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1 Reduction of hypervalent chromium in acidic media by alginic acid

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10 Abstract

11 Selective oxidation of carboxylate groups present in alginic acid by Cr^{VI} affords CO₂, oxidized
12 alginic acid, and Cr^{III} as final products. The redox reaction afforded first-order kinetics in [alginic
13 acid], [Cr^{VI}], and [H⁺], at fixed ionic strength and temperature. Kinetic studies showed that the
14 redox reaction proceeds through a mechanism which combines Cr^{VI}→Cr^{IV}→Cr^{II} and
15 Cr^{VI}→Cr^{IV}→Cr^{III} pathways. The mechanism was supported by the observation of free radicals,
16 CrO₂²⁺ and Cr^V as reaction intermediates. The reduction of Cr^{IV} and Cr^V by alginic acid was
17 independently studied and it was found to occur more than 10³ times faster than alginic acid/
18 Cr^{VI} reaction, in acid media. At pH 1-3, oxo-chromate(V)–alginic acid species remain in solution
19 during several hours at 15 °C. The results showed that this abundant structural polysaccharide
20 present on brown seaweeds is able to reduce Cr^{VI/IV} or stabilize high-valent chromium
21 depending on pH value.

23 Keywords:

24 alginic acid
25 oxidation
26 chromium
27 kinetics

29 1. Introduction

30 The major structural polysaccharide of brown seaweeds (*Phaeophyta*) is alginic
31 acid, a linear copolymer of (1→4)-linked β-D-mannopyranuronic acid (M) and
32 (1→4)-linked α-L-gulopyranuronic acid (G) residues, arranged in
33 heteropolymeric and homopolymeric blocks (**scheme 1**) (Larsen et al., 2003;
34 Leal et al., 2008). The content of uronic acids varies with species and tissues

1 types, and partial acid hydrolysis of alginic acids allows the preparation of
2 fractions enriched in hetero- and homopolymeric blocks (Craigie et al., 1984).
3 The presence of carboxylic acid groups in both monomeric units makes
4 possible its interaction with different metal ions, and in this sense its
5 complexation ability has been studied with heavy metal ions present in
6 wastewaters for water purification. Several authors have proposed interaction
7 models between alginic acid and specific metal ions (De Stefano et al., 2005;
8 Emmerichs et al., 2004; Maureira & Rivas, 2009).

9

10 **Insert scheme 1 here**

11

12 Cr^{VI} is a very important pollutant, and its derivative compounds represent a
13 potential environmental hazard because of their mammalian toxicity and
14 carcinogenicity (Cood, Irwin & Lay, 2003; Levina, Zhang & Lay, 2010). It is well
15 established that reduction of Cr^{VI} to Cr^{III} with a variety of organic and inorganic
16 reductants can occur by a multiplicity of mechanisms which depend on the
17 nature of the reducing agent (Gheju & Iovi, 2006; Mangiameli et al., 2014). The
18 existence of different species of chromium in acid media, Cr^{V} and Cr^{IV} , and the
19 tendency of Cr^{III} to form a variety of complexes, all combine to give systems of
20 considerable complexity (Levina & Lay, 2005).

21 Polyoxygenated compounds, such as polyalcohols and hydroxycarboxylic acids,
22 are effective as non-enzymatic reductants (at low pH) and can stabilize the
23 labile oxidation states of chromium (Codd et al., 2001; Ciésłak-Golonka &
24 Daszkiewicz, 2005). Due to the potential biological and ecological relevance of
25 these kinds of biopolymers, the reduction and stabilization of hypervalent
26 chromium by naturally occurring polysaccharides can provide useful information
27 on the role that these polyoxygenated compounds play in the uptake and
28 transport of chromium (Bellú, et al., 2008). Although the reduction of
29 hypervalent chromium by low molecular weight saccharides has been
30 extensively studied (González et al., 2004; Mangiameli et al., 2010 ; Mangiameli
31 et al., 2011), little is known on the reaction of polysaccharides with Cr^{VI} . Kinetic

1 and mechanistic studies of chromic acid oxidation onto kappa-karrageen;
2 carboxymethyl cellulose and chondroitin-4-sulfate polysaccharides as natural
3 polymers has been reported by Hassan and coworkers (Zaafarany, Khairou, &
4 Hassan, 2009; Hassan et al., 2010; Hassan et al., 2013). Cellulose,
5 hemicellulose and chitin reactions with Cr^{VI} were also studied at acid media (Lin
6 & Wang, 2012) but no redox mechanistic studies were performed in this case.
7 In a previous work we report the mechanism of oxidation of apple pectin by Cr^{VI}
8 in aqueous acid medium (Bellu et al., 2008). The determination of the ability of
9 alginic acid to reduce or stabilize hypervalent chromium will contribute to
10 understand the potential role of this polysaccharide in the biochemistry of this
11 metal. In this work, we report the study of the redox reaction of alginic acid with
12 Cr^{VI} providing information related to the relative reactivity of alginic acid toward
13 Cr^{VI} , Cr^{V} , and Cr^{IV} , the influence of pH on the redox reactions, and the formation
14 of long-lived oxo- Cr^{V} -alginic acid complexes, being characterized by
15 paramagnetic electronic resonance.

16 **2. Experimental**

17 **2.1. Materials**

18 Alginic acid sodium salt (Sigma, p.a.), GSH = L-glutathione reduced (Sigma,
19 98.0%), potassium dichromate (Mallinckrodt p.a.), sodium perchlorate
20 monohydrate (Fluka 98.0%), oxygen (99.99%), nitrogen (99 %), perchloric acid
21 (A. C. S. Baker), Ammonium iron(II) sulfate hexahydrate (Sigma, 99%),
22 acrylamide (Merck, 99.0%), sodium hydroxide (Cicarelli, p.a.),
23 diphenylpicrylhydrazyl (dpph) (Sigma, 99.9%), formic acid (Sigma, 80%),
24 acetone (Anedra 99.5 %), ethanol absolute (Cicarelli, p.a.), ehba = 2-ethyl-
25 hydroxybutanoic acid (Aldrich 99.0%), H_2SO_4 (Sigma, HPLC), were used
26 without further purification.

