

Kinetics of KMnO_4 oxidation of pectin in aqueous KCl solution via cyclic voltammetry

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Abstract: In the present work, The oxidation behavior of the natural polymer "pectin" was examined using potassium permanganate as a strong oxidizing agent via cyclic voltammetry in KCl aqueous solution. A pair of waves was given, as the pectin was oxidized by the permanganate that was reduced, and upon studying a relationship between some physical parameters over time: it was found that most of the reactions follows two steps, the first step is fast, which supports the occurrence of oxidation, and the second is slow, where a complex is formed between permanganate and pectin and their data were discussed.

keywords: Pectin, Cyclic Voltammetry, Potassium permanganate, Solvation Parameters.

1. Introduction

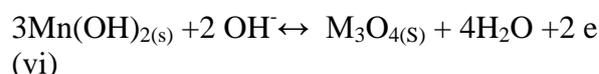
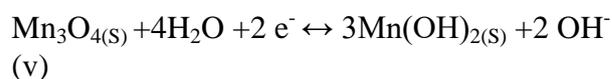
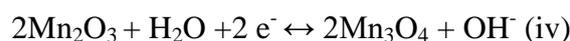
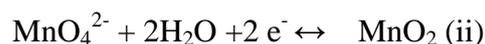
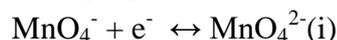
Redox reaction of KMnO_4 in presence of pectin as natural polymer was studied by using cyclic voltammetry in 0.1M KCl. Gold electrode GE was used as working electrode, whereas the other two electrodes are Ag/AgCl standard electrode and platinum wire counter electrode. Potassium permanganate, is very strong oxidizing agent(2), it is has dark purple color. its reduction to divalent manganese to faint pink color. The divalent manganese is further reduced and the product depend on the reaction conditions. Discussion of the effect of oxidation of carboxylic acid or carboxylic natural polymers like pectin by potassium permanganate is necessary for analytical estimation(1-7).

Experimental:

Pectin is a natural polymer, whereas KCl and Potassium permanganate are from Sigma Aldrich Co. Bi distilled water with a conductance of 2.5 micro Siemens, $\mu \text{ ohm}^{-1}$ was used. Cyclic voltammetry potentiostat of the type DY2000 was used for the measurements

Results and discussion:

In low concentration KMnO_4 gave many peaks in the range of 0.625-1.67x10⁻⁵N (8) following equations(i-vi).

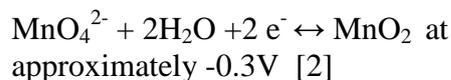
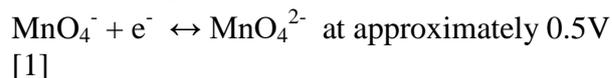


In this work, higher permanganate concentration was used 11.4x10⁻³N was used in 0.1M KCl as supporting electrolyte at 295.75K and gold electrode. The used window range is from 1 volt to -1 V at scan rate 0.1 V/Sec.

The effect of pectin on KMnO_4 waves were observed and given in fig (1).

One reduction wave at approximately -0.5V consuming two electrons (3,8,9).

The suggested electrochemical reduction is as equation [2] after the transfer of MnO_4^- ion to MnO_4^{2-} equation[1] and then to MnO_2 .



The reduction wave following equation [1] need very low KMnO_4 concentration which is not in our range. Need of high KMnO_4 concentration needed for oxidation of pectin with it. the oxidation peak for KMnO_4 in this

