MANSOURA JOURNAL OF CHEMISTRY
Official Journal of Faculty of Science, Mansoura University, Egypt
E-mail: scimag@mans.edu.eg ISSN: 2974-4938

Electrochemical Redox Reaction, Kinetics for KMnO4, Oxidation parameters for Pectin in NaOH solutions Cyclic Voltammetically

Esam A.Gomaa[*], *Elsayed R. H. El-Gharkawy, Mohamed M. Hamouda, Nouran M. Shams*

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt.

Received:1/12/2020
Accepted:28/12/2020

Abstract: Redox reaction of $KMnO_4$ in presence of pectin as a natural polymer was studied cyclic voltammetically in 0.1 M NaOH at 296.85K and scan rate 0.1 v/s. Glassy carbon electrode was used as working electrode, Ag/AgCl reference electrode and platinum wire auxillary electrode were used. The detection of divalent manganese ion was used to detect the reduction oxidation reaction affected by the used polymer in the alkaline 0.1M NaOH solutions. Different kinetic and thermodynamic parameters were obtained at different time measurements by the oxidation of the used natural polymer with $KMnO_4$ and the obtained data were discussed.

keywords: Cyclic Voltammetry, Potassium Permanganate, Pectin, Oxidation.

1.Introduction

In strong alkaline medium, the stable reduction product of permanganate is manganate (VI) ion, MnO_4^{2-} (1) was formed as further reaction:

$MnO_4^- + e^- \leftrightarrow MnO_4^{2-}$ ($\mathcal{E}^\circ$= +0.56V) (1)

In alkaline solutions permanganate reduced to Mn(IV) as follows:

MnO_4- + $2H_2O$ + 3e- ↔ MnO2 + 4OH- ($\mathcal{E}\circ$= +0.6V) (2)

Process Mn(VII)→Mn(IV) in alkaline solutions indicates the formation of colloidal soluble MnO_2 species (2,3). After the complete consumption of permanganate ion, MnO_2 plays important role in auto-catalytic and oscillating reactions (4).

Scheme (I) illustrates the transformstion of Mn(VII) to Mn(V) and rapid oxidation of the hypomanganate ion (4).

Fast

Mn(VII) + S ↔ Mn(V) + P (3)

Fast

Mn(VII) + Mn(V)↔ 2Mn(VI) (4)

(scheme I)

The heptavalent manganese Mn(VII) changes to Mn(IV) in alkaline solution as a final oxidation state.

Our purpose here is to study the oxidation of natural polymer pectin by $KMnO_4$ in alkaline NaOH media kinetically and thermodynamically with suggested redox mechanisms.

2. Experimental:

Potassium Permanganate is provided from Al-Gomhoria Co. Where as pectin is provided from Adwic Chemicals Co.

DY2000 potentiostat was used for measuring the cyclic voltammograms. Glassy carbon electrode GCE was used as working electrode. The other two electrodes for the circuit are Ag/AgCl reference electrode and platinum wire counter electrode. 30 ml of the solutions were measured after passing N_2 gas on it to ensure the removal of dissolved oxygen.

3. Results and discussion:

Cyclic voltammetry of $KMnO_4$ alone in 0.1M NaOH. Many peaks for the used potassium permanganate ranging from concentration 0.332×10^{-3} to 3.23×10^{-3} N in window range from 1 to -1V in 0.1M NaOH as:

$MnO_4^- + e^- \leftrightarrow MnO_4^{2-}$ (i)

$MnO_4^{2-} + 2H_2O + 2e^- \leftrightarrow MnO_2$ (ii)

$MnO_2 + 1/2\ O_2 \leftrightarrow Mn_2O_3$ (iii)

$2Mn_2O_3 + H_2O + 2e^- \leftrightarrow 2Mn_3O_4 + OH^-$ (iv)

$Mn_3O_{4(S)} + 4H_2O + 2e^- \leftrightarrow 3Mn(OH)_{2(S)} + 2OH^-$ (v)

$3Mn(OH)_{2(s)} + 2\ OH^- \leftrightarrow\ M_3O_{4(S)} + 4H_2O + 2\ e^-$ (vi)

The many peaks obtained are appeared in Fig.(1) indicating the developing of many reduction peaks and oxidation peaks on using hydroxide ions medium shifting the equilibrium of the above mentioned equations from (i) to (v) to right side of equations. The different peaks appeared in experimental as redox peaks which appeared are:

1-First reduction wave at ≈ 0.5V corresponding to the equation (1) (5).

