

Oxidation of alginate and pectate biopolymers by cerium(IV) in perchloric and sulfuric acid solutions: A comparative kinetic and mechanistic study



Ahmed Fawzy^{a,b,*}

^a Chemistry Department, Faculty of Applied Sciences, Umm Al-Qura University, Makkah, Saudi Arabia

^b Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

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ABSTRACT

The kinetics of oxidation of alginate (Alg) and pectate (Pec) carbohydrate biopolymers was studied by spectrophotometry in aqueous perchloric and sulfuric acid solutions at fixed ionic strengths and temperature. In both acids, the reactions showed a first order dependence on [Ce(IV)], whereas the orders with respect to biopolymer concentrations are less than unity. In perchloric acid, the reactions exhibited less than unit orders with respect to [H⁺] whereas those proceeded in sulfuric acid showed negative fractional-first order dependences on [H⁺]. The effect of ionic strength and dielectric constant was studied. Probable mechanistic schemes for oxidation reactions were proposed. In both acids, the final oxidation products were characterized as mono-keto derivatives of both biopolymers. The activation parameters with respect to the slow step of the mechanisms were computed and discussed. The rate laws were derived and the reaction constants involved in the different steps of the mechanisms were calculated.

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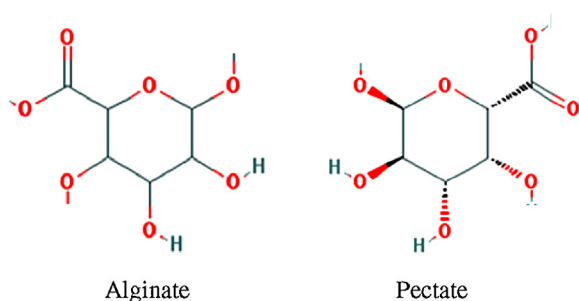
1. Introduction

The study of carbohydrates is one of the most exciting fields of organic chemistry. The biological and economic significance of carbohydrates is responsible for the great interest in studying their biochemical and physicochemical properties. Furthermore, oxidation of carbohydrates is regarded as an important way in which new compounds and materials with interesting properties can be provided. Among these carbohydrates, naturally occurring alginate and pectate biopolymers (Scheme 1) are very attractive. Alginate extracted from seaweed is a copolymer of polyguluronate, polymannuronate and alternating units of both sugars (Sutherland, 1991). The structure of pectate is closely related to that of alginate. The main structural difference between them is the position of the two C-2 and C-3 hydroxyl groups being *cis* in alginate and *trans* in pectate and the carboxylate groups are probably the same in both cases (Aspinal, 1982). The presence of hydroxyl and carboxylate functional groups in alginate and pectate structures allows various chemical and physical modifications. An important feature of alginate and pectate is their gelation in the presence of metal cations.

The gentle gelling property of such biopolymers has a significant impact on medicine (Langer & Vacanti, 1993; Mooney & Mikos, 1999). Alginate and pectate biopolymers are also widely used in the food, cosmetics, agriculture and pharmaceutical industries due to their gelling ability, stabilizing properties and high viscosity in aqueous solutions (Drury & Mooney, 2003; Kong, Smith, & Mooney, 2003). They have been intensively investigated in a variety of biomedical applications including drug delivery and cell transplantation (Bouhadir, Kruger, Lee, & Mooney, 2000; Morgan et al., 1995), dental impression materials (Cook, 1986) and wound dressings (Schmidt, Chung, Andrews, Spyratou, & Turner, 1993). Furthermore, oxidized alginate and pectate biopolymers present more reactive groups and a faster degradation when these biopolymers are used in supports for drug controlled delivery (Boontheekul, Kong, & Mooney, 2005; Bouhadir et al., 2001). The oxidation rates of such biopolymers were found to depend on the oxidant nature and pH of the reaction media. Scanning the literature showed a lack of information as to the kinetic studies on the oxidation of alginate (Gomez, Rinaudo, & Villar, 2007; Makhlof, El-Shatoury, & Hassan, 1992) and pectate (Bellui, Gonzalez, Garcia, Signorella, & Sala, 2008; Khairou & Hassan, 2001) which may be due to the complexity of such studies.

Cerium(IV) is a powerful oxidizing agent in acid media which has been employed in various kinetic and mechanistic studies (Adari, Nowduri, & Parvataneni, 2008; Bolattin, Meti, Nandibewoor,

* Correspondence to: Chemistry Department, Faculty of Applied Sciences, Umm Al-Qura University, Makkah, Saudi Arabia.
E-mail address: afsaad13@yahoo.com



Scheme 1. Structure of alginate and pectate biopolymers.

& Chimatadar, 2015; Byadagi, Naik, Savanur, Nandibewoor, & Chimatadar, 2010; Datt, Nagori, & Mehrotra, 1986; Hardwick & Robertson, 1951; Sumathi, Shanmugasundaram, & Chandramohan, 2013; Thabaj, Chimatadar, & Nandibewoor, 2006; Yadav, Derva, & Rani, 2009). The oxidizing potentialities of Ce(IV) in sulfuric acid solutions have conclusively been established (Adari et al., 2008; Sumathi et al., 2013). Nevertheless, the oxidant has rarely been employed in perchloric acid solutions (Byadagi et al., 2010; Naik, Byadagi, Nandibewoor, & Chimatadar, 2013; Yadav et al., 2009), probably due to presence of dimers and polymers of Ce(IV) species in these solutions (Hardwick & Robertson, 1951; Yadav et al., 2009). However, the reactions of Ce(IV) in perchloric acid solutions proceed much faster than those in sulfuric acid ones. Cerium(IV) oxidation was found to follow different mechanisms, depending upon the substrate nature and acid medium used such as intermediate complex formation and/or free radical mechanism (Sumathi et al., 2013; Thabaj et al., 2006). Generally, oxidation by Ce(IV) is interesting to understand the different pathways of the reactions as well as the different active species of Ce(IV). Although, the kinetic studies on the oxidation of several organic compounds by Ce(IV) in acid media have been a subject of much interest (Adari et al., 2008; Datt et al., 1986; Hosahalli, Savanur, Nandibewoor, & Chimatadar, 2010; Jattinagoudar, Byadagi, Nandibewoor, & Chimatadar, 2015; Sumathi et al., 2013; Yadav et al., 2009), no reports are available about the kinetics of Ce(IV) oxidation of alginate and pectate biopolymers.