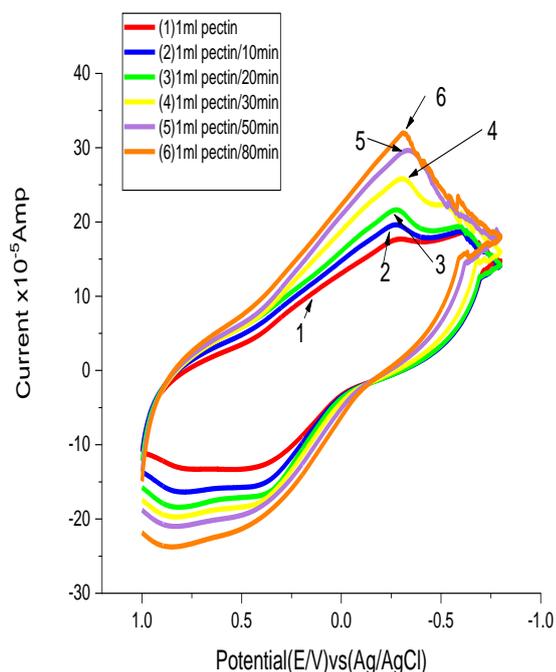
study is broad peak at approximately +0.5V which is opposite of equation[2] consuming also two electrons as:

$MnO_2 \leftrightarrow MnO_4^{2-} + 2H_2O + 2e^-$ at approximately +0.5V [3]

Then studying the resulted redox peaks for potassium permanganate ion is important following the kinetic study of the effect of $KMnO_4$ on pectin natural polymer.

Fig(1): shows the effect of time on pectin+ $KMnO_4$ which explains the increase in the currents for both the anodic, cathodic waves, shift to more positive potentials for the reduction and oxidation peaks. The cyclic voltammograms given in fig(1) indicate the oxidation of pectin by potassium permanganate. After that the potassium permanganate react with pectin by complexation (forming complex and shift in the reduction peak to more negative potentials.

Analysis of the reduction and oxidation peaks the different equations used for the electrochemical.



Fig(1) : Effect of different time of 30ml 0.1 M $KCl+4ml KMnO_4+1ml 11.4 M$ Pectin by using gold electrode at 295.75K and scan rate $0.02V.S^{-1}$.

Voltammetry calculations for the resulted reduction peak and the oxidation peak are

illustrated in the next equations. The cathodic and anodic surface coverage explaining the electrode surface covered by electrostatic species is calculated using equation (4)(10-13):

$$\Gamma_a \text{ or } \Gamma_c = I_{p,c} 4RT / n^2 F^2 A V \quad (4)$$

Where (R) is the universal gas constant, n is the number of electrons in redox reaction, A in cm^2 is electrode surface area, T is the absolute temperature. Q the quantity of electricity need for the redox reaction and can be calculated by applying equation (5) for the anodic and cathodic quantity of electricity(13-18).

$$Q_a, Q_c = n F A \Gamma \quad (5)$$

Diffusion coefficient, anodic and cathodic wave calculated by using equation (6) (19,20)

$$I_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} V^{1/2} \quad (6)$$

Since I_p is the peak current in ampere unit. A in cm^2 is working electrode surface area, and D is the diffusion coefficient. D can be calculated for the cathodic wave and known

as D_c cathodic diffusion coefficient, D_a the anodic diffusion coefficient can be calculated for the anodic peak. V is the scan rate and C is the permanganate normality.

The different between cathodic and anodic peak potential. ΔE_p can be calculated by using equation(7):

$$\Delta E_p = E_{Pa} - E_{Pc} \quad (7)$$

Also for further calculation important parameter K_s , where K_s the heterogenous electron rate constant was calculated by using equation(8)(21-25):

$$k_s = 2.18 (D_c \alpha n_a F V / RT)^{1/2} \exp. \{ \alpha^2 n F (E_{Pc} - E_{Pa}) / RT \}. \quad (8)$$

where α is the charge transfer coefficient, n_a is the number of electrons involved in the anodic, cathodic waves and αn_a can be calculated by using equation (9)(10,11):

$$(E_{Pc} - \{ E_{Pc} / 2 \}) = (1.857RT / \alpha n_a F) \quad (9)$$

Where $E_{Pc}/2$ is the half peak potential and α equal 0.5 as approximation for quasi reversible system. The above parameters were estimated for both the cathodic and anodic peaks of $KMnO_4$ on addition of natural polymer to it 1ml pectin from 1% (W/W) in water. At different time measurements were cited in table (1)

Table (1): Effect of different time of 30ml 0.1 M KCl+4 ml KMnO₄+1ml Pectin by using gold electrode at 295.75K and scan rate 0.02 V.S⁻¹.

