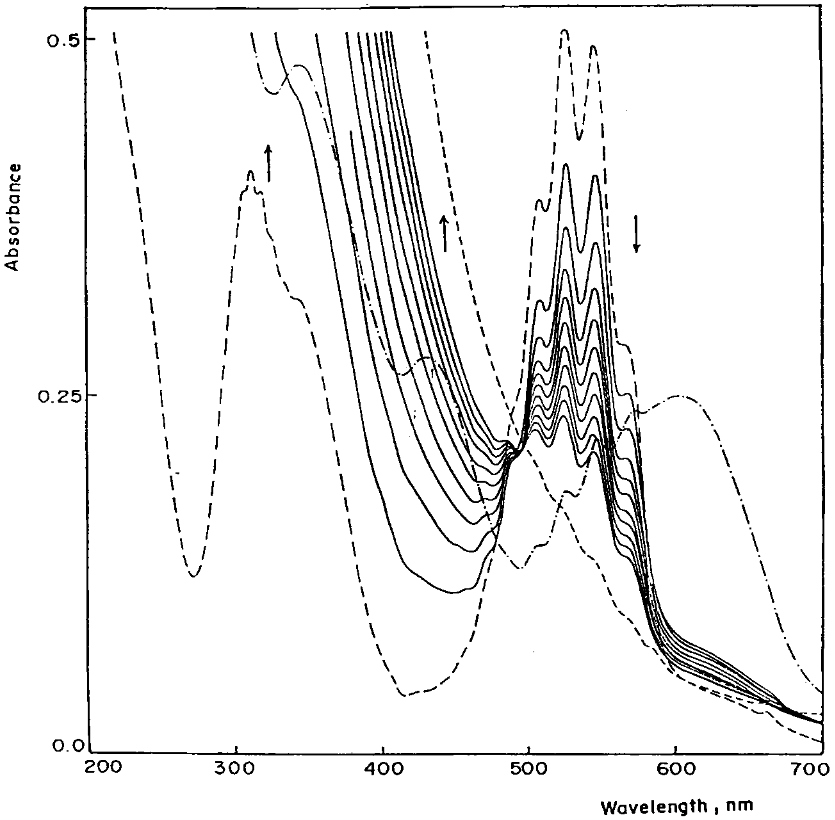


Figure 1. Spectral changes (200~700 nm) in the oxidation of pectate by permanganate ion at $[MnO_4^-] = 2.2 \times 10^{-4}$ $[Pect] = 2.5 \times 10^{-3}$, mol dm^{-1} and 5°C; (---) MnO_4^- ion; (—) intermediate. (-·-·-) using permanganate ion as a reference.