Owing to the forgoing points, the title reactions have been investigated in order to establish the optimum conditions for the oxidation of alginate and pectate biopolymers by Ce(IV) in perchloric and sulfuric acid solutions, to understand the active species of the reactants in both acid media, to examine the effect of the nature of acid medium used, to explore the effect of hydroxyl group

conformational structure in such biopolymers and finally to elucidate the plausible oxidation reaction mechanisms.

2. Experimental

2.1. Materials

The chemicals employed in the present study were Analar or Merck reagents. Stock solutions of the sodium salts of both alginate and pectate biopolymers were prepared by stepwise addition of the samples (BDH) in double distilled water with rapid and continuous stirring to avoid formation of lumpy aggregates. A fresh solution of Ce(IV) was prepared by dissolving ceric ammonium sulfate in a 1.0 mol dm^{-3} sulfuric acid solution, diluted with double distilled water and kept for overnight. Concentration of Ce(IV) was determined by titrating against standard ferrous ammonium sulfate solution and by spectrophotometry. The solution of Ce(IV) was stored in a dark glass bottle and was used after 24 h, since the hydrolysis is negligibly small or ruled out after 12 h of preparation (Hardwick & Robertson, 1951). Cerium(III) solution was prepared by dissolving cerium(III) acetate in water. Sodium perchlorate and sodium sulfate were used to vary the ionic strength in perchloric and sulfuric acid solutions, respectively. Solutions of other reagent were prepared by dissolving the requisite amounts of the samples in doubly distilled water.

2.2. Kinetic measurements

The reactants were formulated such that the reactions were of pseudo-first order kinetics where the biopolymer substrate (S) was added in a large excess relative to Ce(IV). The progress of the reactions was followed by tracing the decay in cerium(IV) absorbance at $\lambda_{\text{max}} = 316 \text{ nm}$, maximum absorption wavelength belonging to Ce(IV), whereas the other constituents of the reactions did not absorb significantly at this wavelength. The absorbance measurements were carried out using Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer. First order plots of $\ln(\text{absorbance})$ versus time were found to be linear up to more than 75% of the reactions completion and the observed first order rate constants (k_{obs}) were calculated as the gradients of such plots. Average values of at least two independent runs of the rate constants were taken for the analysis. The runs were reproducible to within $\pm 4\%$. The reaction orders with respect to the reactants were determined from the slopes of $\log k_{\text{obs}}$ versus $\log(\text{concentration})$ plots by varying the concentrations of the substrates and acids, in turn, while keeping other conditions constant.

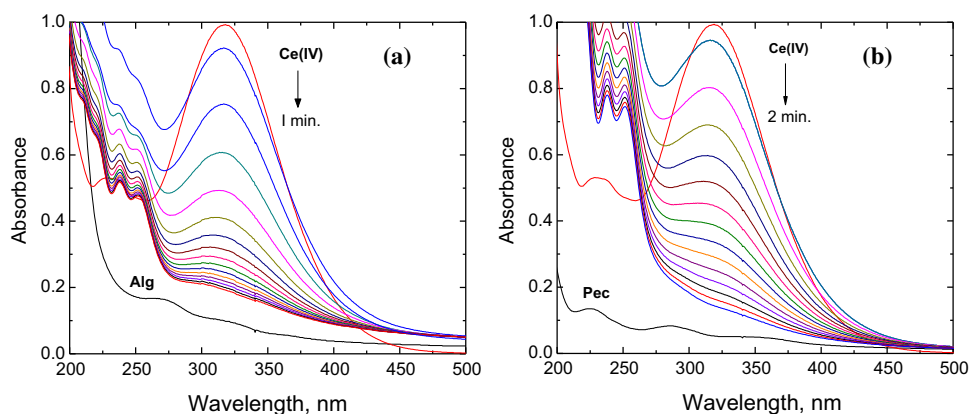


Fig. 1. Time-resolved spectra for the oxidation of alginate and pectate by Ce(IV) in perchloric acid solutions. $[S] = 6.0 \times 10^{-3}$, $[Ce(IV)] = 2.0 \times 10^{-4}$, $[H^+] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

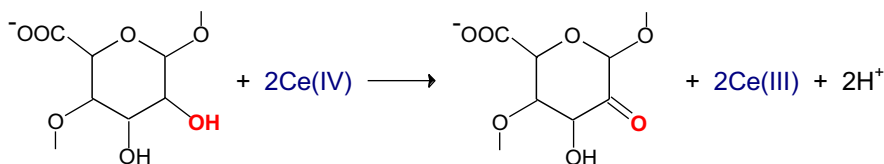
The in situ hydrogen ion concentration in sulfuric acid–sulfate media was calculated by using known ionization constant (Vogel, 1973). In case of perchloric acid solution, $[H^+]$ was maintained by adding required concentration of perchloric acid with subtracting the $[H^+]$ added due to sulfuric acid present in Ce(IV) stock solution.

Some kinetic runs were performed after bubbling purified nitrogen and compared with those taken under air. The results were found to be the same suggesting that the dissolved oxygen did not have any effect on the oxidation rates.

3. Results

3.1. Stoichiometry and product characterization

At fixed acidities, ionic strengths and temperature, the stoichiometry of the oxidation reactions determined by both titrimetry and spectrophotometry indicated consumption of two moles of Ce(IV) per one mole of biopolymer substrate leading to the final oxidation products as shown in the following equation,



The main oxidation products, mono-keto derivatives of both alginate and pectate, were detected via their 2,4-dinitrophenylhydrazone and dioxime derivatives (Vogel, 1973). The products were also confirmed by their IR spectra which showed the appearance of absorption bands at $1708\text{--}1692\text{ cm}^{-1}$ that characterize the carbonyl ($C=O$) stretch.

3.2. Time-resolved spectra

The spectral changes during the oxidation of alginate and pectate biopolymers by Ce(IV) in both perchloric and sulfuric acid solutions are shown in Figs. 1 and 2, respectively. In all cases, the scanned spectra indicated gradual decay of Ce(IV) band at its absorption maximum with time as a result of its reduction to Ce(III).