2-Second reduction peak at -0.3V following equation (5)

$MnO^{2-} + 2H_2O + 2e^- \leftrightarrow MnO_2$ (5)

3-Main oxidation peak at 0.4V following equation (6) (5)

$MnO_2 \leftrightarrow MnO_4^{2-} + 2H_2O + 2e^-$ (6)

We further take in consideration the main reduction peak at -0.3V and the main oxidation peak at 0.4V. This two couple peaks were concentrated in study.

Analysis of reduction and oxidation peaks using the different equations.

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 (7) (6-9):

Γa or $\Gamma c = Ip,c\ 4RT / n^2\ F^2\ A\ V$ (7)

Where (R) is the universal gas constant, n is the number of electrons in redox reaction, A in cm2 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 (8) for the anodic and cathodic quantity of electricity(9-14).

$Qa, Qc = n\ F\ A\ \Gamma$ (8)

Diffusion coefficient, anodic and cathodic wave calculated by using equation (9) (15,16)

$Ip= (2.69x10^5)\ n^{3/2} A\ C\ D^{1/2}\ V^{1/2}$ (9)

Since Ip is the peak current in ampere unit. A in cm2 is working electrode surface area, and D is the diffusion coefficient. D can be calculated for the cathodic wave and known as Dc cathodic diffusion coefficient, Da 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. ΔEp can be calculated by using equation(10):

$\Delta Ep = E_{Pa} - E_{Pc}$ (10)

Also for further calculation important parameter Ks, where Ks the heterogenous electron rate constant was calculated by using equation(11) (17-21):

$k_s = 2.18\ (\ Dc\ \alpha n_a\ F\ V/RT\ )^{1/2}\ exp.\ \{\ \alpha^2\ n\ F(\ E_{Pc} - E_{Pa}\ )/\ RT\ \}$ (11)

where α is the charge transfer coefficient, na is the number of electrons involved in the anodic, cathodic waves and αna can be calculated by using equation (12) (6.7):

$(E_{Pc} - \{\ E_{Pc}\ /2\}) = (1.857RT/\ \alpha naF)$ (12)

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 2ml pectin from 1% (W/W) in water. At different time measurments were cited in table (3) .

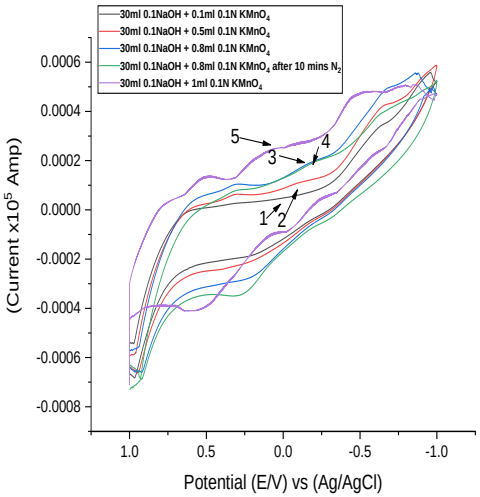


Fig.1. Effect of different concentrations of KMno4 in 0.1M NaOH by using glassy carbon electrode at 296.85K and scan rate 0.1V.S-1.

Effect of scan rate were done for $KMnO_4$ in 0.1M NaOH at scan rate 0.1 and 0.05 and we found that parameters are decrease with the decrease on the scan rate indicating that the electrochemical reaction is diffusion controlled different cyclic voltammetry

Table (1): Effect of different concentrations of KMno4 in 0.1M NaOH by using glassy carbon electrode at 296.85K and scan rate 0.1V.S^{-1}.