27 Aqueous solutions were prepared in milliQ deionized water. Solutions of alginic
28 acid sodium salt were prepared by stepwise addition of the reagent powder to
29 milliQ deionized water while rapidly stirring the solution to avoid the formation of
30 lumps, which dissolves with difficulty.

1 Na[Cr^VO(ehba)₂] \cdot H₂O, [Cr^{IV}O(ehbaH)₂] and K₃[Cr^V(O)(GSH)₂] were synthesized
2 according to the method described in the literature (Krumpolc et al, 1980;
3 Ghosh & Gould,1991; Levina et al., 2003). For experiments performed in the 1-
4 6 pH range, the pH of the solutions was adjusted by addition of HClO₄. In
5 experiments performed at constant ionic strength (μ = 0.50 M) and different
6 hydrogen ion concentrations; sodium perchlorate and perchloric acid solution
7 mixtures were used. The concentration of stock solutions of perchloric acid was
8 determined by titration employing standard analytical methods.

9
10 **Caution: Cr^{VI}, Na[Cr^VO(ehba)₂] \cdot H₂O, [Cr^{IV}O(ehbaH)₂] and dpph are human**
11 **carcinogens. Contact with skin and inhalation must be avoided.**

12 13 **2.2. Alginate acid stability**

14 Stability of polysaccharide in acidic conditions was studied by HPLC. The
15 chromatograms were obtained on a Varian Polaris 200 chromatograph provided
16 with a cc Star 9000 HPLC pump. The separation was carried out on an Aminex
17 HPX-87X (300 x 7.8mm², Bio-Rad Lab) HPLC column, using H₂SO₄ as eluent
18 (pH 1.5) and a flow rate of 0.6 mL/min, at 30°C. The samples were filtered
19 through a 0.2 mm membrane prior to the injection into the chromatographic
20 system. The effluent was monitored with a UV-vis detector (Prostar 325 UV-vis
21 detector, λ = 220 nm). Chromatograms, recorded after incubation of the standard
22 sample in 1.0 M HClO₄ (higher than the highest [H⁺] used in the kinetic
23 measurements) at 60 °C during 3.0 h, showed only one peak (tr: 5.65 min)
24 assigned to alginate acid. No others peaks were observed suggesting the stability
25 of the polysaccharide under the present experimental conditions.

26 27 **2.3. Measurement of free carboxylic groups of alginate acid**

28
29 Measurements of free carboxylic groups of alginate acid were performed by acid
30 base titration employing NaOH as titrant and phenolphthalein as visual indicator
31 (Kolthoff et al., 1969). Titration of 10.00 mL solution containing 20.00 g/L alginate

1 acid with 0.08704 M NaOH until change colour from colourless to pink afforded
2 10.75 mL of NaOH consumed which corresponds to 87.6 mM of free carboxylic
3 groups. The employed polysaccharide contains an average of 4.38 mmol free
4 carboxylic groups per gram of polymer.

5

6 **2.4. Product analysis**

7 Carbon dioxide was measured from a mixture of alginic acid (33.1 mg/mL), Cr^{VI}
8 (5.0 mM) and HClO₄ (0.50 M). The temperature was kept constant at 60°C and
9 the reaction mixture was continuously stirred and flushed with pure nitrogen.
10 The gaseous products were passed through three flasks containing NaOH (0.02
11 M). After reaction, in order to determine the yield of carbon dioxide, the NaOH
12 solutions were titrated with standard HCl (0.0232 M). Aliquots of the reaction
13 mixture of alginic acid/Cr^{VI} were analyzed by HPLC, using the same
14 experimental conditions and column mentioned at Section 2.2. No peak
15 corresponding to HCOOH (tr: 13.2 min) was observed.

16

17 **2.5. Polymerization test**

18 Detection of free organic radical generation, during the oxidation of alginic acid
19 by hypervalent chromium, was tested employing acrylamide. In a typical
20 experiment, a solution of Cr^{VI} (1.0 mL, 0.010 M) was added to 10.0 mL of a
21 solution 2.70 g/L of alginic acid, 0.50 M HClO₄ and 0.70 M of acrylamide. When
22 [Cr^{VI}] became negligible, the precipitation of a white polymer of polyacrylamide
23 was observed. Control experiments showed that no polymerization of
24 acrylamide took place under the same experimental conditions with either
25 K₂Cr₂O₇ or alginic acid alone. Possible reactions of Cr^V and Cr^{IV} with acrylamide
26 were tested with Na[Cr^VO(ehba)₂] and [Cr^{IV}O(ehbaH)₂]. No precipitation
27 occurred on mixing Cr^V or Cr^{IV} complexes with acrylamide under the conditions
28 used in the Cr^{VI}/alginic acid reaction.

29

30 **2.6. Kinetic measurements**

1 Kinetic measurements were performed by monitoring absorbance changes on a
2 Jasco V-550 spectrophotometer with fully thermostated cell compartments (± 0.2
3 $^{\circ}\text{C}$). The reactions were followed under pseudo-first-order conditions, at 60°C ;
4 using excess of alginic acid over $\text{Cr}^{\text{VI}}/\text{Cr}^{\text{V}}$. Reactant solutions were thermally
5 equilibrated at 60°C prior to the experiment and NaClO_4 was used to maintain a
6 constant ionic strength (μ).