3.3. Effect of $[Ce(IV)]$ on the oxidation rates

The oxidant Ce(IV) was varied in all reactions in the range of $(1.0\text{--}8.0) \times 10^{-4}\text{ mol dm}^{-3}$ at fixed concentration of the substrates (S), ionic strengths and temperature. The non significant variation of the pseudo-first order rate constants at various initial concentrations of Ce(IV) (Tables 1 and 2) indicates that the reactions order with respect to Ce(IV) was unity. The first order kinetics was also confirmed by the linearity of the plots of $\ln(\text{absorbance})$ versus time for up to 75% completion of the reactions.

3.4. Effect of $[S]$ on the oxidation rates

The observed rate constants (k_{obs}) were measured at different initial concentrations of the biopolymer substrates (S) while other variables were kept constant. It was found that increasing $[S]$ increased the rates (Tables 1 and 2). The plots of k_{obs} versus $[S]$ in both acid solutions were linear with positive intercepts (figures not shown) confirming the fractional-first order dependences with respect to the substrates concentration.

3.5. Effect of $[H^+]$ on the oxidation rates

To explore the effect of hydrogen ion concentration on the rates of the reactions, kinetic runs were carried out by varying the hydrogen ion concentration in the range of $0.1\text{--}1.0\text{ mol dm}^{-3}$ in case of perchloric acid and from 0.05 to 0.3 mol dm^{-3} in case of sulfuric acid while maintaining other variables constant. It was observed that the increase in $[H^+]$ increased the oxidation rates of the biopolymers in perchloric acid solutions (Table 1) and decreased them in case of sulfuric acid (Table 2). The plots of k_{obs} versus $[H^+]$ were linear with positive slopes for perchloric acid and with negative slopes for sulfuric acid (figures not shown) confirming the positive and negative fractional-first order dependences with respect to $[H^+]$ in perchloric and sulfuric acids, respectively.

3.6. Effect of ionic strength and dielectric constant on the oxidation rates

At constant concentrations of the reactants and with other conditions constant, the ionic strength was varied between 1.0

and 3.0 mol dm^{-3} by addition of sodium perchlorate in case of perchloric acid and from 0.3 to 0.8 mol dm^{-3} using sodium sulfate in case of sulfuric acid. The results inserted in Tables 1 and 2 indicate that the observed rate constants increased with increasing the ionic strength in perchloric acid solutions while unchanged significantly in case of sulfuric acid. Thus, in case of perchloric acid, the Debye–Huckel plots were linear with positive slopes (Fig. S1).

In order to examine the effect of the dielectric constant (D) of the reaction media on the oxidation rates, the reactions were studied in water–organic solvent mixtures of different compositions (vol%) of organic co-solvent viz. acetic acid up to 40% acetic acid content at fixed concentrations of all other reactants, ionic strengths and temperature. At different compositions, the dielectric constant of the medium was calculated using the equation of Laidler and Eyring (Amis & Hinton, 1973): $D = D_1V_1 + D_2V_2$, where V_1 and V_2 are volume fractions and D_1 and D_2 are dielectric constants of water and acetic acid as 78.5 and 6.15 at $25\text{ }^\circ\text{C}$, respectively. In perchloric acid solutions, the rate constants clearly decreased as the dielectric constant of the reaction medium decreased, i.e., increasing acetic acid content, and the plots of $\log k_{\text{obs}}$ versus $1/D$ were linear with negative slopes (Fig. S2). In case of sulfuric acid, the rate constants were found to increase negligibly with decreasing the dielectric constant of the reaction medium.

3.7. Effect of initially added product on the oxidation rates

The effect of added cerium(III) product was studied in the concentration range of $(1.0\text{--}8.0) \times 10^{-4}\text{ mol dm}^{-3}$ at fixed concentrations of the oxidant, reductants and acids. It was found that Ce(III) did not alter the oxidation rates in both perchloric and sulfuric acid solutions.

3.8. Effect of temperature on the oxidation rates

The rates of the biopolymers oxidation are measured at five temperatures between 293 K and 313 K at constant concentrations of the reactants and other conditions being constant. The results indicated that the observed first order rate constants were increased

Table 1Effect of variation of $[Ce^{IV}]$, $[S]$, $[H^+]$ and ionic strength, I , on the observed first order rate constants (k_{obs}) in the oxidation of alginate and pectate by Ce(IV) in perchloric acid solutions at 25 °C.

$10^4 [Ce(IV)]$ (mol dm ⁻³)	$10^3 [S]$ (mol dm ⁻³)	$[H^+]$ (mol dm ⁻³)	I (mol dm ⁻³)	$10^4 k_{obs}$ (s ⁻¹)	
				Alginate	Pectate
1.0	6.0	0.5	1.0	163.0	78.3
2.0	6.0	0.5	1.0	160.2	76.1
3.0	6.0	0.5	1.0	162.0	77.1
4.0	6.0	0.5	1.0	155.7	74.6
6.0	6.0	0.5	1.0	161.2	74.9
8.0	6.0	0.5	1.0	158.9	75.8
2.0	2.0	0.5	1.0	71.1	36.6
2.0	4.0	0.5	1.0	116.2	60.1
2.0	6.0	0.5	1.0	160.2	76.1
2.0	8.0	0.5	1.0	199.4	96.0
2.0	10.0	0.5	1.0	234.6	120.9
2.0	12.0	0.5	1.0	265.2	136.0
2.0	6.0	0.1	1.0	57.9	27.6
2.0	6.0	0.3	1.0	112.0	57.1
2.0	6.0	0.5	1.0	160.2	76.1
2.0	6.0	0.7	1.0	198.2	92.3
2.0	6.0	0.9	1.0	233.4	111.2
2.0	6.0	1.0	1.0	249.2	120.8
2.0	6.0	0.5	1.0	160.2	76.1
2.0	6.0	0.5	1.4	181.1	89.2
2.0	6.0	0.5	1.8	205.3	97.0
2.0	6.0	0.5	2.0	233.7	111.6
2.0	6.0	0.5	2.5	251.1	118.9
2.0	6.0	0.5	3.0	269.2	123.2

Experimental error $\pm 4\%$.**Table 2**Effect of variation of $[Ce^{IV}]$, $[S]$, $[H^+]$ and ionic strength, I , on the observed first order rate constants (k_{obs}) in the oxidation of alginate and pectate by Ce(IV) in sulfuric acid solutions at 25 °C.