[N] x10^3 mol.L^{-1}	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-) Ip,a x10^5 Amp	Ip,c x10^5 Amp	Ip,a/Ip,c	E° Volt	Da x10^{10} cm^2.s^{-1}	Dc x10^{10} cm^2.s^{-1}	αnac	Ksc x10^2	Γ c x10^9 mol.cm^{-2}	(+) Qc x10^5 C	Γ a x10^9 mol.cm^{-2}	(-) Qa x10^5 C
0.332	0.2086	-0.1686	0.3772	5.85	6.26	0.935	0.01999	5429x10^3	6210x10^3	0.1849	7290	5.2866	3.20	4.9444	3.00
1.64	0.1958	-0.1039	0.2997	4.10	4.72	0.869	0.04590	1096x10^2	1450x10^2	0.4408	379	3.988	2.42	3.46736	2.10
2.60	0.2499	-0.1301	0.3800	5.48	7.43	0.737	0.059877	77790	1430x10^2	0.4306	1790	6.28084	3.81	4.62752	2.80
2.60After 10 mins N2	0.2722	-0.2289	0.5011	8.01	7.29	1.099	0.02166	0.166638	0.138	0.3583	17	6.16046	3.73	6.77268	4.10
3.23	0.5814	-0.1334	0.6175	17.5	3.66	4.785	0.22399	5165x10^2	226x10^2	0.4602	75700	3.0948	1.88	1.48081	8.97

Table (2): Effect of different scan rates of(3.23x10^{-3} N) KMno4 in 0.1M NaOH by using glassy carbon electrode at 296.85K.

v V.S^{-1}	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-)Ip,a x10^5 Amp	Ip,c x10^5 Amp	Ip,a/Ip,c	E° Volt	Da x10^{10} cm^2.s^{-1}	Dc x10^{10} cm^2.s^{-1}	αna	ksc x10^2	Γ c x10^9 mol.cm^{-2}	(+)Qc x10^{5}C	Γ ax10^9 mol.cm^{-2}	(-) Qa x10^{5}C
0.1	0.5814	-0.1334	0.6175	17.5	3.66	4.785	0.22399	5165x10^2	226x10^2	0.4602	75700	3.0948	1.88	1.48081	8.97
0.05	0.21295	-0.2330	0.4459	13.1	11.3	1.160	0.01001	0.5738	0.426	0.2573	6.10	19.0248	11.5	22.073	13.4

Table (3): Effect of Time on 2ml 1%Pectin + 30ml 0.1M NaOH + 1ml 0.1N $KMnO_4$ by using glassy carbon electrode at 296.85K and scan rate 0.1V.S^{-1}.

Time min	[N] x10^3 mol.L^{-1}	[P] x10^3 mol.L$^-$	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-) Ip,a x10^5 Amp	Ip,c x10^5 Amp	Ip,a/Ip,c	E° Volt	Da x10^{10} cm^2.s^{-1}	Dc x10^{10} cm^2.s^{-1}	αnac	Ksc x10^{-2}	Γ c x10^9 mol.cm^{-2}	(+) Qc x10^5 C	Γ a x10^9 mol.cm^{-2}	(-) Qa x10^5 C
0	3.03	6.06	0.4467	-0.2260	0.6727	39.8	4.49	8.860	0.1103	3.02	0.0384	0.7029	0.0364	3.7923	2.3	33.601	20.4
5	3.03	6.06	0.4760	-0.2237	0.6997	37.8	5.24	7.203	0.1262	2.72	0.0524	0.6954	0.0716	4.4276	2.68	31.891	19.3
7	3.03	6.06	0.4910	-0.2214	0.7124	34.8	3.50	9.923	0.1348	2.30	0.0234	0.8147	0.0664	2.9578	1.79	29.349	17.8
10	3.03	6.06	0.5096	-0.2195	0.7291	38.7	3.98	9.741	0.1450	2.86	0.0301	0.8762	0.108	3.3565	2.03	32.695	19.8
15	3.03	6.06	0.5027	-0.2153	0.7180	36.5	4.48	8.141	0.1437	2.54	0.0383	0.8089	0.0945	3.7841	2.29	30.805	18.7
17	3.03	6.06	0.4718	-0.2071	0.6789	32.5	4.05	8.020	0.1323	2.01	0.0312	0.8439	0.0406	3.4186	2.07	27.418	16.6
30	3.03	6.06	0.5060	-0.2051	0.7111	32.8	4.62	7.098	0.1505	2.05	0.0406	0.8414	0.0867	3.8982	2.36	27.67	16.8
40	3.03	6.06	0.5056	-0.2072	0.7127	36.3	3.98	9.117	0.1492	2.51	0.0301	0.8704	0.0784	3.3588	2.04	30.623	18.6