7 ***Alginic acid/ Cr^{VI} reactions.***

8 Disappearance of Cr^{VI} was followed by DPC method (Clesceri, Greenberg, &
9 Eaton, 1998); monitoring the absorbance at 540 nm until at least 80%
10 conversion. In the kinetic measurements, the concentration of Cr^{VI} and μ were
11 kept constant at 1.0 mM and 0.50 M, respectively, while carboxylic group/ Cr^{VI}
12 ratio was varied from 20:1 to 60:1, at various $[\text{HClO}_4]$. The experimental
13 pseudo-first-order rate constants (k_{6exp}), obtained from nonlinear least-square
14 fits of kinetic data, were averages of at least three determinations and were
15 within $\pm 5\%$ of each other. The first-order dependence of the rate upon $[\text{Cr}^{\text{VI}}]$ was
16 verified in a set of experiments where the $[\text{Cr}^{\text{VI}}]_0$ was varied between 0.30 and
17 2.0 mM, keeping temperature, [alginic acid], $[\text{H}^+]$, and μ constant. Ionic strength
18 effect was studied in a set of experiments where $[\text{Cr}^{\text{VI}}]_0$, [alginic acid], $[\text{H}^+]$ and T
19 were kept constant and μ was varied from 0.20 M to 1.0 M.

20 ***Alginic acid/ Cr^{V} reactions.***

21 Kinetic measurements for the oxidation of alginic acid by Cr^{V} was performed by
22 ligand exchange reaction, employing $\text{K}_3[\text{Cr}^{\text{V}}(\text{O})(\text{GSH})_2]$. In a typical experiment,
23 100 μL of the oxo- Cr^{V} complex solution (24 mM) were mixed with 2.3 mL of a
24 solution containing alginic acid (4.57 g/L), $[\text{H}^+]$ (0.30 M) and $\mu = 0.50$ M
25 (NaClO_4) at 15°C . The reaction was followed at 350 nm, until at least 80 %
26 conversion.

27 ***Alginic acid/ Cr^{IV} reactions.***

28 The oxidation of alginic acid by Cr^{IV} (CrO_2^{2+}) was spectrophotometrically
29 monitored following the appearance of CrO_2^{2+} as a final redox product. Alginic
30 acid/ CrO_2^{2+} mixtures showed an increase of two intense absorption bands at

1 290 and 247 nm, with relative intensity $Abs_{247}/Abs_{290} = 2.2$ characteristic of
2 CrO_2^{2+} (Scott, Bakac, & Espenson, 1991). The kinetic data were collected
3 spectrophotometrically by following the formation of CrO_2^{2+} at 290 nm ($\epsilon = 3100$
4 $M^{-1}cm^{-1}$) at 25 °C (Scott, Bakac, & Espenson, 1992). At this wavelength, neither
5 alginic acid nor the oxidized products absorb. In the kinetics measurements,
6 $[Cr^{IV}]$, μ , $[O_2]$, and temperature were kept constant at 0.207 mM, 0.50 M, 1.26
7 mM and 25 °C respectively. The concentration range of alginic acid used was
8 chosen in order to avoid CrO^{2+} disproportionation. The carboxylic group/ Cr^{IV}
9 ratio was varied from 50:1 to 400:1. The experimental pseudo first order rate
10 constants (k_{4exp}), obtained from nonlinear least square fits of absorbance data
11 at 290 nm were averages of at least five determinations and were within $\pm 10\%$
12 of each other. Data used to calculate the kinetic constant, k_{4exp} , correspond to
13 80% of the total experimental values. The first order dependence of the rate
14 upon $[Cr^{IV}]$ was verified in a set of experiments where the $[Cr^{IV}]_0$ was varied
15 between 0.10- 0.50 mM, but T, [alginic acid], and μ were kept constant.

17 **2.7. Detection of superoxo- Cr^{III} during the reaction of alginic acid with Cr^{VI}**

18 The possible formation of Cr^{II} in alginic acid/ Cr^{VI} mixtures was examined by UV-
19 vis periodic scanning (220- 600 nm) of solutions of 0.78 g/L alginic acid, 0.0797
20 mM Cr^{VI} and 3.0 M $HClO_4$ saturated with oxygen ($[O_2] = 1.26$ mM), at 25 °C.
21 Spectra were collected every 2 min. If Cr^{II} forms, it is converted rapidly by
22 dioxygen to CrO_2^{2+} , which has characteristic absorption bands (Scott, Bakac, &
23 Espenson, 1991; Scott, Bakac, & Espenson, 1992) and can be detected at low
24 $[Cr^{VI}]$. Periodic scanning of the reaction mixture showed that the Cr^{VI} band at
25 350 nm decreased in intensity, while two new peaks at 290 nm and 247 nm
26 characteristic of CrO_2^{2+} grew in. When $[Cr^{VI}]$ was negligible, 0.091 mM Fe^{2+}
27 was added.

29 **2.8. Chromate esters**

1 Chromate esters were investigated by UV-vis spectrophotometry in the 320-
2 450 nm region in which these compounds show characteristic absorption
3 bands. Reactions were performed at pH 6.0, where the redox reaction is slow
4 enough to enable the observation of the ester formation. The instrument was
5 zeroed to an arrangement of the reference and sample beams passing through
6 matched cell, both containing 0.5 mM Cr^{VI} at pH 6.0. The solution in the sample
7 cell was replaced with the reaction solution containing 0.5 mM Cr^{VI} and 0.228-
8 0.457 g/L alginic acid at pH = 6.0, $\mu = 0.50$ M and T = 25 °C. Spectra obtained
9 at 30 minutes after mixing showed a characteristic absorption at 375 nm.

