



2017

International Journal of ChemTech Research CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555 Vol.10 No.7, pp 341-349,

Kinetics of Oxidation of few organic substrates by chromium (VI) compounds – A Review

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Abstract : Chemical Kinetics is the study of time as a prime factor that adds interest and difficulty to this branch of chemistry. The testing of rate theories, the measurment of equilibrium constants, the analysis of solution, including the solutes and solvents and their properties depend upon the rate of the reaction. The highly toxic chromium (VI) compounds are converted into environmental friendly non- toxic chromium (III) compounds by using several oxidants like Nicotinum dichromate, Piperidinium chlorochromate, Quinolinium fluorochromate, Quinolinium dichromate. The reaction kinetics and rate constant for various chemical reactions are studied and the activation parameters have been evaluated. The key to the application of kinetics is also to determine the quality loss of deterioration of food. Key Words: Chemical kinetics, Rate constant, Nicotinium dichromate, Piperidinium chlorochromate, Quinolinium fluorochromate, Quinolinium dichromate.

Introduction

The metal chromium has both beneficial and detrimental properties. Cr (III) is essential in human nutrition in glucose metabolism. But most of the hexavalent compounds are toxic, and cause lung cancer^{1,2, 3, 4}. Economically the advantages of chromium have wide applications in industries, such as the production of stainless steel, in electroplating, tanning, pigment and chemical industry, etc.,. The soil, groundwater and surface water are contaminated with anthropogenic Cr (VI)^{5,6}. To understand the mechanistic aspect of reduction of Cr (VI) to Cr (III), several kinetics studies of chromic acid oxidation of different types of organic substrates have been carried out by different workers^{7, 8}. The source of Cr (VI) is being chromium trioxide, sodium or potassium dichromate. The structure of chromium trioxide has been determined by X-ray analysis⁹ to be a linear polymer of chromium and oxygen atoms, with two additional oxygen atoms linked to each chromium atom. It is polymerised in water and forms strong acid¹⁰

 $(CrO_3)_n + n H_2O \longrightarrow n H_2CrO_4$ $H_2CrO_4 \longrightarrow H^+ + HCrO_4$ $K_1 = 1.21 \text{ mol/lit.}$ $HCrO_4^- \implies H^+ + CrO_4^{2-}$ $K_2 = 3.0 \times 10^{-7} mol/lit.$

Oxidation States of Chromium Metal

 Cr^{+2} , Cr^{+3} , Cr^{+6} are the stabe states and in nitrosyls, carbonyls group ⁻², ⁻¹ state is seen. Cr^{+4} , Cr^{+5} are unstable in water and they form Cr^{+3} , Cr^{+6} . Cr^{+6} is used as an oxidant for various reactions and the source is mentioned above. Organic compounds are oxidised in presence of acids like H₂SO₄, CH₃COOH, acetone, DMSO and ethers if the compounds are water soluble. Chromium (VI) exists as aceto chromate ion in presence of 97% acetic acid³⁸. New chromium species are formed on adding anions like Cl⁻, Br⁻, F⁻, and SO₄²⁻ anions.



Experimental and Discussion

1. Nicotinium Dichromate - Oxidation of Few Amino Acids by NDC:

Nicotinum Dichromate (NDC) is a mild, non-hygroscopic, stable and selective oxidizing reagent in synthetic organic chemistry ^{11, 12, 13}. The author has used NDC as oxidant to oxidise essential amino acids in aqueous medium in the presence of perchloric acid which resulted in the formation of a complex giving corresponding aldehyde¹⁴. The effect of Temperature was studied by the author at 303K, 313K, 323K and 333K. He observed the rate constant of the reaction increased with increasing temperature and the reaction followed pseudo-first order kinetics as shown in the Table 1. The negative sign¹⁵ of the entropy change $\Delta S^{\#}$, suggests that the transition state is more orderly when compared with the reactants.