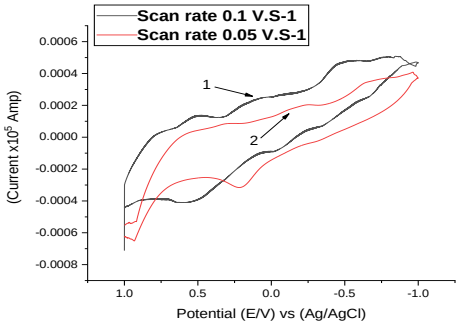
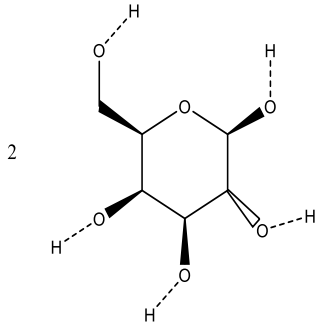


Fig.2. Effect of different scan rates of (3.23x10^{-3} N) KMno4 in 0.1M NaOH by using glassy carbon electrode at 296.85K

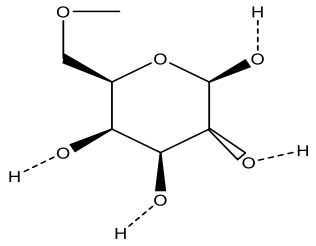
1) Increase in Ip_a.

The oxidation mechanism proceed through equations (13) and (15). Equation (14) is an important intermediate.



(2*R*,3*S*,4*S*,5*R*,6*R*)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2,3,4,5-tetraol

(Pectin)



Beta-D- Gluco-pyranuronic acid beta-D-glucuronic acid

…..(13)

[P] is pectin concentration.

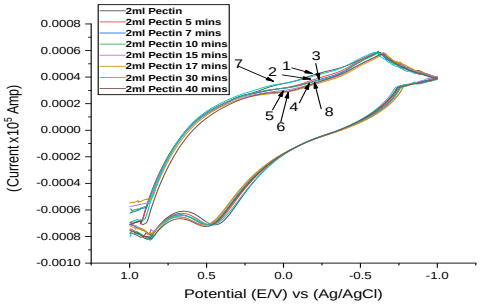


Fig.3. Effect of Time on 2ml 1%Pectin + 30ml 0.1M NaOH + 1ml 0.1N $KMnO_4$ by using glassy carbon electrode at 296.85K and scan rate 0.1V.S^{-1}.

Kinetic oxidation parameters for pectin by $KMnO_4$ in alkaline medium (0.1M NaOH). the applications of equations (7) to (12) on the oxidation of pectin by $KMnO_4$ in 0.1M NaOH were done and the different data were tabulated

in table (3) at the used different times interval at 296.85K. all measurements were done on the use 1%(w/w) for pectin solution in H_2O. The difference between anodic and cathodic peaks ΔE_p at all time intervals is in the range of 0.7V indicating the quasi reversible redox reaction which is very near to the reversible one 0.59V. This indicates that the reaction is quasi reversible.. Two sharp peaks are obtained, one reduction at -0.3V and one oxidation at 0.4V which indicate agreement of specific reaction of the selected species.

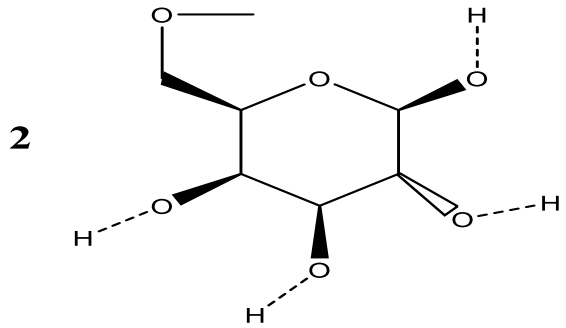
We noticed that oxidation mechanism for pectin by $KMnO_4$ was observed and supported by:

2) Shift of Ep_c to more positive values.

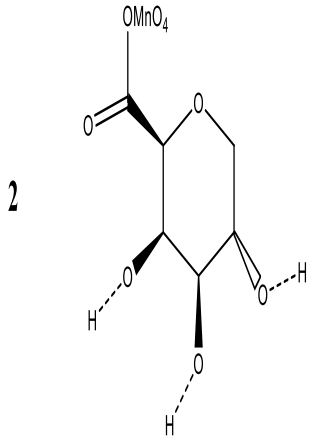
3) Increase of Ip_c.

4) Shift of Ep_a to more positive values.