10

11 **2.9. EPR measurements**

12 The EPR spectra were obtained with a Bruker ESP 300 E computer-controlled
13 spectrometer operating at X-band frequencies (~ 9.4-9.8 GHz). Microwave
14 generation was by means of a klystron (ER041MR) and frequencies were
15 measured with a built-in frequency-counter. Spectra were recorded as first
16 derivatives of the microwave absorption in 1024 points at 288 K, using 10 mW
17 microwave power and 100 kHz modulation frequency. Power values used in the
18 EPR experiments did not overcome 10 mW in order to avoid signal saturation.
19 In EPR measurements, scanning speed and number were fixed in order to
20 reduce the time used in each measurement. This was done to avoid fluctuations
21 in the EPR signal during the sample scanning. *g*-values were determined by
22 reference to diphenylpicrylhydrazyl (dpph) ($g_{iso} = 2.0036$) as an external
23 standard. Long-lived oxo-Cr^V-alginic acid complexes were generated in two
24 different ways: a) by reaction of K₂Cr₂O₇ with an aqueous solution containing
25 alginic acid; b) by mixing reduced glutathione (GSH) and K₂Cr₂O₇ where [Cr^{VI}] =
26 [GSH] and an excess of alginic acid.

27

28 **3. Results and discussion**

29 **3.1. Oxidation of alginic acid by Cr^{VI}**

30 **3.1.1. Rate studies**

1 The reaction kinetic of alginic acid with Cr^{VI} was examined by the
 2 diphenylcarbazide (DPC) (Clesceri, Greenberg, & Eaton, 1998) method, in
 3 excess of alginic acid over Cr^{VI} , in the 0.10- 0.50 M HClO_4 range. DPC can
 4 react with Cr^{V} and probably with Cr^{IV} (Eckert et al., 1991), therefore it is very
 5 important to probe that no accumulation of these species occurs in the alginic
 6 acid/ Cr^{VI} reaction mixtures. Under experimental conditions employed in this
 7 work, both species Cr^{IV} and Cr^{V} , decay rates are much higher than Cr^{VI} (as
 8 shown below) and do not accumulate in the reaction alginic acid/ Cr^{VI} . This result
 9 allows the use of DPC method for measuring Cr^{VI} without any interference by
 10 other chromium species. A monophasic decrease of $[\text{Cr}^{\text{VI}}]$ with time was
 11 observed, and the kinetic profiles could be adequately described by a single
 12 exponential decay from which Cr^{VI} pseudo-first-order rate constants ($k_{6\text{exp}}$) were
 13 calculated. **Table 1** summarizes $k_{6\text{exp}}$ values for various concentrations of
 14 alginic acid and HClO_4 .

15 **Table 1: Experimental pseudo-first-order rate constants for different**
 16 **$[\text{HClO}_4]$ and $[\text{alginic acid}]$.**^[a]

$[\text{H}^+](\text{M})$	0.1	0.2	0.3	0.4	0.5
$[\text{alginic acid}]$ (g/L)	$10^2 \times k_{6\text{exp}}^{\text{[b]}}$				
4.57	0.817±0.006	1.00±0.04	1.57±0.18	1.80±0.03	2.28±0.04
6.85	1.26±0.01	1.53±0.04	2.05±0.07	2.49±0.14	3.12±0.19
9.13	1.62±0.02	2.01±0.02	2.63±0.06	3.53±0.09	4.16±0.26
11.4	2.10±0.04	2.35±0.08	3.55±0.17	4.43±0.02	5.63±0.13
13.7	2.64±0.03	3.02±0.05	4.22±0.09	5.30±0.06	6.60±0.14

17 ^[a]T = 60 °C; $[\text{Cr}^{\text{VI}}] = 1.0 \text{ mM}$; $\mu = 0.50 \text{ M}$. The values of $k_{6\text{exp}}$ are expressed in
 18 min^{-1} . ^[b]Mean values from multiple determinations (estimated errors are lower
 19 than 10%). Rate constants were obtained using Sigma Plot 11.0 Program.

20

1 The value of $k_{6\text{exp}}$ did not vary with different $[\text{Cr}^{\text{VI}}]_0$ at fixed T , μ , [alginic acid]
 2 and $[\text{HClO}_4]$, confirming the first-order rate dependence on $[\text{Cr}^{\text{VI}}]$. When μ is
 3 varied from 0.20 M to 1.0 M but $[\text{Cr}^{\text{VI}}]_0$, T , [alginic acid] and $[\text{HClO}_4]$ are fixed,
 4 the value of $k_{6\text{exp}}$ increased with the increase of μ . The effect of ionic strength
 5 on the rate constants of reactions involving ions is well understood applying the
 6 Bronsted- Debye- Hückel equation (Espenson, 2002):

$$7 \log_{10} k = \log_{10} k_0 + 2 A Z_A Z_B F_\mu \quad (1)$$

8 Where A is a constant equals to 0.73 for water at 333 K ($A = 1.87 \times 10^6 / (\epsilon T)^{3/2}$,
 9 Z_A , Z_B are the charges of reactive A and B respectively, and F_μ is the ionic
 10 strength function $\mu^{1/2} / (1 + \mu^{1/2})$. The quantity k_0 is the limiting rate constant at zero
 11 ionic strength. The value of $Z_A Z_B$ obtained from the slope of the plot $\log_{10} k$ vs
 12 F_μ was 1.01 ± 0.01 (see Supplementary material **Fig S1**), which is in agreement
 13 with two reactive ionic species with a charge value of $Z_A = Z_B = -1$.

14 It is well known that the trivalent metal cation Cr^{III} have a high tendency to make
 15 complexation with alginic acid or its derivatives to give the corresponding
 16 coordination biopolymeric cross-linked trivalent metal-alginate complexes
 17 (Ibáñez & Umetsu, 2004). Since Cr^{III} is one of the oxidation products, its
 18 influence on the oxidation rates was examined. **Table 2** showed the values of
 19 $k_{6\text{exp}}$ obtained with and without Cr^{III} perchlorate salts added to the reaction
 20 mixtures.