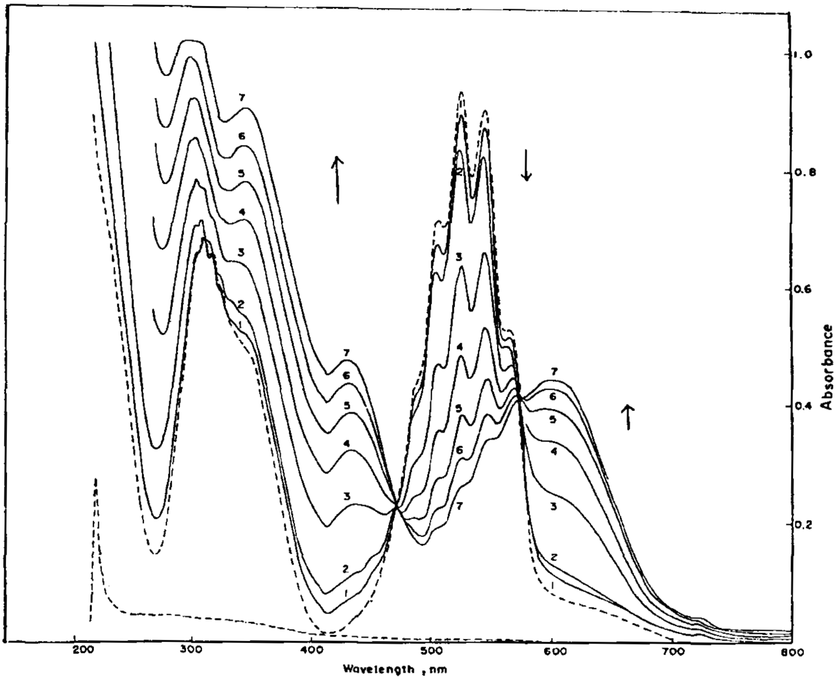


Figure 2. Spectral changes (200 -800 nm) in the oxidation of poly(vinyl alcohol) by permanganate ion. $[MnO_4^-] = 4.31 \times 10^{-4}$, $[PVA] = 5.01 \times 10^{-3}$, $[OH] = 2.5 \times 10^{-2}$ dm^{-3} mol^{-1} and T = 22°C; (---):$[MnO_4^-]$; (—·—·—): PVA

wavelengths of 606, 435, and 350 nm. To our knowledge, the 606 nm band represents the transient Mn(VI) species which absorbed in the visible region.(17-20,28) At this wavelength, the absorption of MnO_4^- is much weaker, thus the detection of MnO_4^{2-} may have no difficulty.

As the concentration of Mn(VI) increases, the intermediate formed at a wavelength of 606 nm decays to give rise to the reaction products as shown in Figures 3 and 4. The isobestic point, which is seen at 575 nm

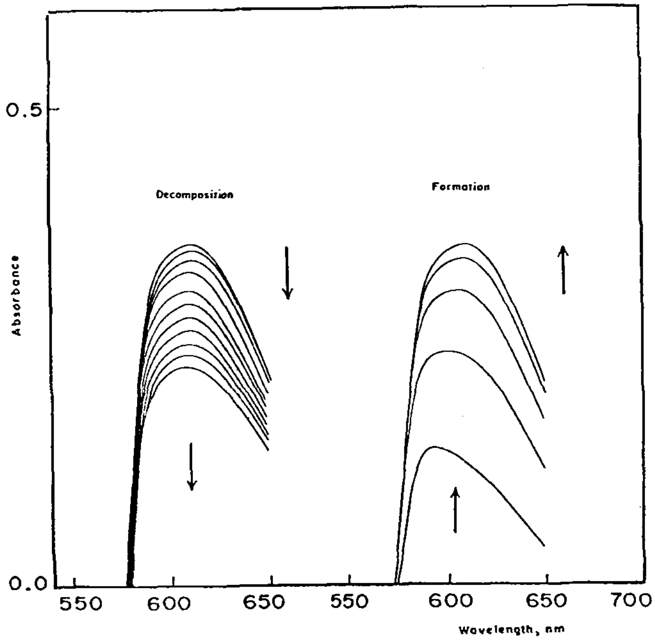


Figure 3. Spectral changes during (a) the formation and (b) the decomposition of the intermediates in the oxidation of pectate by permanganate ion. $[MnO_4^-]$ = 2.2×10^{-4} $[OH^-]$ = 1.1×10^{-3} [Pect] = 2.5×10^{-3}, and 5oC; (a) formation, (b) decomposition.

during the course of reactions, indicates the conversion of MnO_4^- to MnO_4^{2-}, whereas that of ~ 475 nm reveals that the MnO_4^- and Mn(IV) formed, which have absorptions in the visible region, do not necessarily exclude the formation of the detectable manganate(VI) intermediate. Hence, an equilibrium between MnO_4^{2-} and Mn(IV) is suggested. Again, the change in the intensity of the bands observed at wavelengths of 435