MnO_4^- + Na^+ ↔ $NaMnO_4$ …… (14)



+$NaMnO_4$ →



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

Na + e^- .(15)

The reaction between the permangante ion and the Na^+ in NaOH to form neutral molecule. Then the charge on the formed complex will be decreased owing to either presence of Na^+ cation or Mn-O bond polarization (22,23).

This means that the above two processes facilitate the attack of the oxidant on the center of the polymer substrate.

Kinetic oxidation of pectin by $KMnO_4$ in alkaline medium:

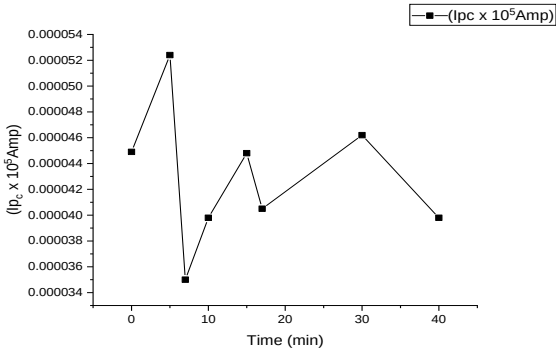


Fig.4. The relation between Time and Ip_c for Pectin+$KMnO_4$.

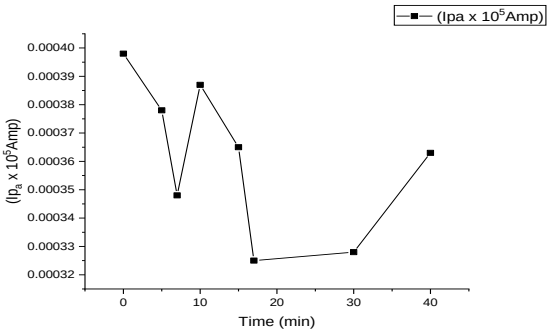


Fig.5. The relation between Time and Ipa for Pectin+$KMnO_4$.

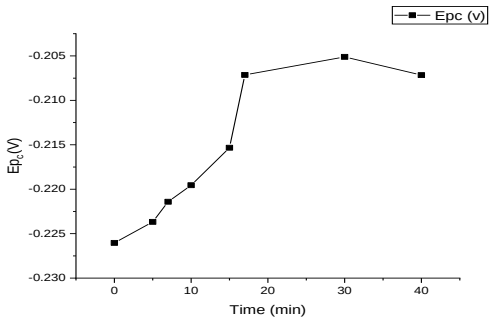


Fig.6. The relation between Time and Epc for Pectin+$KMnO_4$.

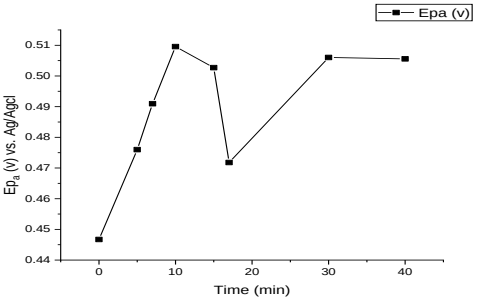


Fig.7. The relation between Time and Epa for Pectin+$KMnO_4$.

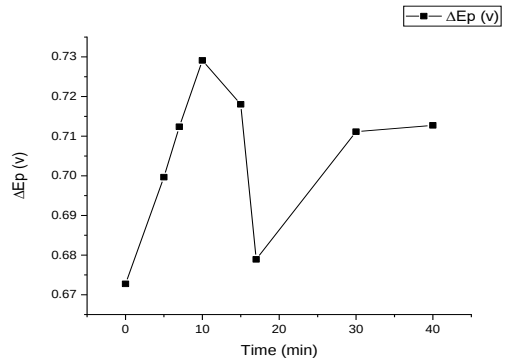


Fig.8. The relation between Time and ΔEp for Pectin+$KMnO_4$.

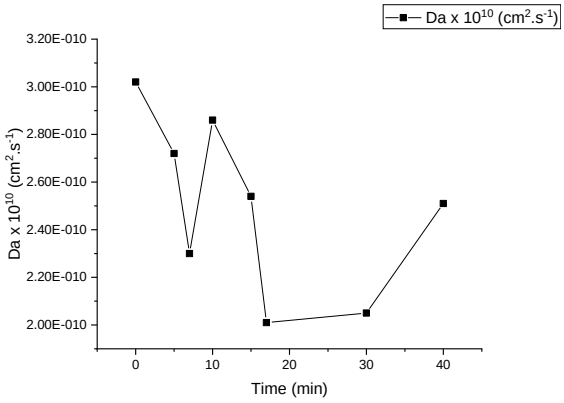


Fig.9. The relation between Time and Da for Pectin+$KMnO_4$.