[NDC]10 ⁻³ mol dm ⁻³	[Amino acid]10 ² mol dm ⁻³	[H ⁺]10 ² mol dm ⁻³	Valine k 1 10 ⁴ s ⁻¹	Leucine k ₁ 10 ⁴ s ⁻¹	Histidine k ₁ 10 ⁴ s ⁻¹
6.0	2.0	5.0	4.34	4.46	9.25
8.0	2.0	5.0	4.30	4.43	9.20
10.0	2.0	5.0	4.37	4.40	9.29
12.0	2.0	5.0	4.29	4.49	9.23
14.0	2.0	5.0	4.30	4.46	9.27
6.0	2.0	5.0	4.34	4.46	9.25
6.0	3.0	5.0	5.32	5.45	11.20
6.0	4.0	5.0	6.14	6.28	12.80
6.0	5.0	5.0	6.88	7.04	14.70
6.0	6.0	5.0	7.60	7.80	15.90
6.0	2.0	5.0	4.34	4.46	9.25
6.0	2.0	7.5	8.23	10.30	17.60
6.0	2.0	10.0	15.16	17.80	30.00
6.0	2.0	12.5	23.23	27.80	49.30
6.0	2.0	15.0	30.99	38.70	87.00

Table 1.Rate constant for the oxidation of few amino acids by NDC at 313 K in perchloric acid ¹⁴

1.1 Oxidation of Aniline by NDC

The kinetics of oxidation of aniline¹⁶ and para-(Me, OMe, COMe, NHCOMe, NO₂, Br, Cl, F) and meta-(Me, COOH, NO₂, Et, OMe, COMe) substituted anilines were carried by the author under pseudo-first-order condition and from the least squares method, the rate constants were found and the linear plots, $r \ge 0.96$ of log [NDC] vs time and $\Delta G^{\#}$ is 8 kJ mol⁻¹, $\Delta S^{\#}$ varies from 0.1305 to 0.8599 JK⁻¹mol⁻¹. The product azobenzene was identified by its melting point 66 ^oC, IR and UV spectra. The Thermodynamic parameters of few substituted aniline is shown in the Table 2.



			Mole fraction of benzene in 2-methylpropan-2-ol						
Substituent in aniline moiety	TP ^a	0.1305	0.1465	0.1766	0.317	0.4192	0.5199	0.6679	0.8599
Н	Ea	13.6	15.1	9.6	27.8	23.4	32.7	45.3	50.8
	$\Delta H^{\#}$	11.5	13	7.6	25.8	21.4	30.7	43.3	48.8
	$\Delta S^{\#}$	-28	-283	-299	-231	-243	-211	-167	-148
	$\Delta G^{\#}$	98.1	97.9	97.2	94.9	94.3	94	93.4	93.1
p-Me	Ea	9	10	14.1	14.6	19.9	21.5	24.8	32.9
-	$\Delta H^{\#}$	7.9	7.9	12	12.6	17.8	1.4	22.7	30.9
	$\Delta S^{\#}$	-300	-299	-285	-282	-263	-255	-245	-216
	$\Delta G^{\#}$	97.7	97.6	97.4	97	96.6	95.9	95.9	95.6
p-OMe	$\mathbf{E}_{\mathbf{a}}$	8.8	9	11.7	10.7	21.5	31.9	31.1	40
_	$\Delta H^{\#}$	6.7	7	9.7	8.6	19.5	29.8	29	37.8
	$\Delta S^{\#}$	-295	-294	-284	-285	-247	-211	-211	-178
	$\Delta G^{\#}$	95.1	94.9	94.7	93.8	93.6	93.1	92.4	91.1

Table 2. Oxidation of aniline by NDC in benzene/2-methylpropan-2-ol mixture ¹⁶ - Thermodynamic parameters

1.2 Oxidation of substituted benzaldehydes by NDC

The author investigated the kinetics and mechanism of oxidation of para- and meta- substituted benzaldehydes with NDC in an acidic medium ¹⁷. The author maintained the substrate concentration in excess over NDC, first order conditions shown in Table 3. The high solvation of transition state over the reactants showed the entropies of activation $\Delta S^{\#}$, are negative. Also the rate data for oxidation of the substituted benzaldehydes gave a good correlation, r = 0.996, $\rho = +0.55$ with the Hammett σ value at 300K.