$10^4 [Ce(IV)]$ (mol dm ⁻³)	$10^3 [S]$ (mol dm ⁻³)	$[H^+]$ (mol dm ⁻³)	I (mol dm ⁻³)	$10^4 k_{obs}$ (s ⁻¹)	
				Alginate	Pectate
1.0	6.0	0.1	0.3	51.6	34.1
2.0	6.0	0.1	0.3	52.3	32.1
3.0	6.0	0.1	0.3	55.1	31.6
4.0	6.0	0.1	0.3	52.7	30.9
6.0	6.0	0.1	0.3	50.9	32.7
8.0	6.0	0.1	0.3	51.8	31.5
2.0	2.0	0.1	0.3	28.2	19.5
2.0	4.0	0.1	0.3	41.1	26.4
2.0	6.0	0.1	0.3	52.3	32.1
2.0	8.0	0.1	0.3	62.8	38.2
2.0	10.0	0.1	0.3	71.4	42.5
2.0	12.0	0.1	0.3	79.2	46.4
2.0	6.0	0.05	0.3	76.9	37.9
2.0	6.0	0.10	0.3	47.1	32.1
2.0	6.0	0.15	0.3	31.3	28.2
2.0	6.0	0.20	0.3	24.8	25.2
2.0	6.0	0.25	0.3	19.6	21.6
2.0	6.0	0.30	0.3	16.5	19.9
2.0	6.0	0.1	0.3	52.3	32.1
2.0	6.0	0.1	0.4	49.2	29.4
2.0	6.0	0.1	0.5	46.0	27.5
2.0	6.0	0.1	0.6	44.1	25.3
2.0	6.0	0.1	0.7	41.8	23.9
2.0	6.0	0.1	0.8	40.6	22.8

Experimental error $\pm 4\%$.**Table 3**Activation parameters of the second order rate constants (k_2) in the oxidation of alginate and pectate by Ce(IV) in perchloric and sulfuric acid solutions.

Acid	Substrate	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger_{298} (kJ mol ⁻¹)	E_a^\ddagger (kJ mol ⁻¹)
Perchloric	Alginate	-98.94	41.15	70.63	43.73
	Pectate	-118.89	37.25	72.68	39.90
Sulfuric	Alginate	-167.11	23.36	73.16	26.08
	Pectate	-176.26	21.86	74.38	24.56

Experimental error $\pm 5\%$.

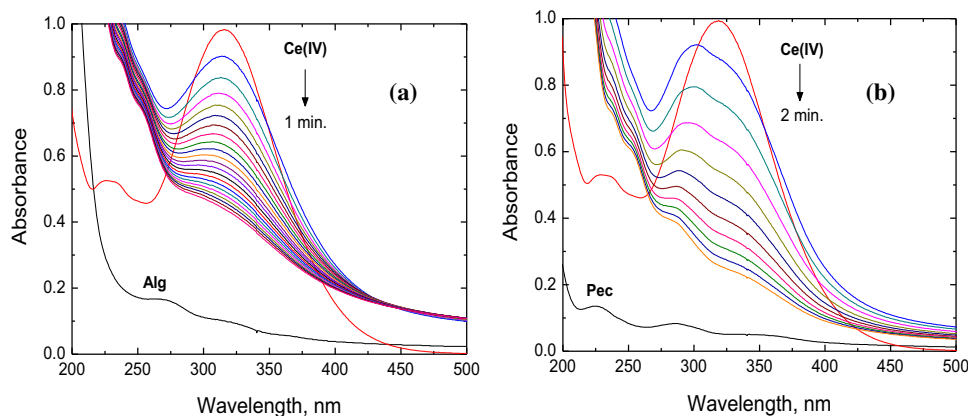


Fig. 2. Time-resolved spectra for the oxidation of alginate and pectate by Ce(IV) in sulfuric acid solutions. $[S] = 6.0 \times 10^{-3}$, $[Ce(IV)] = 2.0 \times 10^{-4}$, $[H^+] = 0.1$ and $I = 0.3 \text{ mol dm}^{-3}$ at 25°C .

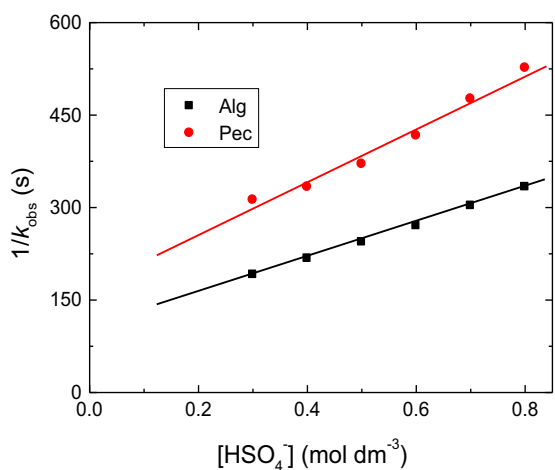


Fig. 3. Plots of $1/k_{\text{obs}}$ versus $[HSO_4^-]$ in the oxidation of alginate and pectate by Ce(IV) in sulfuric acid solutions. $[S] = 6.0 \times 10^{-3}$, $[Ce(IV)] = 2.0 \times 10^{-4}$, $[H^+] = 0.1$ and $I = 0.3 \text{ mol dm}^{-3}$.

with raising temperature. The activation parameters of the second order rate constant of slow step of Scheme (k_2) are calculated using Eyring and Arrhenius plots (Figs. S3 and S4) and are listed in Table 3.