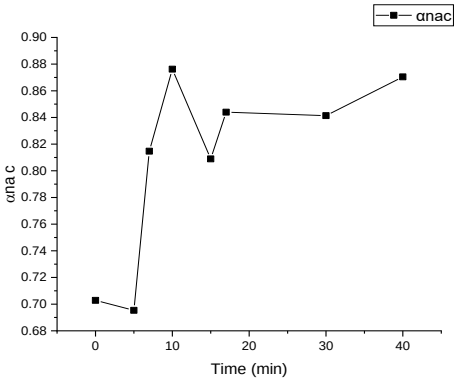


Fig.10. The relation between Time and αna for Pectin+$KMnO_4$.

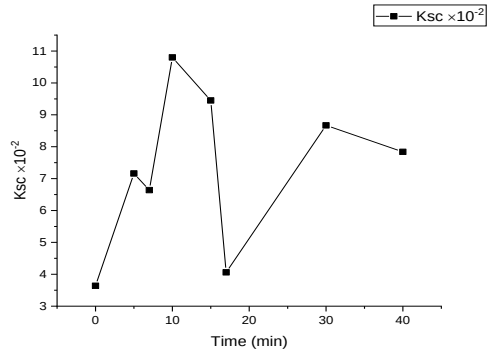


Fig.11. The relation between Time and K_s for Pectin+$KMnO_4$.

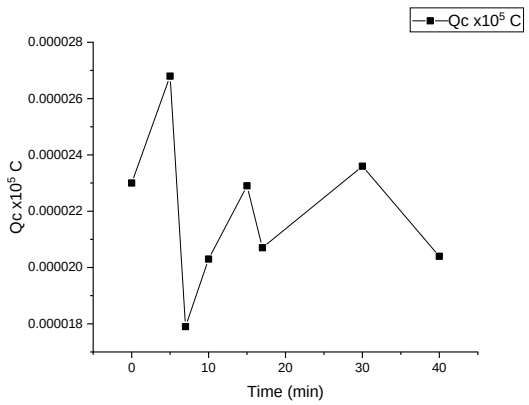


Fig.12. The relation between Time and Q_c for Pectin+$KMnO_4$.

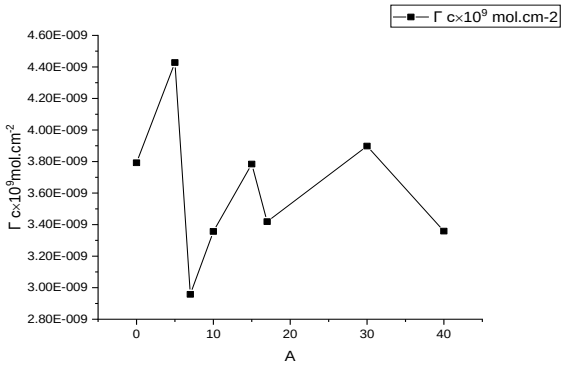


Fig.13. The relation between Time and Γ_c for Pectin+$KMnO_4$.

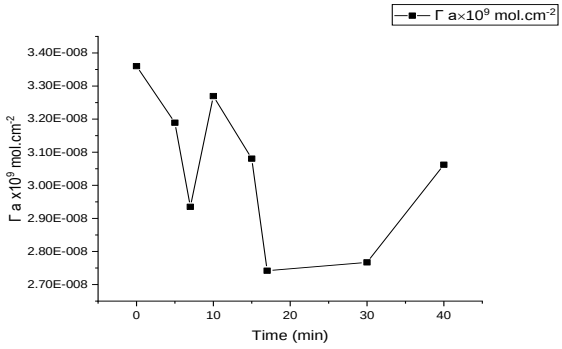


Fig.14. The relation between Time and Γ_a for Pectin+$KMnO_4$.