Table 3.	. Effect of	concentration	of reactants o	n reaction	rates at 30)0K [H ⁺]	= 1.50 mol	dm ⁻³ , 70%	acetic
acid – w	vater (v/v)	17							

10 ² [Benzaldehyde] /mol/dm 3	10 ⁴ [NDC] /mol/dm 3	$10^4 k_{ m obs/s-1}$
2.0	7.5	3.43
2.0	10.0	3.60
2.0	12.5	3.38
2.0	15.0	3.27
2.0	20.0	3.51
1.5	10.0	2.75
2.5	10.0	4.26
3.0	10.0	5.13
3.5	10.0	6.02
4.0	10.0	6.76

2. Piperidinium chlorochromate - Oxidation of α-hydroxy acids by PipCC

The kinetics of oxidation of α -hydroxy acids by piperidinium chlorochromate was investigated by the author at several concentrations of the reactants. The author found at 313K glycolic acid was oxidised in 50% acetic acid-water medium and he states that the reaction was found to be first order as evidenced by a linear plot

of log absorbance *versus* time ¹⁸ shown in Fig 1. The plot of [PipCC] *versus* $1/k_1$ is linear and as the concentration of substrate increased the author states, the rate also increased and the reaction was found to be first order with respect to substrate evidenced by the unit slope, r = 0.998 of the plot of log k_1 *versus* log [substrate]. The rate constants are shown in Table 4.

[PipCC] 10 ³ (mol dm ⁻³)	[Glycolic Acid] 10 ² (mol dm ⁻³)	$k_1 10^4 (s^{-1})$	$\frac{\mathbf{k}_2}{(s^{-1} mol^{-1} dm^3)}$
3.3	7.5	11.87	-
4.4	7.5	10.62	-
5.5	7.5	9.38	-
6.6	7.5	8.44	-
7.7	7.5	7.39	-
4.4	5	7.01	0.14
4.4	7.5	10.62	0.141
4.4	10	14.32	0.143
4.4	12.5	17.78	0.142
4.4	15	21.25	0.141

Table 4: Rate Constants for the Oxidation of Glycolic Acids by PipCC at 313 K¹⁸

 $[H^+] = 6.8 \times 10^{-2} mol \ dm^{-3}$ AcOH : $H_2O = 50 : 50 \ (v/v)$



Fig 1: Plot of 1/k₁ versus [PipCC]¹⁹

2.1. Oxidation of S-phenylmercaptoacetic acid by Piperidinium Chlorochromate

The author prepared piperidinium chlorochromate and S-phenyl mercapto acetic acid and its purity was checked iodometrically by finding the Cr (VI) concentration²⁰. UV-Visible spectro-photometer at 470 nm was used to determine the kinetic runs and the temperature was maintained at desired value to an accuracy of ± 0.1 ^oC. From the slope of log absorbance versus time plots the pseudo-first order rate constants were calculated by the investigator. At constant temperature, constant concentration of (oxidant) perchloric acid, the rate of reaction increased with increase in the concentration of the substrate as shown by the author in the Table 5. By using Eyring's plot of log k₂/T *versus* 1/T, the thermodynamic and activation parameters were calculated and reported by the author, $\Delta H^{\#} = 4.78$ kJmol⁻¹, $\Delta S^{\#} = -184.57$ JK⁻¹mol⁻¹, $\Delta G^{\#} = 62.55$ kJmol⁻¹²⁰.

Table 5. Oxidation S-phenyl mercaptoaceticacid by piperidinium chlorochromate at 313 K and the Rate Constants²⁰

[PipCC] 10 ³ (mol dm ⁻³)	[PMAA] 10^{3} (mol dm ⁻³)	$[H^+] 10^2$ (mol dm ⁻³)	$[NaClO_4]10^2$ (mol dm ⁻³)	AcOH : H ₂ O v/v	$[MnSO_4]10^2$ $(mol \ dm^{-3})$	$k_1 \ 10^4 (s^{-1})$
3.3 - 7.7	7.5	0.68		50:50	-	9.11 - 9.24
4.4	5.0 - 17.5	0.68		50:50	-	6.34 - 19.91
4.4	7.5	0.68 - 3.41		50:50	-	7.43 - 15.98
4.4	7.5	0.68	0.00-20.04	50:50	-	9.05 - 9.06