21 **Table 2: Effect of $[\text{Cr}^{\text{III}}]_0$ over $k_{6\text{exp}}$.**^[a]

$[\text{Cr}^{\text{III}}]_0$ (M)	0.000	0.010	0.050
[alginic acid] (g/L)		$10^2 \times k_{6\text{exp}}$ ^[b]	
4.57	1.00±0.04	1.06±0.05	1.07±0.08
13.7	3.02±0.05	3.08±0.08	3.03±0.06

22 ^[a] $T = 60 \text{ }^\circ\text{C}$; $[\text{Cr}^{\text{VI}}] = 1.0 \text{ mM}$; $[\text{H}^+] = 0.20 \text{ M}$; $\mu = 0.50 \text{ M}$. The values of $k_{6\text{exp}}$
 23 are expressed in min^{-1} . ^[b]Mean values from multiple determinations

1 (estimated errors are lower than 10%). Rate constants were obtained
2 using Sigma Plot 11.0 Program.

3

4 As it showed in **Table 2** no significant variation of $k_{6\text{exp}}$ values was obtained at
5 fixed $[\text{H}^+]$, [alginic acid], T and μ . These results demonstrate that Cr^{III} -
6 alginates, if it is formed, they don't modify the oxidation rates of alginic
7 acid by Cr^{VI} .

8 Plots of $k_{6\text{exp}}$ versus [alginic acid] afforded good straight lines (**Fig. 1**) from
9 which values of $k_{6\text{S}}$ were determined. A linear dependence of $k_{6\text{S}}$ values on
10 $[\text{HClO}_4]$ was observed, (**inset, Fig. 1**).

11 **Insert Fig. 1 here**

12 The rate constant k_6 and $k_{6\text{H}}$ calculated from plot of $k_{6\text{S}}$ versus $[\text{H}^+]$ were found
13 to be $(0.21 \pm 0.03) \text{ min}^{-1}\text{M}^{-1}$ and $(1.72 \pm 0.08) \text{ min}^{-1}\text{M}^{-2}$, respectively.
14 Consequently, the complete rate law for the Cr^{VI} consumption can be expressed
15 as:

$$16 \quad -\frac{d[\text{Cr}^{\text{VI}}]}{dt} = (k_6 + k_{6\text{H}}[\text{H}^+])[\text{alginic acid}][\text{Cr}^{\text{VI}}]_{\text{T}} \quad (2)$$

17 Under conditions used in the kinetic studies, CO_2 was detected as product of
18 oxidation. Quantitative analysis of CO_2 showed that the reaction yielded 0.60
19 mol of CO_2 per mole of Cr^{VI} . In alginic acid structure, the functional group being
20 oxidized is the carboxylic group and can be rationalized taking into account the
21 relative reactivity of functional groups in saccharides toward Cr^{VI} :

22 $-(\text{H})\text{C}(\text{OR})\text{OH}_{\text{hemiacetal}}$ (Signorella et al., 1999) > $-\text{CO}_2\text{H}$ (Bellú et al., 2008) >
23 $-\text{H}_2\text{COH}_{\text{primary}}$ (Roldán et al., 2000) >> $(\text{H})\text{COH}_{\text{secondary}}$ (Santoro et al., 2007);
24 $(\text{H})\text{COR}_{\text{glycoside}}$ (Signorella et al., 2000); $\text{RCO}_2\text{R}_{\text{ester}}$ (Sala et al., 1993).

25 Stoichiometry of the oxidation of alginic acid by Cr^{VI} is shown in **Scheme 2**.

26 **Insert scheme 2 here**

27 **3.1.2. Detection of Cr^{VI} esters**

1 Chromate esters were investigated by differential UV-vis spectra of alginic
2 acid/Cr^{VI} mixtures. The mixtures exhibited an absorption band with $\lambda_{\max} = 375$
3 nm consistent with that described for oxo-Cr^{VI}-ester (Mitewa & Bontchev, 1985;
4 Mangiameli et al., 2010; Mangiameli et al., 2014). At pH 6.0, the redox reaction
5 of Cr^{VI} with alginic acid proceeds very slowly, with negligible reduction of Cr^{VI}.
6 Thus, at this pH value, the ester formation step can be clearly distinguished
7 from the electron transfer reaction. Spectra obtained within 30.0 min after
8 mixing revealed a distinctive absorption band at 375 nm, **Fig. 2**.

9 **Insert Fig. 2 here**

10 Alginic acid/Cr^{VI} mixtures with [alginic acid] 0.228- 0.457 g/L, at pH 6.0, showed
11 that the absorbance at 375 nm increased with increasing [alginic acid], probably
12 as a result of a shift towards the ester in the esterification equilibrium.

13

14 **3.1.3. Intermediacy of Cr^V**

15 EPR spectroscopy is the most specific and sensitive technique to detect micro
16 molar concentrations of paramagnetic ions such as Cr^V species. Therefore, the
17 presence of oxo-Cr^V complexes can be identified with great sensitivity by EPR
18 spectroscopy at room temperature in X-band spectra. The EPR spectral
19 parameter, g_{iso} , values of the EPR signal of Cr^V complexes depend on the Cr^V
20 coordination number and the nature of the donor groups bound to oxo-Cr^V
21 (Barr-David et al., 1995). EPR spectra of alginic acid/ Cr^{VI} reaction mixtures
22 showed complex and less resolved signals than in the other systems (Sala et
23 al., 2011). In general, the signals were very broad, which indicates the
24 contribution of several Cr^V isomers; **Fig. 3**. The signal belongs to species where
25 the oxo-Cr^V was coordinated to alcoholate and carboxylate groups which may
26 belong to the same or different polymeric chain, thus affording a complex EPR
27 signal.