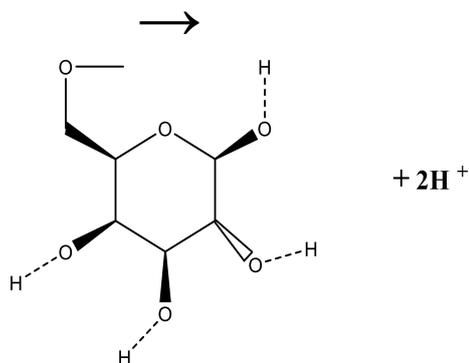
Time (min.)	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-) Ip,a x10 ⁵ Amp	Ip,c x10 ⁵ Amp	Ip,a/Ip,c	E ^o Volt	Da x10 ⁵ cm ² .s ⁻¹	De x10 ⁶ cm ² .s ⁻¹	Anac	ksc x10 ²	Γ c x10 ⁸ mol.cm ⁻²	(+) Qc x10 ⁵ C	Γ a x10 ⁸ mol.cm ⁻²	(-) Qa x10 ⁴ C
0	0.343	0.276	0.619	5.79	2.11	2.7496	0.0333	0.224	0.296	0.5865	1.54E+02	0.8863	5.37	2.43716	1.48
10	0.356	0.260	0.616	8.09	4.11	1.9712	0.0475	0.437	1.12	0.4296	2.42E+02	1.7268	10.5	3.40397	2.06
20	0.311	0.263	0.575	8.90	4.92	1.8078	0.0239	0.528	1.62	0.3925	1.24E+02	2.0705	12.5	3.74314	2.27
30	0.335	0.273	0.608	7.65	8.06	0.9501	0.0310	0.391	4.33	0.2792	3.25E+02	3.3880	20.5	3.21923	1.95
50	0.345	0.323	0.668	6.60	7.14	0.9245	0.0111	0.291	3.40	0.3108	9.82E+02	3.0047	18.2	2.7779	1.68
80	0.345	0.305	0.651	5.84	9.10	0.6421	0.0200	0.228	5.53	0.3168	9.10E+02	3.8279	23.2	2.458	1.49

The difference between cathodic and anodic peaks ΔEp at all the time intervals measured is 0.616 volt indicate the quasi reversible redox reaction which is very near to the reversible value 0.59V. this indicate the redox reaction is light quasi reversible Reaction. Shape peak is obtained for permanganate ion reduction consuming two electrons at approximately -0.3V. the oxidation peak gave broad peak at approximately 0.5V. which splitted into two for indicating the appearance of two electrons mechanism oxidation at intervals with small time difference.

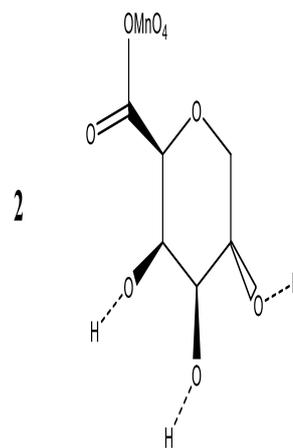
We noticed that oxidation mechanism for pectin by KMnO₄ was observed and supported by:

- (1) Shift of E_{Pc} to more positive values.
- (2) Increase in I_{Pc}.
- (3) Shift of E_{Pa} to more positive values.
- (4) Increase in I_{Pa}: suggested oxidation by KMnO₄.