4.4	7.5	0.68	55:45-30:70	-	6.82-16.61
4.4	7.5	0.68	50:50	0.00-20.04	9.05-6.41

3. Quinolinium Dichromate - Oxidation of Diols using QDC

Oxidation of Ethylene Glycol to yield an R-hydroxy carbonyl compound such as

 $HOCH_2CH_2OH + HCrO_4^- + H^+ \rightarrow HOCH_2CH_2OCrO_3H + H_2O$

$HOCH_2CH_2OCrO_3H \rightarrow HOCH_2CHO + Cr (IV)$

The investigator reported the kinetics of trans-1, 2-cyclohexanediol²¹ into R-hydroxy carbonyl compound in acid medium with QDC. The author conducted the reaction at temperature 0.1 K. He also studied the kinetic runs with UV-vis absorption band at 440 nm. The sharp band at 1687 cm⁻¹, shows the hydrogen bonded C=O group and absorption band at 3050 cm⁻¹ showed the presence of the OH group from the Infra Red Spectroscopy. The product was confirmed by the author as 2-hydroxycyclohexanone and with respect to QDC the reaction follows first order kinetics and the rate constants are shown in the Table 6.

Table 6. Rate Constants on Oxidant Concentration Diols (0.01 M), H_2SO_4 (1.0 M) T = 323K and rate constants on substrate concentration QDC (0.001 M), H_2SO_4 (1.0 M), T=323 K²¹

10 ⁴ [QDC] (M)	10^4k_1 (s ⁻¹) for 1,2 cyclohexanediol	10 ² [diol] (M)	$10^{4}k_{1} (s^{-1}) \text{ for } 1,2$ cyclohexanediol
1.0	7.75	1.0	7.67
5.0	7.52	5.0	38.5
7.5	7.36	7.5	58.0
10.0	7.67	10.0	77.1
20.0	7.62	20.0	155

3.1. Quinolinium Dichromate - Oxidation of 2-furaldehydes²³

The investigator prepared quinolinium dichromate and its purity was checked by spectral analysis, where IR spectrum exhibited bands at 930, 875, 765 and 730 cm⁻¹ and reactions were carried at temperature 0.1 K and the UV-visible absorption band was recorded at 440 nm. From the linear plots, r > 0.996, of log [QDC] against time the rate constants were found by the author. The oxidized products 2-furancarboxylic acids were obtained with yields 85– 90%. The thermodynamic and activation parameters were calculated and reported by the author, $\Delta H^{\#} \pm 2 \text{ kJmol}^{-1} \Delta S^{\#} \pm 5 \text{ Jmol}^{-1} \text{K}^{-1}$. The rate of oxidation of substituted 2-furaldehydes at 313 K is shown in the Table 7.

[Substrate] (10 ² M)	[QDC](10 ³ M)	[H ₂ SO ₄](M)	2- Furaldehyde 10 ⁴ k (s-1)	5-Bromo-2- furaldehyde 10 ⁴ k (s-1)	5-Methyl-2- furaldehyde 10 ⁴ k (s-1)
1	1	0.5	1.25	1.1	1.5
2.5	1	0.5	3.12	2.6	3.8
5	1	0.5	6.21	5.6	7.8
7.5	1	0.5	9.32	8.3	12.1
10	1	0.5	12.5	11	15.6
1	0.75	0.5	1.22	1.12	1.52
1	0.5	0.5	1.25	1.09	1.5
1	0.25	0.5	1.24	1.1	1.45
1	0.1	0.5	1.27	1.15	1.43
1	1	0.75	1.88	1.7	2.3
1	1	1	2.5	2.15	3.1
1	1	1.25	3.2	2.7	3.7
1	1	1.5	3.8	3.4	4.6

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4. Quinolinium fluorochromate - Oxidation of benzaldehyde by QFC

QFC of molecular formula C₉H₇NH[CrO₂F]⁴¹ was prepared by the author and its purity was checked by iodometric method and oxidation of mono substituted benzaldehyde by QFC in Dimethyl sulphoxide²² was reported by the investigator. The reactions were carried at temperature ±0.1K and spectrphotometrically monitoring the decrease in concentration of QFC at 354 nm, and pseudo-first order rate constant (k_{obs}) was evaluated from the linear (r^2 =0.990-0.999) plots of log [QFC] and second order rate constant(k_2) was derived from $k_2=k_{obs}$ /[aldehyde]. The rate constants of oxidation of benzaldehyde by QFC is shown in the Table 8.