28

29 **Insert Fig. 3 here**

30

1 After 30 min of reaction multiplicity of EPR signals of alginic/Cr^{VI} reaction
 2 mixture at pH 1- 3 could not be resolved, even with low modulation amplitude,
 3 because the superhyperfine coupling constants were lower than the line width.
 4 Spectra were simulated with four singlets in order to obtain information from the
 5 g_{iso} values (**Table 2**) of oxo-Cr^V species in the reaction mixture. The simulation
 6 of the EPR spectra showed that the complex signal of the alginic acid/Cr^{VI}
 7 reaction mixture came from the contribution of, at least, four species of oxo-Cr^V
 8 species. Additionally, it must be noted that the average g_{iso} value were in the
 9 range of that expected for five-coordinated oxochromate(V) complexes (see
 10 Supplementary material **Fig. S2** and **Table 2**). The signal with average g_{iso}
 11 1.9780 (species A) is consistent with those for five-co-ordinated oxo-Cr^V
 12 complexes having two carboxylate and two alcoholate donor groups, (Barr-
 13 David, et al., 1995) [Cr^VO(R-COO⁻,R-OH)₂]. Meanwhile the signal with average
 14 g_{iso} 1.9790 belongs to five-co-ordinated oxo-Cr^V mixed species [Cr^VO(R-COO⁻
 15 ,OH)(R-OH)₂] (species B) where the oxo-Cr^V group is being coordinated by
 16 three alcoholate and one carboxylate groups.

17 **Table 2**

species	coordination	g_{iso}	g_{iso} (calculated)	line width (G)	%
A	[Cr ^V O(R-COO ⁻ ,R-OH) ₂]	1.9780	1.9783	2.90	45.0
B	[Cr ^V O(R-COO ⁻ ,OH)(R-OH) ₂]	1.9790	1.9791	3.90	35.4
C	[Cr ^V O(R-OH) ₂ (R-OH) ₂]	1.9803	1.9800	2.40	14.7
D	[Cr ^V O(R-COO ⁻) ₂ (H ₂ O) ₂]	1.9750	1.9749	5.00	4.6

18 T = 15 °C; [alginic acid] = 4.57 g/L; [Cr^{VI}] = 1.0 mM; μ = 0.50 M; pH = 2.0;
 19 Center Field = 3410 G ; Modulation amplitude = 2.0 G ; resolution = 1024
 20 points ; Frequency = 9.4312 GHz

21

22 Unlike the results observed in the acid sacharides/Cr^V complexes, (Gonzalez et
 23 al., 2009; Gonzalez et al., 2010), at pH 2.0, there was approximately a 15% of
 24 species, where the oxo-Cr^V group is being coordinated with four alcoholate
 25 groups (species C). Finally, a fourth species (D) with a g_{iso} 1.9750 could be
 26 related with oxo-Cr^V coordinated by two carboxylates and molecules of waters.

1 Anyway, the predominant species with g_{iso} values 1.9780 and 1.9791, during
2 reaction time, indicated that the coordination mode of oxo-Cr^{VO} by carboxylate
3 and diolates (belonging to β -D-mannopyranuronic and α -L-gulopyranuronic acid
4 residues,) was the most suitable from the thermodynamic point of view at acidic
5 pH.

6

7 **3.1.4. Intermediacy of Cr^{II}**

8 The fact that Cr^{II} is involved in the oxidation mechanism of several alcohols and
9 tiols by Cr^{IV} and Cr^{VI} in HClO₄ was demonstrated by conversion to CrO₂²⁺ upon
10 reaction with dioxygen (Scott et al., 1991; Scott et al., 1992; Al-Ajlouni et al.,
11 1994; Pérez Benito et al., 1994; Pérez Benito & Arias, 1993). In appropriate
12 experimental conditions, such as high [O₂] = 1.26 mM and low [Cr^{VI}] = 0.08 mM,
13 the reaction of Cr^{II} (if any) with O₂ to give CrO₂²⁺ can compete successfully with:
14 a) the reaction of Cr^{II} with Cr^{VI} and b) the autocatalytic consumption of CrO₂²⁺
15 by Cr^{II}. If Cr^{II} is an intermediate species in the alginic acid/Cr^{VI} redox reaction,
16 CrO₂²⁺ should be detected (Scott et al., 1992).

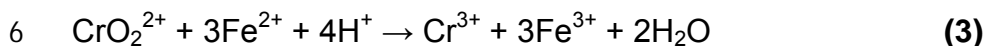
17 We examined the presence of intermediate Cr^{II} in the reaction of alginic acid
18 with Cr^{VI}, by monitoring the formation of CrO₂²⁺, using [Cr^{VI}]₀ low enough to
19 avoid the Cr^{VI} + Cr^{II} competitive reaction, and 3.0 M HClO₄ to accelerate the
20 alginic acid/Cr^{VI} reaction at a temperature lower than used in the kinetics
21 experiments.

22 A periodic scanning of the O₂-saturated solution (1.26 mM O₂) of a alginic
23 acid/Cr^{VI} reaction mixture in 3.0 M HClO₄ over a period of 60 min, showed that
24 the band at 350 nm, characteristic of Cr^{VI}, decreased in intensity meanwhile two
25 absorption bands at λ_{max} 247 and 290nm appeared (**Fig. 4**).