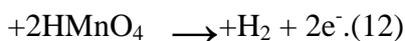
The oxidation mechanism proceed through equations (10) and (12). Equation (11) is an important intermediate.



Beta-D- Gluco-pyranuronic acid beta-D-glucuronic acid
(Pectin)(10)



tetraoxomanganio (2S,3R,4R,5R)-3,4,5-trihydroxytetrahydro-2H-pyran-2-carboxylate



Kinetic oxidation of pectin by KMnO₄:

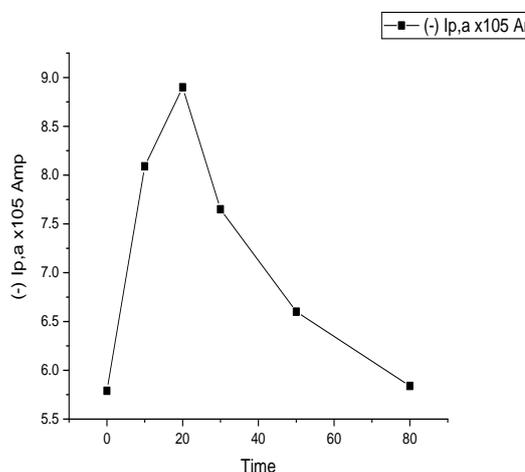


Fig.2. shows the relation between Time and I_{pa} for pectin

As explained in fig(2) the relation between I_{pa} and time increase firstly till 20 minute and decrease afterwards. The first part is the increase in I_{pa} with time due to the oxidation of pectin and then decrease due to complexation reaction between permanganate ion and natural polymer pectin.

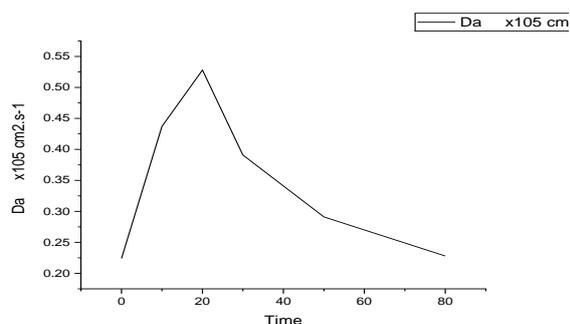


Fig.3. shows the relation between Time and Da for pectin.

Fig (3) the relation between Da for the anodic wave and time in minutes gave the same trend as explained in fig(2) supporting that mechanism given in former section.

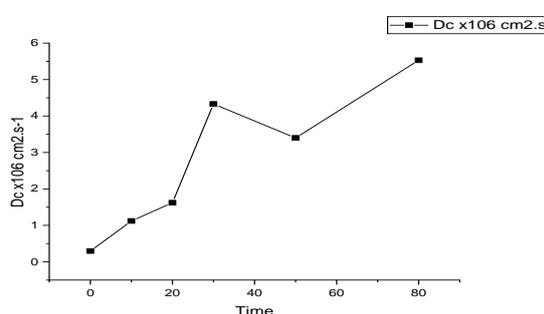


Fig.4. shows the relation between Time and Dc. for pectin

Fig (4) the relation between Dc for the cathodic wave and time in minutes for the reaction between KMnO_4 + pectin is approximately increase by increase in time indicating oxidation reaction mechanism.

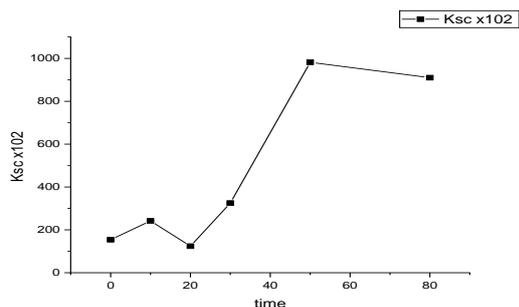


Fig.5. shows the relation between Time and ksc. for pectin

Fig(5) The relation between Ks and time show two mechanisms oxidation and complexation.