10 ³ [QFC] (mol dm	[Aldehyde] (mol dm ⁻	[TsOH] (mol	10 ⁴ k obs (s ⁻¹)
1.0	0.10	0.0	4.46
1.0	1.20	0.0	6.59
1.0	1.40	0.0	8.66
1.0	1.60	0.0	9.67
1.0	1.80	0.0	10.30
1.0	1.00	0.0	10.70
1.0	1.50	0.0	11.20
1.0	3.00	0.0	11.90
2.0	0.40	0.0	8.82
4.0	0.40	0.0	8.25
6.0	0.40	0.0	9.00
8.0	0.40	0.0	8.46

 Table 8. Rate constants for the oxidation of benzaldehyde by QFC at 298K²²

Application of Chemical Kinetics

Deterioration of Food^{24, 25, 26}

The investigator depicts that in the food science literature, quality changes are usually modeled by means of a zero-, 1st-, or 2nd-order reaction, as pioneered by Labuza and Karel, for n = 0 for a decomposition reaction 24,25,26 the equation can be written as,

-dc/dt = k

 $C = C_{o}-kt$

Zero-order reactions are rather frequently reported for changes in foods, especially for formation reactions when the amount of product formed is only a small fraction, or for decomposition reactions where only a small amount of product is formed from a reactant. The reactant is large and its concentration remains constant and the rate appears to be independent of the concentration.



Fig 2. Decomposition of a component for a reaction of varying order n having same initial concentration and rate constant ²⁴

Toxicity of Chromium-(VI) and (III)

Chromium (Cr) was discovered in the year 1798 by the French chemist Vauquelin³³.

It is a transition element located in the group VI-B of the periodic table with a ground-state electronic configuration of Ar $3d^54s^1$. Naturally occurring in soil, Cr ranges from 10 to 50 mg. kg⁻¹ depending on the parental material. In fresh water, Cr concentrations generally range from 0.1 to 117 µg L⁻¹, whereas values for seawater range from 0.2 to 50 µg L⁻¹. Nutrient solution with 9.6 µM Cr (VI) decreased the uptake of K, Mg, P, Fe and Mn in the roots of few plants like soybean³⁴. Chromium (III) is cationic and can easily adsorbs on the clay particles, organic matter, and other negatively charged particles ^{35,36} and Cr(VI) adsorb more tightly to oxide than anions like Cl⁻, NO⁻³, and sulfate. Also Cr(VI) and (III) are causing lethal effects to Earthworms³⁷. Hexavalent chromium (Cr⁶⁺) is mobile, can penetrate the cell wall and cause various cancer diseases^{27, 29}. Also short term exposure causes Ulcer, skin irritation and Long-term exposure causes damage to internal organs like liver, kidney, blood circulation, nerve tissue and death ^{28, 29}. Cr (III) accumulates in the cell membrane ^{29, 30, 31, 32}.





Conclusion

The study of chemical kinetics deals with the limit of extent to which a reaction occur, the sequence of steps by which the reaction proceeds, rates of the steps, factors, nature of reactants, concentration and temperature which affect the rate. The oxidation of various chromium compounds studied by different investigators and the kinetics, rate constants, toxicity and applications are reported above. The more active oxidants are made passive by using suitable oxidants and their kinetics studied are discussed above.