3.9. Effect of $[HSO_4^-]$

To study the effect of bisulfate ion on the rates of the reactions proceeded in sulfuric acid solutions, kinetic runs were carried out at different concentrations of bisulfate in the range of $0.3\text{--}0.8 \text{ mol dm}^{-3}$, at constant other variables. It was observed that the increase in $[HSO_4^-]$ decreased the oxidation rates and the order with respect to $[HSO_4^-]$ was negative. This is confirmed by the linear plot of $1/k_{\text{obs}}$ versus $[HSO_4^-]$ with positive intercept (Fig. 3).

3.10. Test for free radicals intervention

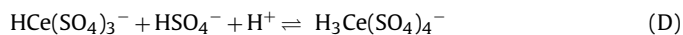
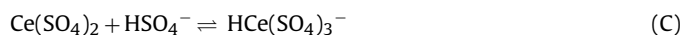
The possibility of free radicals intervention was examined by polymerization test. The reaction mixtures, to which known quantities of acrylonitrile were added, were kept in inert atmosphere for 4 h at room temperature. When the reaction mixtures were diluted with methanol, progressive white precipitates were formed suggesting that there were participation of free radicals in the present oxidation reactions. When the experiments were repeated in the absence of the biopolymers under similar conditions, the tests were negative. This indicates that the reactions were routed through free radical paths.

4. Discussion

4.1. Kinetically active cerium(IV) species in both perchloric and sulfuric acids

A survey on the earlier literature on the nature of cerium(IV) species in perchloric acid solutions (Heidt & Smith, 1948; King & Pandow, 1952; Sherill, King, & Spooner, 1943) showed that the active species of Ce(IV) was found to be either free monomeric species Ce^{4+} , its hydrolyzed forms, $Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$ or dimeric species $(Ce-O-Ce)^{6+}$ and $(HO-Ce-O-CeOH)^{4+}$. Spectrometric measurements (Offner & Skoog, 1966) showed that Ce^{4+} is the predominant species at $[H^+] \geq 1.0 \text{ mol dm}^{-3}$ up to the concentration of $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ of Ce(IV), whereas the hydrolyzed forms and dimers are the more predominant at $[H^+] < 0.8 \text{ mol dm}^{-3}$. However, increasing the reaction rates with the increase in hydrogen ion concentration suggests that Ce^{4+} may be more reactive than its hydrolyzed form. Therefore, under our experimental conditions, Ce^{4+} may be regarded as the kinetically active form of Ce(IV).

In sulfuric acid solutions, and depending upon the concentrations of H^+ , HSO_4^- and H_2SO_4 , cerium(IV) forms several sulfate complexes such as $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $HCe(SO_4)_3^-$ and $H_3Ce(SO_4)_4^-$, although their role has not received much attention so far (Sumathi et al., 2013; Thabaj et al., 2006). Owing to the effect of $[H^+]$ and $[HSO_4^-]$ on the oxidation rates, one or other of these species were treated to be the kinetically active species of Ce(IV). The following equilibria (Chimatadar, Madawale, & Nandibewoor, 2007) lead to formation of Ce(IV) sulfate complexes,



The observations that both H^+ and HSO_4^- ions retard the rates of the oxidation reactions point to the fact that $HCe(SO_4)_3^-$ (equilibrium D) may be considered as the kinetically active species which shows parallelism with variation of k_{obs} with both $[H^+]$ and $[HSO_4^-]$ in the present investigation. Generally, as the sulfuric acid concentration increased in the reaction mixtures, both $[H^+]$ and $[HSO_4^-]$ also increased. If the rate is inversely dependent on $[HSO_4^-]$ to a great extent, the overall effect of adding sulfuric acid would lower the rate as obtained experimentally (Table 2). Similar behavior has been reported elsewhere (Chimatadar et al., 2007).

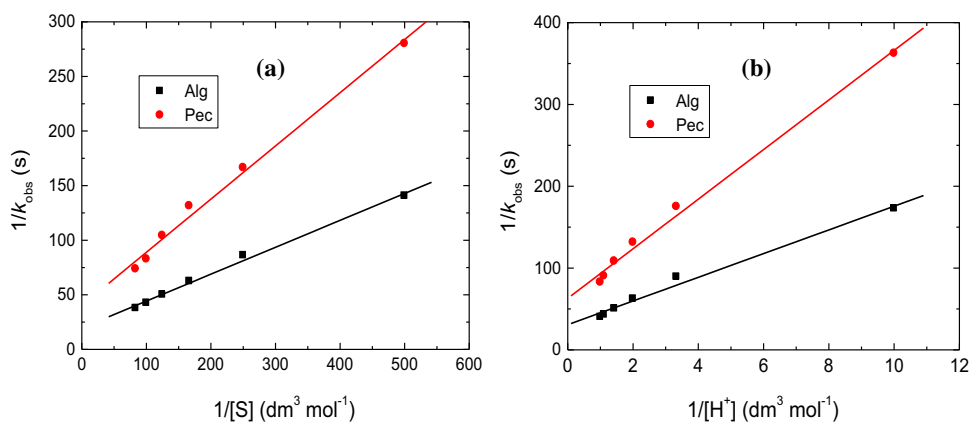
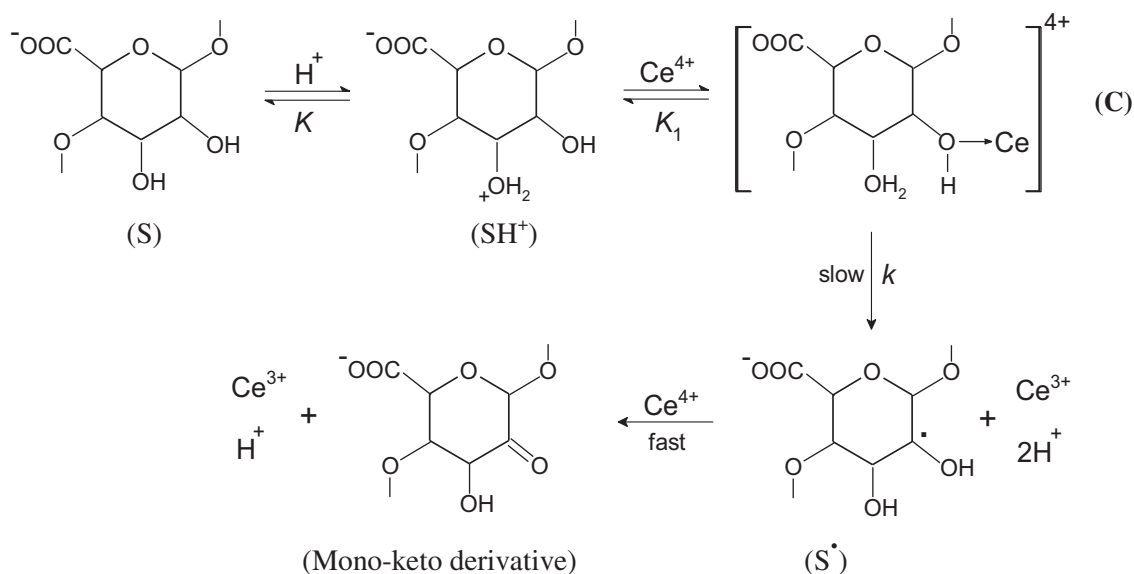