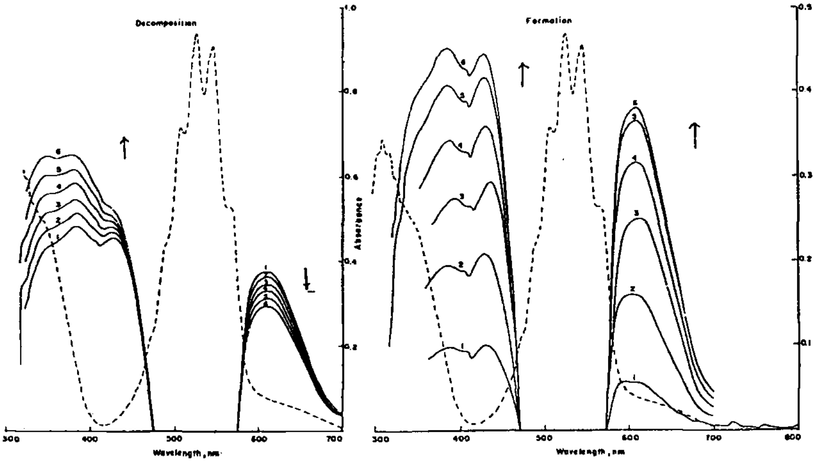


Figure 4. Spectral changes for the formation and decomposition of the intermediate in the oxidation of polyvinyl alcohol by permanganate ion. $[MnO_4^-] = 4.31 \times 10^{-4}$; $[PVA] = 5.01 \times 10^{-3}$; $[OH^-] = 2.5 \times 10^{-2}$ dm^{-3} mol^{-1} and T = 22°C; Reference = $[MnO_4^-]$ and $[OH^-]$ as the same reaction mixture

and 350 nm is due to the increase of the soluble Mn(IV) concentration which does not absorb above 540 nm but which has gradually increasing absorpitivity below this region.

Furthermore, the change in color of the mixture as the reaction proceeded from purple – pink to blue to green may confirm the formation of the stable Mn(VI) and/or Mn(V) short-lived intermediates.

The failure to detect hypomanganate (V) short-lived intermediate may be interpreted by its extreme short lifetime.(20) This suggestion is not without precedent, as the formation of longer- lived Mn(V) is conceivable with sterically rigid olefines(29) and sulfite ion.(16) However, in most other redox reactions, Mn(V) is still postulated as a short-lived intermediate.(20,30,31)

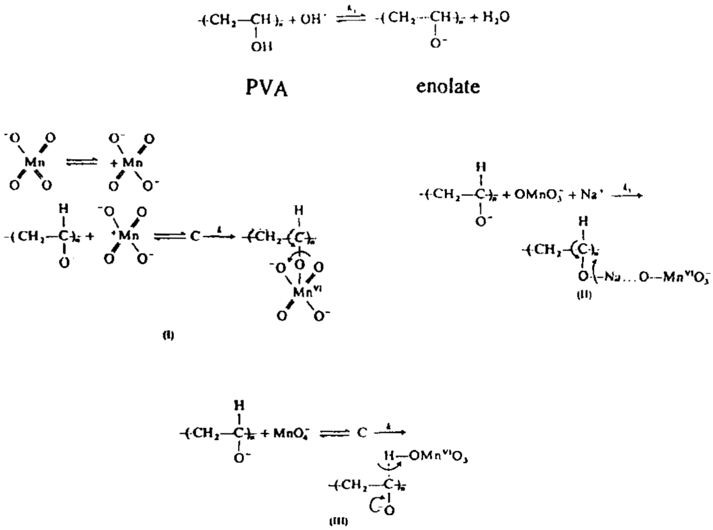
One question that remains to be considered is the nature of intermediate formed from the reaction of MnO_4^- and PVA or MnO_4^- and pectin substrates. Preliminary experiments indicated the formation of keto-derivatives as reaction products for MnO_4^- - PVA and MnO_4^- - pectin redox reactions. These products could be separated from the reaction mixtures, and its presence confirmed by IR and elemental analyses.(32) Hence, reaction mechanisms in good consistency with the experimental observations were suggested in Schemes (A) and (B), respectively.

It was reported that the oxidation of poly (vinyl alcohol) by permanganate ion in alkaline solutions occurs via formation of the intermediate complexes(I), (II) and/or (III)(23,24). Hence, two alternative mechanisms for the formation of the intermediates may be suggested. The first corresponds to the removal of H^+ ion from PVA by the base to give an enolate form, followed by the attack of MnO_4^- ion to the enolate centre (I), or direct attack of MnO_4^- on the enolate centre via Na^+ cations as bridges in order to reduce the net charge of the intermediate complex(II).