References

- 1. Katz SA, Salem H. The Biological and Environmental Chemistry of Chromium; VCH: New York, 1994.
- 2. Nriagu JO, Nieboer E. Chromium in the Natural and Human Environments; Eds.; Wiley & Sons, New York, 1988, 571.
- 3. Mertz W, Murti CRK, Bingheng C, Gopalan HNB, Massoud A, Sanotsky IV, Sto⁻⁻ ber W. Chromium, World Health Organization, Geneva, 1988.
- 4. Toxicology Profile for Chromium, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Washington, DC, 1991.
- 5. Calder LM, Nriagu JO, Nieboer. In Chromium in the Natural and Human Environments, Eds.; Wiley & Sons, New York, 1988, 215-229.
- 6. Palmer CD, Wittbrodt PR. Environ. Health Perspect. 1991, 92, 25-40.
- 7. Gonzalaz JC, Garvia S, Mamana N, Sala LF and Sinorella SJ. Evidence for the invovlement of Cr(ll) and free radicals as intermediates in the reduction of HCrO₄ by saccharides, alcohols and hydroxyacids .Inorg. Chem. Commun., 2006, 9; 437-440, 2006.
- 8. Chimatadar SA, Koujalagi SB and Nandibewoor ST. Kinetics and Mechanism of Palladium (II) Catalysed Chromium (VI) Oxidation of mercury (I) in aqueous sulphuric acid. Trans. Met. Chem., 2001, 26; 662-667.
- Bystrom A and Wilheni KA. The Crystal Structure of Chromium Trioxide. Acta Chem. Scand., 1950, 4; 1131.
- 10. Pourbaix M, Atlas of Electro Chemical Equilibria in Aqueous Solutions., 2nd Ed, Oxford, Pergamon press, 1966, 261.
- 11. Chockalingam Karunakaran, Vaithiyalingam Chidambaranathan. Linear Free energy relationship near Isokinetic Temperature. Oxidation of Organic sulphides with Nicotinium Dichromate. Creat. Chem. Acta., 2001, 74, 51-59.
- 12. Bhuvaneshwari DS, Elango KP. Correlation Analysis of reactivity in the oxidation of anilines by Nicotinium Dichromate in non aqueous media. Int. J. Chem. Kinet., 2006, 38, 657-665.
- 13. Palaniappan AN, Arulmozhi varman A, Srinivasan S, Senthilkumar S. J. Kinetics and Mechanism of Oxidation of Anthranyl Styryl Ketone by Nicotinium Dichromate in aqusous acetic acid medium. Chem. Pharm. Res., 2012, 4; 2874-2878.
- 14. Vivekanandan K, Lakshmi Narayanan R. Oxidative Decarboxylation and Deamination of Essential Amino Acids by Nicotinium Dichromate A Kinetic Study. International Letters of Chemistry, Physics and Astronomy, 2015, 45; 66-72.
- 15. Frost AA, Pearson RG. Kinetics and Mechanism, Wiley Eastern, New Delhi, 1970.
- Durvas S, Bhuvaneshwari, Kuppanago, Elango P. Effect of Preferential Solvation on the Kinetics and Thermodynamics of Oxidation of Anilines by Nicotinium Dichromate. Naturforsch Z., 2005, 60b; 1105 – 1111.
- 17. Sekar KG, Kinetic studies on the oxidation of some para and meta-substituted benzaldeydes by nicotinium dichromate. Journal of Chemical Research., 2002, 2; 626-627.
- Anbarasu K, Selvi P. Reactivity of α-hydroxy Acids towards Piperidinium Chlorochromate Oxidation. Oriental Journal of Chemistry, 2013, 29; 247-252.
- 19. Anbrarasu K, Selvi P. Mechanism of Glycolic acid towards Piperidinium chlorochromate Oxidation. Rasayan J.Chem., 2014, 7; 365-369.
- 20. Anbrarasu K, Selvi P. Oxidation of *S*-Phenylmercaptoacetic Acid by Piperidinium Chlorochromate. Chem Sci Trans., 2013, 2(S1); S83-S86.
- 21. Bernadette Kuotsu, Enboklin Tiewsoh, Abhijit Debroy, Mahendra K. Mahanti. Quinolinium Dichromate Oxidation of Diols: A Kinetic Study. Journal of Organic Chemistry, 1996, 61; 8875-8877.
- 22. Jagrity Khatri A, Choudhary P, Purohit R, Kumbhat, Vinita Sharma. Correlation Analysis of Reactivity in the Oxidation of Substituted Benzaldehydes by Quinolinium fluorochromate. Eur. Chem. Bull., 2012, 1; 49-57.
- 23. Girija S. Chaubey, Bansiewdor Kharsyntiew and Mahendra K. Mahanti. Oxidation of substituted 2furaldehydes by quinolinium dichromate: a kinetic study. Phys. Org. Chem., 2004, 17; 83–87.
- 24. Martinus AJS, van Boekel. Kinetic Modelling of Food Quality: A Critical Review. Comprehensive Reviews in Food Science and Food safety, 2008, 7; 144-158.
- 25. Labuza TP. Application of chemical kinetics to deterioration of foods. J.Chem.Ed., 1984, 61; 348-58.