Fig. 4. Verification of rate law (1) in the form of: (a) Eq. (4), and (b) Eq. (5) in the oxidation of alginate and pectate by Ce(IV) in perchloric acid solutions. $[S] = 6.0 \times 10^{-3}$, $[Ce(IV)] = 2.0 \times 10^{-4}$, $[H^+] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .



Scheme 2. Mechanism of oxidation of alginate and pectate by Ce(IV) in perchloric acid solutions.

4.2. Reaction mechanism in perchloric acid

The reactions of alginate and pectate biopolymers with Ce(IV) in perchloric acid solutions have a stoichiometry of 1:2, i.e., one mole of biopolymer consumed two moles of Ce(IV). The reactions exhibited first order dependence with respect to $[Ce(IV)]$, less than unit order each with respect to $[H^+]$ and $[S]$. The less than unit orders in $[H^+]$ may be an indication of the protonation of biopolymers in the first step to form more reactive species of the reductants. No effect of added product, Ce(III), was observed suggesting absence of any fast equilibrium with the product preceding the rate-determining step. The latter should be irreversible as is generally the case for one electron oxidants (Leal, Domingo, Garcla, & Ibeas, 1993) and the oxidation takes place through generation of free radicals as obtained experimentally. Also, the fractional-first order kinetics with respect to biopolymer concentrations presumably due to formation of complexes between the kinetically active Ce(IV) species (Ce^{4+}) and the protonated substrates (SH^+) prior to the slow (rate-determining) step. Complexes formation was proved kinetically by the non-zero intercepts of the plots of $1/k_{obs}$ versus $1/[S]$ (Michaelis & Menten, 1913) as shown in Fig. 4a. Furthermore, increasing the oxidation rates with the increase in both ionic strength and dielectric constant of the reaction media indicates that the reactions occur between

two similarly charged ions (Amis, 1966; Frost & Person, 1973), i.e. between Ce^{4+} and SH^+ . The formed complexes are slowly decomposed in the slow step leading to formation of free radicals derived from the biopolymer substrates (S^*) in addition to Ce(III). The substrate radical reacts with another Ce^{4+} species in a subsequent fast step to yield the final oxidation products as shown in Scheme 2.

The suggested mechanism leads to the following rate law (see Appendix A),

$$\text{Rate} = \frac{kK_1[Ce(IV)][S][H^+]}{1 + K[H^+] + KK_1[S][H^+]} \quad (1)$$

This rate law is consistent with all the observed orders with respect to the different species.

Under pseudo-first order condition, the rate-law can be expressed by Eq. (2),

$$\text{Rate} = \frac{-d[Ce(IV)]}{dt} = k_{obs}[Ce(IV)] \quad (2)$$

Comparing Eqs. (1) and (2), the following relationship is obtained,

$$k_{obs} = \frac{kK_1[S][H^+]}{1 + K[H^+] + KK_1[S][H^+]} \quad (3)$$

Table 4
Values of the rate constant of the slow step and the equilibrium constants in the oxidation of alginate and pectate by Ce(IV) in perchloric and sulfuric acid solutions at 25 °C.

Perchloric acid			Sulfuric acid		
Constant	Alginate	Pectate	Constant	Alginate	Pectate
$10^3 k$ (s ⁻¹)	43.41	25.60	$10^3 k_1$ (s ⁻¹)	16.13	6.25
K (dm ³ mol ⁻¹)	0.93	0.87	$10^{-3} K_2$ (dm ³ mol ⁻¹)	158.81	7.96
$10^{-2} K_1$ (dm ³ mol ⁻¹)	2.96	2.50	$10^{-2} K_3$ (dm ³ mol ⁻¹)	17.22	4.45

Experimental error = ± 4%.

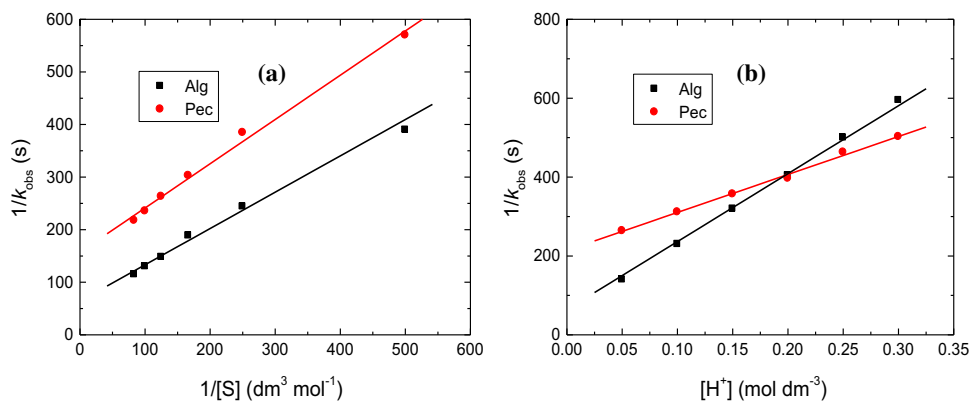


Fig. 5. Verification of rate law (6) in the form of: (a) Eq. (9), and (b) Eq. (10) in the oxidation of alginate and pectate by Ce(IV) in sulfuric acid solutions. $[S]=6.0 \times 10^{-3}$, $[Ce(IV)]=2.0 \times 10^{-4}$, $[H^+]=0.1$, $[HSO_4^-]=0.3$ and $I=0.3$ mol dm⁻³ at 25 °C.