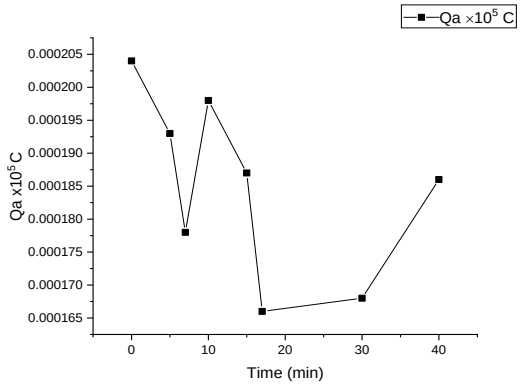


Fig.15. The relation between Time and Q_a for Pectin+$KMnO_4$.

The different relations were done above and the obtained curves and data cited in table (3) prove the following remarks:

1) ΔEp values are almost the same indicate that the reaction is not complexation but oxidation reaction.
2) Ip_c decrease by time indicating more oxidation of pectin by adding $KMnO_4$ in alkaline 0.1M NaOH.
3) Ep_c is shifted to less negative potentials by time indicating increase of the oxidation process by time.
4) Ep_a values are shifted to more positive values by time indicating also more oxidation by time.
5) Da, Diffusion coefficient values are decreased by time indicating increase of diffusion characters.
6) αna increase by time for the reaction of $KMnO_4$ + pectin indicating the increase of the quasi reversible reaction towards irreversible one.
7) The anodic quantity of electricity Qa for pectin +$KMnO_4$ are decreased by time indicating little quantity of electricity needed by time.

Table (4): Oxidation constant for (2 ml Pectin) by $KMnO_4$ in 0.1M NaOH

Time min	[N] $x10^3$ mol..L^{-1}	[L] $x\ 10^3$ mol.L^{-1}	(Ep,1/2)M	(Ep,1/2)C	ΔE v	J (L/J)	Log βj	ΔG (KJ/mol)
0	3.03	6.06	0.223999	0.110330	0.113669	2	8.294124	-47.14238
5	3.03	6.06	0.223999	0.126163	0.097836	2	7.756569	-44.08701
7	3.03	6.06	0.223999	0.134776	0.089223	2	7.481926	-42.27815
10	3.03	6.06	0.223999	0.145011	0.078988	2	7.116674	-40.44996
15	3.03	6.06	0.223999	0.143690	0.080309	2	7.161525	-40.70489
17	3.03	6.06	0.223999	0.132321	0.091678	2	7.547510	-42.89876
30	3.03	6.06	0.223999	0.150456	0.073543	2	6.931813	-39.39924
40	3.03	6.06	0.223999	0.149207	0.074792	2	6.974218	-39.64026

The oxidation constant (β_{ox}) for interaction of $KMnO_4$ with pectin in 0.1M NaOH was evaluated by using equation (16)

$$(E½)_{ox}-(E½)_{M}=(2.303RT/nF)(Log\beta_{ox})+(2.303RT/nF)\ Log\ C_x \text{..}\ (16)$$

Knowing that $(E½)_M$ is the half wave potential for $KMnO_4$ in absence of pectin. $(E½)_{ox}$ is the half wave potential in presence of pectin at different time intervals. The oxidation Gibbs free energies for interaction of $KMnO_4$ with pectin in 0.1M NaOH were evaluated by the use of equation (17)

$$\Delta G_{ox}=2.303RT Log\ \beta_{ox} \ldots (17)$$

The evaluated thermodynamic parameters β_{ox}

and ΔG_{ox} for interaction of $KMnO_4$ + pectin are represented in table (4).

The data on table (3)&(4) and Fig. (3) indicate the oxidation of Pectin by $KMnO_4$ in alkaline medium and the mechanism of Pectin by $KMnO_4$ took place by two mechanisms, on step fast and followed by slow one for each electron one electron consumed in oxidation redox reaction.

Conclusion:

Pectin is oxidized by $KMnO_4$ by two electron mechanism processes. One electron fast and followed by other slow. The Gibbs free energies of oxidation for pectin+$KMnO_4$ indicate big oxidation parameters.

4. References

1. Timmanagoounder, P. L., Hiremath, G. A. A., Nandibewoor, S. T., (1997), Trans. Met. Chem., **22**, 193-196.
2. Simandi, L.I., Jáky, M., Savage, C.R., Schelly,Z.A., (1985) *J.Am.Chem.Soc*., ,**107**,4220_4224.
3. Pode, J. S. F.,Waters, W.A.,(1956) *J.Chem,Soc*.,717_725.
4. Panari, R.G., Chougale, R.B., Nandibewoor, S.T., (1998) *Polish J.Chem*., ,**72**,99_107.
5. Bratsch, S.G, *(*1989) *J. Phys. Chem. Ref. Data,* **18**,1_21,.
6. Gosser, D. K. (1993) Cyclic Voltammetry: Simulation and Analysis of Reaction Mechanisms; VCH New York,; Vol. **43**.