- 26. Saguy I, Karel M. Modeling of quality deterioration during food processing and storage. Food Technol., 1980, 34; 78–85.
- 27. Gil RA, Cerutti S, Gasquez JA, Olsina RA and Martinez LD. Preconcentration and speciation of chromium in drinking water samples by coupling of on-line sorption on activated carbon to ETAAS determination. Talanta., 2006, 68; 1065-1070.
- 28. Kotas J and Stasicka Z. Chromium occurrence in the environment and methods of its speciation. J. Environ. Pollut., 2000, 107; 263-283.
- 29. Sethuraman C, Srinivas K, Sekaran G. Conversion of Hazardous Leather Solid Waste into Fuels and Products. IEEE., 2013, 274-278.
- 30. Jannette KW. The role of metals in carcinogenesis, biochemistry and metabolism. Environ. Health Perspect., 1981, 40; 233–252.
- 31. Martell AE. Chemistry of carcinogenic metals. Environ. Health Perspect., 1980, 40; 207-226.
- 32. Shen H, Wang Y.T. Biological reduction of chromium by E. coli. J.Environ. Eng., 1994, 120; 560–572.
- 33. Arun K. Shanker, Carlos Cervantes, Herminia Loza-Tavera, Avudainayagam S. Chromium toxicity in plants, Review article. Environment International., 2005, 31; 739–753.
- Clijsters H, Van Assche F. Inhibition of photosynthesis by heavy metals. Photosynth Res., 1985, 7; 31– 40.
- 35. Turner MA, Rust RH. Effects of chromium on growth and mineral nutrition of soybeans. Soil Sci Soc Am Proc 1971, 35; 755–758.
- 36. Bartlett RJ, Kimble JM. Behaviour of chromium in soils: II.Hexavalent form. J. Environ. Qual. 1976, 5; 386.
- 37. Sivakumar S, Subbhuraam CV. Toxicity of chromium(III) and chromium(VI) to the earthworm Eisenia fetida. Ecotoxicology and Environmental Safety., 2005, 62; 93–98.
- Mihir K. Chaudhuri, Shiv K. Chettri, Synjukta Lyndem, Pradio C. Paul and Pendyala Srinivas. Quinilinium Fluorochromate (QFC), C₉H₇NH[CrO₃F]: An Improved Cr(VI)-Oxidant for Organic Substrates. Bull. Chem. Soc. Jpn., 1994, 67; 1894-1898.
- 39. Lopez C, Gonzalez A, Cossio FP and Palomo C. 3- carboxy Pyridinium Dichromate and 4- carboxy Pyridinium Dichromate: Two new mild, stable, efficient and in expensive chromium (VI) oxidation reagents. Synth. Commun., 1985, 15; 1197-1211.
- 40. Sheik HN, Sharma M and Kalsotra BL. Kinetics and Mechanism of Oxidation of Alcohols by Piperidinium Chlorochromate. J.Indian Chem. Soc., 2005, 82; 913-916.
- 41. Balasubramanian K and Prathiba V. Quinolinium Dichromate A New Reagent for Oxidation of Alcohols. Indian J.Chem, 1986, 25B; 326-327.
- 42. Chaudhri MK, Chetti SK, Lyndem S, Paul PC and Srinivas P. Quinolinium Fluorochromate. An Improved Cr (VI) Oxidant for Organic Substrates. Bull. Chem. Soc., 1994, 67; 1894-1898.