Increase in the heterogenous electron rate constant and time in three steps, slow step till time 30minute, fast increase till 50 minute and slow step almost constant above 50 minute.

The steps are:

- (1) Slow oxidation of pectin by KMnO_4 till 30 minute.

- (2) Fast oxidation step of pectin by KMnO_4 from time 30 to 50 minutes.
- (3) Slow complexation step which indicate the constancy of Ks values above 50 minute.

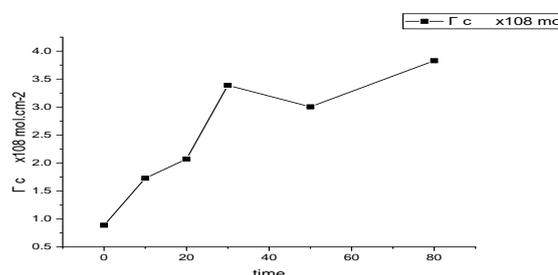


Fig.6. shows the relation between Time and rc. for pectin

Fig(6) The relation between Γ_c ,cathodic surface coverage and time in minutes show increase in the cathodic surface coverage with time do not differentiate between the oxidation and complexation processes.

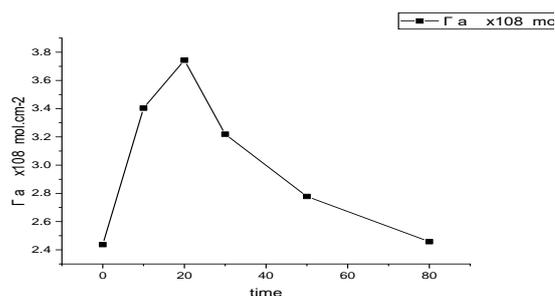


Fig.7. shows the relation between Time and ra. for pectin.

Fig (7) is the relation between Γ_a ,anodic surface coverage and time in minutes show

Two mechanisms, two trends, the first till 20 minute supporting the oxidation mechanism and then decrease above 20 minute. The decrease in Γ_a supports the complexation mechanism at which the electrode is fully covered with complex formed from reaction KMnO_4 with pectin.

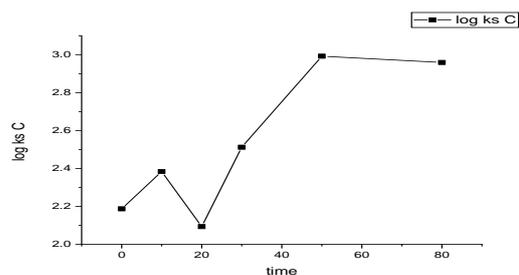


Fig.8. shows the relation between Time and $\log(k_s c)$ for pectin.

The curve drawn in fig (8) and is the relation between $\log K_s$ and time in minutes gave the same trend as curve K_s versus time in minutes.

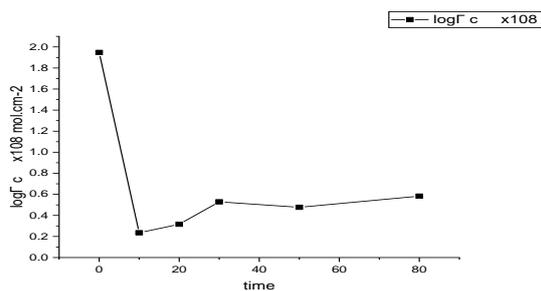


Fig.9. shows the relation between Time and $\log(r c)$ for pectin

Fig (9) is the relation between $\log \Gamma c$ and time in minutes support also the two mechanisms, oxidation and then complexation for the reaction of $KMnO_4$ with pectin.