7. Bamford, C. H.; Tipper, C. F. H.; Compton, R. G (1986.) Electrode Kinetics: Principles and Methodology; Elsevier,; Vol. **26**.
8. Brownson, D. A. C.; Banks, C. E. (2014) ;Interpreting Electrochemistry. In The handbook of graphene electrochemistry; Springer, pp 23–77.
9. Gomaa, E. A.; Mousa, M. A.; El-Khouly, A. A. (1985)Association, Dissociation and Hydrogen Bonding of Salicylic Acid in Water N, N-Dimethylformamide Mixtures. Thermochim. Acta, **89,** 133–139.
10. Gomaa, E. A.; Ghandour, M. A.; Abo-Doma, R. A. (1985) Polarographic Behaviour of Uranyl Ion in Maleic Acid and Maleate Buffer Solutions. Monatshefte für Chemie/Chemical Mon., **116 (1),** 33–42.
11. Mousa, M. A.; El-Khouly, A. A.; Gomaa, E. A.; Aly, A. A. M. (1986) Electrical Conduction in $γ$-Irradiated-and Unirradiated-Pure and Doped Samples of Cr2O3. Zeitschrift für Phys. Chemie, **267 (1)**, 125–130.
12. Gomaa, E. A.; Hafez, M. A.; Moussa, M. N. H. (1986) Conductivity of Anisaldehyde Carbohydrazone Methyl Trimethyl Ammonium Chloride Complexes of Some Transition Metals in DMF at 25 OC. Bull. Soc. Chim. Fr. 1986, No. 3, 361–363.Gomaa, E. A. solubility of tetraphenyl derivatives Ph4C, Ph4Ge and Ph4AsBPh4 in aqueous hexamethylphosphotriamide solutions at 25-degrees-c. *Indian J. Techno*l., **24 (11),** 725–726.
13. Gomaa, E. A.; ELASKLANY, A. H.; Moussa, M. N. H. (1987), dissociation of KCl in mixed hexamethylphosphortriamide water solvents. Rev. Roum. Chim. **32 (3)**, 243–247.
14. pimiento .V. , lavabre.D., levy.G., Micheau.J.C. (1994) *J. Phys.Chem*., ,**98**,13294.
15. Mata-Perez, F., Perez-Benito, J.F., land(1985), *J. chem*, ,**63**,988.
16. Gomaa, E. A.; Abuelnader,H.M,BUELNADER,Partition, (1987) association and interaction of trichloroacetic acid in various organic solvents. *Indian J.of Technology*, pp 297–298.
17. Gomaa, E. A. (1987) Solute-Solvent Interactions of Some Univalent-Univalent Salts with Various Organic Solvents at 25oC. Thermochim. Acta, **120**, 183–190.
18. Gomaa, E. A. (1988) The Polarographic Electroreduction of Uranyl Ion in Arsenic Acid Solution. Monatshefte für Chemie/Chemical Mon., **119 (3)**, 287–293.
19. Wang, Y.; Hernandez, R. M.; Bartlett, D. J.; Bingham, J. M.; Kline, T. R.; Sen, A.; Mallouk, T. E. (2006) Bipolar Electrochemical Mechanism for the Propulsion of Catalytic Nanomotors in Hydrogen Peroxide Solutions. Langmuir, **22 (25),** 10451–10456.
20. Gomaa, E. A. (1988) Theoretical Contribution of Solvation of AgBr in Some Organic Solvents at 25^{o}C. Thermochim. Acta, **128**, 99–104.
21. Zaafarany, I.A., (2013) *Journal of American Science*, ,**9(12),**233_247
22. Malik, M.A., Ilyas, M., Khan, Z., Indian (2009) *Journal of Chemistry*, **48**, 189_193
23. Jáky, M., Simandi, L.I., React. Kinet. (1981) Catal. Lett., , **18**, 485_489 .
24. Cherry, A.K., Am. (1962) Water Works Assoc., **54**, 417_424 .
26 Stewart, B.,"oxidation in Organic Chemistry" part A, Wiberg, K.B.(Edn), Academic Press, New York, Chapter 1,1965