Eq. (3) can be verified by rearranging it to the following equations,

$$\frac{1}{k_{obs}} = \left(\frac{1 + K[H^+]}{kKK_1[H^+]} \right) \frac{1}{[S]} + \frac{1}{k} \quad (4)$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{kKK_1[S]} \right) \frac{1}{[H^+]} + \left(\frac{1}{kK_1[S]} + \frac{1}{k} \right) \quad (5)$$

According to Eqs. (4) and (5), the plots of $1/k_{obs}$ versus $1/[S]$ at constant $[H^+]$, and $1/k_{obs}$ versus $1/[H^+]$ at constant $[S]$ should be linear with positive intercepts and are found to be so as shown in Fig. 4a and b, respectively. From the slopes and intercepts of such plots, the values of the rate constant of the slow step of Scheme 2 (k) and the equilibrium constants (K and K_1) are calculated and are listed in Table 4.

4.3. Reaction mechanism in sulfuric acid

The kinetics of reduction of Ce(IV) by alginate and pectate biopolymers in sulfuric acid solutions is consistent with that observed in perchloric acid solutions regarding to the reactions stoichiometry, reaction orders with respect to both the oxidant and reductant concentrations, free radical test and the effect of Ce(III) product. In contrast with perchloric acid, the reactions of the biopolymers with Ce(IV) in sulfuric acid solutions exhibited negative fractional-first order kinetics in $[H^+]$, and their rates were independent of both ionic strength and dielectric constant of the reaction media. Also, the increase in bisulfate concentration decreased the oxidation rates.

In view of the above arguments, the oxidation of biopolymer substrates by Ce(IV) in sulfuric acid solutions is suggested to proceed through formation of complexes (similar to that suggested in perchloric acid) between the neutral biopolymer substrates (S) and the kinetically active Ce(IV) species ($HCe(SO_4)_3^-$) prior to the rate-determining step. Such reactions between neutral substrates and negatively charged Ce(IV) species are supported by the independence of the reaction rates on both ionic strength and dielectric constant of the reaction media [37, 38]. Complexes formation was

also proved kinetically by the non-zero intercepts of the plots of $1/k_{obs}$ versus $1/[S]$ as shown in Fig. 5a. The formed complexes are slowly decomposed in the slow step to yield biopolymer free radicals (S^\bullet) and Ce(III). The substrate radical reacts with another $HCe(SO_4)_3^-$ species in a subsequent fast step leading to the final oxidation products as illustrated in Scheme 3.

The suggested mechanism leads to the following rate law (Appendix B in the supplementary materials),

$$\text{Rate} = \frac{k_1 K_3 [Ce(IV)][S]}{1 + K_2 [HSO_4^-][H^+] + K_3 [S]} \quad (6)$$

This rate law is also consistent with the observed orders with respect to the different species.

Under pseudo-first order condition,

$$\text{Rate} = \frac{-d[Ce(IV)]}{dt} = k_{obs}[Ce(IV)] \quad (7)$$

Comparing Eqs. (6) and (7), the following relationship is obtained,

$$k_{obs} = \frac{k_1 K_3 [S]}{1 + K_2 [HSO_4^-][H^+] + K_3 [S]} \quad (8)$$

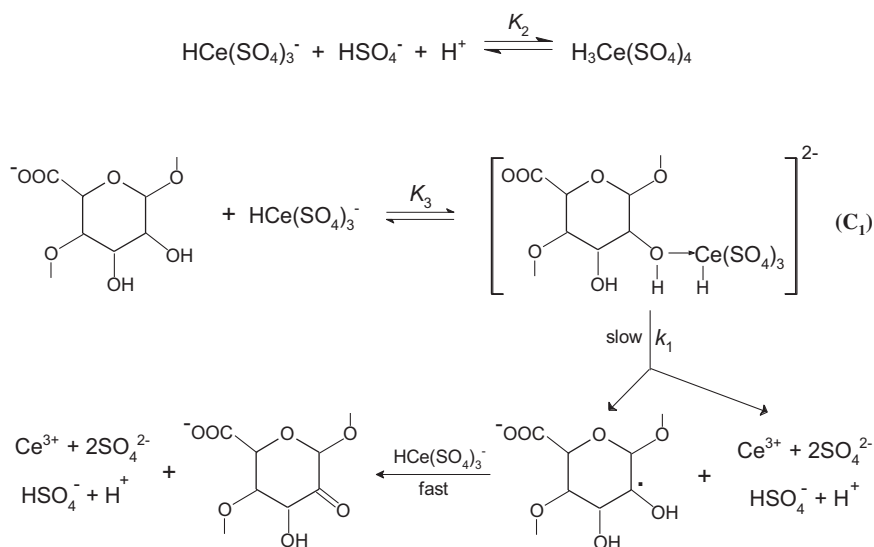
Equation (8) can be verified by rearranging it to Eqs. (9) and (10),

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_2 [HSO_4^-][H^+]}{k_1 K_3} \right) \frac{1}{[S]} + \frac{1}{k_1} \quad (9)$$

$$\frac{1}{k_{obs}} = \left(\frac{K_2}{k_1 K_3} \right) [HSO_4^-][H^+] + \left(\frac{1}{k_1 K_3 [S]} + \frac{1}{k_1} \right) \quad (10)$$

Thus, the plots of $1/k_{obs}$ versus $1/[S]$ at constant $[H^+]$, and $1/k_{obs}$ versus $[H^+]$ at constant $[S]$ should be linear with positive intercepts and are found to be so as shown also in Fig. 5a and b, respectively. From the slopes and intercepts of such plots, the values of the rate constant of the slow step of Scheme 3 (k_1) and the equilibrium constants (K_2 and K_3) are also calculated and are listed in Table 4.