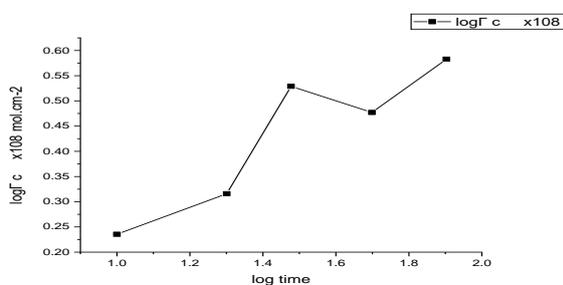


Fig.10. shows the relation between \log Time and $\log(r c)$ for pectin

Fig (10) is the relation between $\log \Gamma c$ and \log time in minutes supports only the oxidation mechanism.

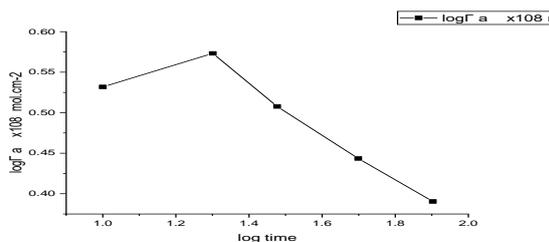


Fig.11. shows the relation between \log Time and $\log(r a)$ for pectin.

Fig (11) is the relation between $\log \Gamma a$ and \log time is the opposite curve of fig (10).

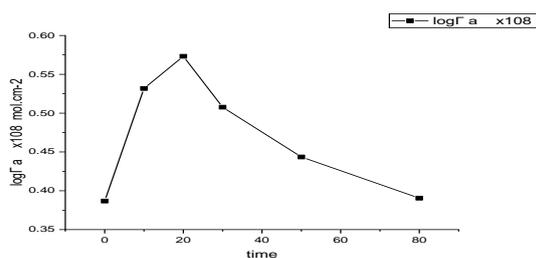


Fig.12. shows the relation between Time and $\log(r a)$ for pectin

The data given in figure 12, which is the relation between $\log \Gamma a$ and time gave two opposite trends with inflection at minute 20, which the time for the differentiation between oxidation and complexation mechanisms.

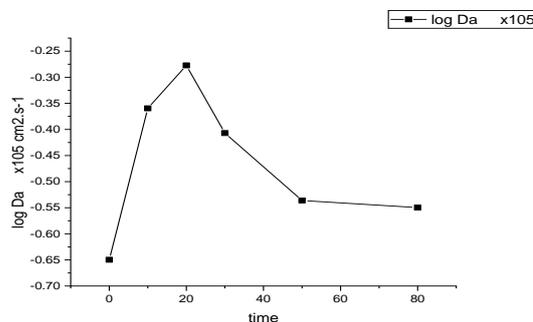


Fig.13. shows the relation between Time and $\log(Da)$ for pectin

Fig (13) same trend as fig (12).

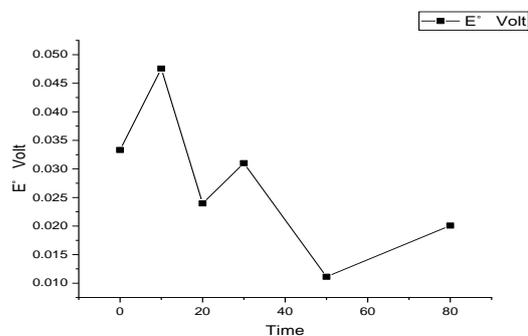


Fig.14. shows the relation between Time and E^0 volt for pectin.

The relation between E^0 and time for reaction of $KMnO_4$ with pectin.

Fig (14) shows no specific trend other than decrease in values due to the electrode interactions.

Conclusion:

Cyclic voltammetry of Pectin was done and the redox peaks were explained. Oxidation of Pectin by $KMnO_4$ was illustrated and examined. Oxidation stability constant and Gibbs free energy of oxidation were evaluated and their data were explained. Also complexation is suggested for the interaction of $KMnO_4$ with Pectin after oxidation process.

4. References

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