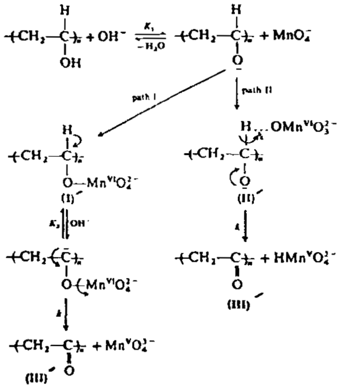
The second mechanism corresponds to the attack of MnO_4^- on the C-H bond(18,20) and the formation of the intermediate (III).

Accordingly, two alternative mechanisms for the decomposition of the intermediates may be considered. The first corresponds to a fast

Formation

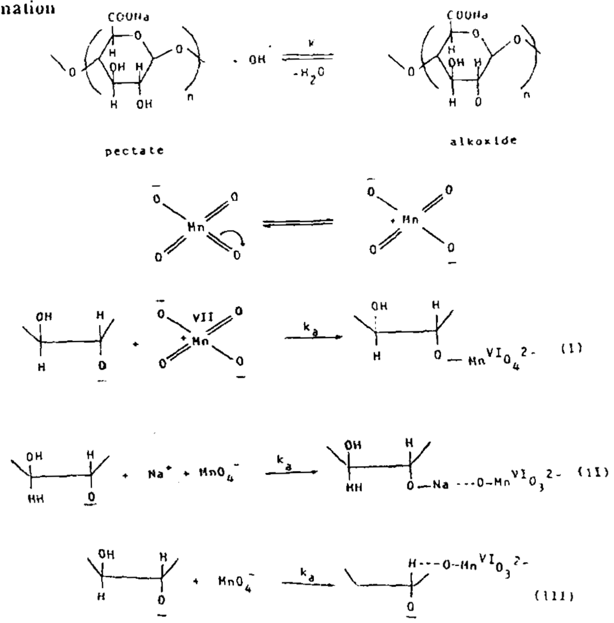


Decomposition

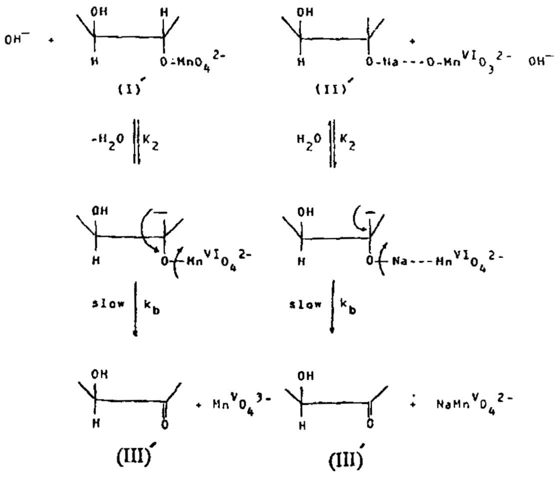


Scheme (A)

Formation



Decomposition



Scheme (B)

deprotonation of the intermediate by the alkali followed by electron transfer from PVA to Mn(VI) as illustrated by reaction - path (I)′. The second mechanism represents the transfer of hydride ion from PVA to MnO_4^{2-} as the rate – determining step as shown in reaction path (II)′.

Reaction paths (I)′ and (II)′ lead to the formation of poly (vinyl ketone) (III)′ as the final product of oxidation of the substrate. Again, the hypomanganate (V) formed may be decomposed as follows

$$2Mn^{V}O_4^{3-} \rightarrow Mn^{IV}_{sol} + Mn^{VI}O_4^{2-}$$

The yellow color which remains even after completion of reaction may be considered as an evidence for the formation of soluble manganese (IV) rather than colloidal MnO_2.(6,7,10,33)

Similarly in the oxidation of pectin by MnO_4^- ion, the experimental observations suggest the formation of alkoxide form of pectate prior to the attack of permanganate ion. This takes place by the removal of a proton from OH groups by the alkali, followed by the attack of MnO_4^- ion to the alkoxide center as discussed previously. The mechanisms of formation and decomposition of the intermediate are illustrated in Scheme (B).

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