The obtained activation parameters listed in Table 3 can be discussed as follows. The negative values of ΔS^\ddagger suggest interaction of reacting ions of similar charges to form intermediate complexes



Scheme 3. Mechanism of oxidation of alginate and pectate by Ce(IV) in sulfuric acid solutions.

of inner-sphere nature (Freeman et al., 1981; Hicks, Toppen, & Linck, 1972). These values are within the range of radical reactions and have been ascribed to the nature of the electron pairing and unpairing process and to the loss of degree of freedom formerly available to the reactants upon formation of a rigid transition state (Walling, 1957). The values of ΔH^\ddagger and ΔS^\ddagger are both favorable for electron transfer processes. On the other hand, the positive values of both ΔH^\ddagger and ΔG^\ddagger indicate endothermic formation of the complexes and their non-spontaneities, respectively.

Conclusions

The oxidation rates in perchloric acid solutions are found to be higher than those observed in sulfuric acid solutions and the oxidation rates of alginate are higher than those of pectate in both acids. Ce^{4+} and $\text{HCe}(\text{SO}_4)_3^-$ are regarded as the kinetically active species of cerium(IV) in perchloric and sulfuric acid solutions, respectively. In both cases, the final oxidation products are characterized as mono-keto derivatives of both biopolymers.

Appendix A. Appendix A

Derivation of rate law in case of perchloric acid

According to Scheme 2,

$$\text{Rate} = \frac{-d[\text{Ce(IV)}]}{dt} = k[\text{C}] \quad (\text{A.1})$$

$$K = \frac{[\text{SH}^+]}{[\text{S}][\text{H}^+]}, \quad [\text{SH}^+] = K[\text{S}][\text{H}^+] \quad (\text{A.2})$$

and

$$K_1 = \frac{[\text{C}]}{[\text{Ce}^{4+}][\text{SH}^+]}, \quad [\text{C}] = K_1[\text{Ce}^{4+}][\text{SH}^+] = KK_1[\text{Ce}^{4+}][\text{S}][\text{H}^+] \quad (\text{A.3})$$

Substituting Eq. (A.3) into Eq. (A.1) leads to,

$$\text{Rate} = kKK_1[\text{Ce}^{4+}][\text{S}][\text{H}^+] \quad (\text{A.4})$$

The total concentration of the substrate is given by,

$$[\text{S}]_T = [\text{S}]_F + [\text{SH}^+] + [\text{C}] \quad (\text{A.5})$$

where 'T' and 'F' stand for total and free concentrations.

Substituting Eqs. (A.2) and (A.3) into Eq. (A.5) and rearrangement gives,

$$[\text{S}]_T = [\text{S}]_F + K[\text{S}][\text{H}^+] + KK_1[\text{Ce}^{4+}][\text{S}][\text{H}^+] \quad (\text{A.6})$$

$$[\text{S}]_T = [\text{S}]_F(1 + K[\text{H}^+] + KK_1[\text{Ce}^{4+}][\text{H}^+]) \quad (\text{A.7})$$

Therefore,

$$[\text{S}]_F = \frac{[\text{S}]_T}{1 + K[\text{H}^+] + KK_1[\text{Ce}^{4+}][\text{H}^+]} \quad (\text{A.8})$$

In view of low $[\text{Ce}^{4+}]$, the third denominator term in the above equation is neglected. Therefore,

$$[\text{S}]_F = \frac{[\text{S}]_T}{1 + K[\text{H}^+]}. \quad (\text{A.9})$$

Also,

$$[\text{Ce(IV)}]_T = [\text{Ce}^{4+}]_F + [\text{C}] \quad (\text{A.10})$$

Substituting Eqs. (A.3) into Eq. (A.9),

$$[\text{Ce(IV)}]_T = [\text{Ce}^{4+}]_F + KK_1[\text{Ce}^{4+}][\text{S}][\text{H}^+] \quad (\text{A.11})$$

$$[\text{Ce(IV)}]_T = [\text{Ce}^{4+}]_F(1 + KK_1[\text{S}][\text{H}^+]) \quad (\text{A.12})$$

$$[\text{Ce}^{4+}]_F = \frac{[\text{Ce(IV)}]_T}{1 + KK_1[\text{S}][\text{H}^+]} \quad (\text{A.13})$$

Because of high $[\text{H}^+]$,

$$[\text{H}^+]_T = [\text{H}^+]_F \quad (\text{A.14})$$

Substituting Eqs. (A.9), (A.13) and (A.14) into Eq. (A.4) (and omitting 'T' and 'F' subscripts) leads to,

$$\text{Rate} = \frac{kKK_1[\text{Ce(IV)}][\text{S}][\text{H}^+]}{(1 + K[\text{H}^+])(1 + KK_1[\text{S}][\text{H}^+])} \quad (\text{A.15})$$

$$\text{Rate} = \frac{kKK_1[\text{Ce(IV)}][\text{S}][\text{H}^+]}{1 + K[\text{H}^+] + KK_1[\text{S}][\text{H}^+] + K^2K_1[\text{S}][\text{H}^+]^2} \quad (\text{A.16})$$

For low substrate concentration, the denominator term, $K^2K_1[\text{S}][\text{H}^+]^2$, in Eq. (A.16) can be neglected, resulting to Eq. (A.17),

$$\text{Rate} = \frac{kKK_1[\text{Ce(IV)}][\text{S}][\text{H}^+]}{1 + K[\text{H}^+] + KK_1[\text{S}][\text{H}^+]} \quad (\text{A.17})$$

Under pseudo-first order condition,

$$\text{Rate} = \frac{-d[\text{Ce(IV)}]}{dt} = k_{\text{obs}}[\text{Ce(IV)}] \quad (\text{A.18})$$

Comparing Eqs. (A.17) and (A.18), the following relationship is obtained,

$$k_{\text{obs}} = \frac{kKK_1[S][H^+]}{1 + K[H^+] + KK_1[S][H^+]} \quad (\text{A.19})$$

and with rearrangement, the following equations are obtained,

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1 + K[H^+]}{kKK_1[H^+]} \right) \frac{1}{[S]} + \frac{1}{k} \quad (\text{A.20})$$

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{kKK_1[S]} \right) \frac{1}{[H^+]} + \left(\frac{1}{kK_1[S]} + \frac{1}{k} \right) \quad (\text{A.21})$$

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2015.10.076.

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