26 **Insert Fig. 4 here**

27 These two bands are characteristic of CrO₂²⁺ formed as a long-lived
28 intermediate (Scott et al., 1991), that then slowly transforms into the final Cr^{III}
29 (as shown below). Since CrO₂²⁺ can be exclusively formed by reaction of Cr^{II}
30 with O₂, and, in turn, Cr^{II} had previously been demonstrated to form exclusively

1 through two-electron reduction of Cr^{IV} (Scott et al., 1992; Al-Ajlouni et al., 1994),
 2 our spectroscopic results provide evidence that Cr^{II} and Cr^{IV} are involved in the
 3 redox mechanism of the reaction between Cr^{VI} and alginic acid. When the
 4 absorbance at 350 nm was negligible, 0.091 mM of Fe^{II} was added to bring
 5 about the following reaction:



7 The spectrum of the reaction mixture was subtracted from the corresponding
 8 one prior to Fe^{II} addition. As shown in **Fig. 4 inset**, there is a negative
 9 absorbance difference around 290 nm, consistent with the presence of CrO_2^{2+} .

10

11 **3.2. Oxidation of alginic acid by Cr^{V}**

12 The reaction of alginic acid with Cr^{V} was examined by ligand exchange
 13 employing the complex $\text{K}_3[\text{Cr}^{\text{V}}(\text{O})(\text{GSH})_2]$, and following the decrease in
 14 absorption at 350 nm. The ligand exchange reaction was verified by EPR
 15 measurements and it was completed in a few seconds. Comparing the alginic
 16 acid/ Cr^{VI} and alginic acid/ Cr^{V} reactions, at the same conditions (μ , [alginic acid]
 17 and $[\text{Cr}^{\text{VI}}]_0$) except T (15 °C for Cr^{V} reaction and 60 °C for Cr^{VI} reaction) it was
 18 observed that alginic acid/ Cr^{V} reaction is very fast (see Supplementary material
 19 **Fig S3**).

20 As it is showed in **Fig. S3**, Cr^{V} decays with time very fast and is expected that
 21 no accumulation of this species occurs in the alginic acid/ Cr^{VI} systems. After 2.0
 22 min, only 6 % of Cr^{VI} consumption was achieved while 85% of Cr^{V} consumption
 23 occurs. **Fig. S3** showed a monophasic decrease of $[\text{Cr}^{\text{V}}]$ with time. The oxo- Cr^{V} -
 24 alginic acid species kinetic profile could be adequately fitted to a single
 25 exponential decay from which Cr^{V} pseudo-first-order rate constant ($k_{5\text{exp}}$) was
 26 calculated. The value of $k_{5\text{exp}}$ estimated in this way resulted to be $(2.14 \pm 0.06) \times$
 27 10^{-2} s^{-1} . EPR and electronic spectroscopy show that Cr^{III} is the ultimate fate of
 28 chromium in these reactions.

29 **3.3. Reaction of CrO_2^{2+} with alginic acid**

1 The addition of variable quantities of alginic acid to O₂-saturated solutions
 2 containing 0.30 mM of CrO₂²⁺ resulted in the increase of the CrO₂²⁺ spectrum
 3 intensity. The formation of CrO₂²⁺ was followed at 290nm and the monotonic
 4 increase of absorbance was found to follow first-order kinetics. The
 5 experimental rate constants $k_{4\text{exp}}$ were calculated by nonlinear least-square fit of
 6 absorbance-time data to the equation:

$$7 \quad Abs_t = Abs_{\infty} + (Abs_0 - Abs_{\infty})e^{(-k_{4\text{exp}} t)} \quad (4)$$

8 where Abs_{∞} and Abs_0 were absorbance at infinite time and initial absorbance,
 9 respectively.

10 **Fig. 5** shows spectral scanning of alginic acid/Cr^{IV} mixtures and the right fitting
 11 of the absorbance data vs. time at 290 nm employing **eqn 4**, (**inset Fig. 5**).

12 **Insert Figure 5 here**

13 The value of $k_{4\text{exp}}$ did not vary with different [Cr^{IV}]₀, but fixed T, μ , [alginic acid],
 14 and [HClO₄], confirming the first-order dependence of rate on [Cr^{IV}]. **Table 3**
 15 summarizes values of $k_{4\text{exp}}$ for various concentrations of alginic acid and HClO₄.

16 **Table 3: Experimental pseudo-first-order rate constants ($k_{4\text{exp}}$) for different**
 17 **concentrations of HClO₄ and alginic acid.**^[a]

[H ⁺](M)	0.2	0.3	0.4	0.5
[alginic acid] (g/L)	$10^2 \times k_{4\text{exp}}^{[b]}$			
2.28	1.80±0.11	1.90±0.18	1.89±0.12	1.85±0.15
4.57	3.20±0.16	3.00±0.17	2.80±0.14	3.05±0.08
6.85	4.04±0.04	4.10±0.06	3.89±0.13	4.06±0.05
9.13	4.45±0.18	4.60±0.15	4.50±0.12	4.52±0.13
11.4	4.90±0.12	5.20±0.11	5.00±0.09	5.05±0.10

1 $^{[a]}T = 25\text{ }^{\circ}\text{C}$; $[\text{Cr}^{\text{IV}}] = 0.20\text{ mM}$; $\mu = 0.50\text{ M}$. The values of $k_{4\text{exp}}$ are expressed in
 2 s^{-1} . $^{[b]}$ Mean values from multiple determinations (estimated errors are lower than
 3 10%). Rate constants were obtained using Sigma Plot 11.0 Program.

4 Experimental conditions were chosen so that the alginic acid/ Cr^{IV} reaction was
 5 much faster than Cr^{IV} disproportionation into Cr^{VI} and Cr^{III} . In the absence of
 6 alginic acid, or when the alginic acid concentration was too low,
 7 disproportionation of Cr^{IV} was evidenced by the grow-up of absorbance at 350
 8 nm due to formation of Cr^{VI} . Using reactant concentrations of **Table 3**, Cr^{VI} was
 9 not detected. Values of $k_{4\text{exp}}$ are independent of $[\text{H}^+]$ in the range 0.20- 0.50 M,
 10 followed by saturation kinetic with [alginic acid] (see Supplementary material **Fig.**
 11 **S4**).

12 Non-linear curve fit of kinetic data allowed to calculate values of k_1 and k_2
 13 applying the equation:

$$14 \quad k_{4\text{exp}} = \frac{k_1[\text{alginic acid}]}{1+k_2[\text{alginic acid}]} \quad (5)$$

15 Consequently, the complete rate law for the Cr^{IV} consumption can be expressed
 16 as in the equation:

$$17 \quad \frac{d[\text{CrO}_2^{2+}]}{dt} = -\frac{d[\text{Cr}^{\text{IV}}]}{dt} = \left(\frac{k_1[\text{alginic acid}]}{1+k_2[\text{alginic acid}]} \right) [\text{Cr}^{\text{IV}}]_{\text{T}} \quad (6)$$

18 With $k_1 = 66 \pm 1\text{ M}^{-1}\text{s}^{-1}$ and $k_2 = 1120 \pm 30\text{ M}^{-1}$

19 Reaction mixtures containing excess of alginic acid over CrO_2^{2+} in 0.20 M HClO_4
 20 were analyzed for CO_2 as reaction product. Quantitative analysis of CO_2
 21 showed that the reaction yielded 1.0 mol of CO_2 per mole of Cr^{IV} .

22 **Scheme 3** shows a proposed reaction mechanism for the oxidation of alginic
 23 acid by CrO_2^{2+} .

24 **Insert scheme 3 here**

25 We proposed that a reactive alginic acid- Cr^{IV} ester is formed in a first step of the
 26 reaction pathway. This very reactive intermediate is in stationary state so its
 27 formation and decomposition rates are equals. Taking into account the
 28 proposed mechanism, the rate law takes the form:

$$1 \quad -\frac{d[\text{Cr}^{\text{IV}}]}{dt} = k_4[\text{Cr}^{\text{IV}} - \text{ester}] \quad (10)$$

2 Applying stationary state concept:

$$3 \quad [\text{Cr}^{\text{IV}} - \text{ester}] = \frac{k_a[\text{alginic acid}][\text{Cr}^{\text{IV}}]}{k_{-a}+k_4} \quad (11)$$

4 Considering total analytical concentration of Cr^{IV} :

$$5 \quad [\text{Cr}^{\text{IV}}]_T = [\text{Cr}^{\text{IV}}] + [\text{Cr}^{\text{IV}} - \text{ester}] \quad (12)$$

6 Replacing and making the corresponding mathematical arrangements, **eqn 10**
7 transforms into **eqn 13**.

$$8 \quad -\frac{d[\text{Cr}^{\text{IV}}]}{dt} = \frac{k_a k_4 [\text{alginic acid}][\text{Cr}^{\text{IV}}]_T}{k_{-a} + k_4 + k_4 [\text{alginic acid}]} \quad (13)$$

9 The rate law for the disappearance of Cr^{IV} takes the form of **eqn 13** which is in
10 total agreement with the experimental rate law, **eqn 6** where $k_1 = \frac{k_a k_4}{k_{-a} + k_4}$ and

$$11 \quad k_2 = \frac{k_4}{k_{-a} + k_4}.$$

13 3.4. Reaction mechanism for the oxidation of alginic acid by Cr^{VI}

14 In the range of substrate and acid concentration used in the kinetic
15 measurements, the oxidation of alginic acid by Cr^{VI} is a complex reaction that
16 yields Cr^{III} , CO_2 , and oxidized alginic acid as final redox products. CrO_2^{2+} was
17 detected in the reaction of alginic acid with Cr^{VI} under aerobic conditions. This
18 fact indicates that Cr^{IV} and Cr^{II} were involved in the mechanism of the redox
19 reaction Cr^{VI} /alginic acid. Cr^{II} was originated exclusively by two-electron
20 reduction of Cr^{IV} species affording indirect evidence of participation of Cr^{IV} in the
21 redox mechanism. The observation of oxo- Cr^{V} species at pH higher than used
22 in the kinetic measurements, indicate that oxo- Cr^{V} -alginic acid intermediate
23 species were formed in the reaction of Cr^{VI} with alginic acid. However, under
24 conditions used in the kinetic measurements, Cr^{IV} and Cr^{V} react with alginic acid
25 much faster than Cr^{VI} and do not accumulate in the reaction mixture. Reduction
26 of Cr^{IV} by alginic acid at 0.30 M HClO_4 and 25 °C is 5.5×10^3 times faster than

1 reduction of Cr^{VI} at 60 °C. Cr^V also oxidizes alginate faster than Cr^{VI} does. In
 2 0.30 M HClO₄, and T = 15 °C, Cr^V oxidizes alginate 160 times faster than
 3 Cr^{VI} at 60 °C.

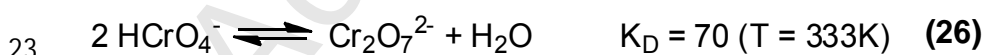
4 Thus, the concentration-time profiles of the Cr^{VI}-alginate mixtures reflect the
 5 [Cr^{VI}] monotonic decay without interference of [Cr^{IV}] and/or [Cr^V]. Oxidation of
 6 alginate by HClO₄ was excluded because this strong acid acts as oxidant
 7 only at high concentration (higher than 50 %) and at high temperature (near to
 8 the boiling point) (Diehl and Smith, 1959).

9 In **Scheme 4**, we propose a mechanism that combines Cr^{VI}→Cr^{IV}→Cr^{II} and
 10 Cr^{VI}→Cr^{IV}→Cr^{III} pathways, and takes into account: (a) kinetic results, (b) the
 11 polymerization of acrylamide added to the reaction mixture, (c) detection of
 12 intermediate of oxo-Cr^V-alginate species, (d) spectroscopy detection of
 13 CrO₂²⁺, and (e) formation of CO₂, Cr^{III}, and oxidized alginate as final redox
 14 products.

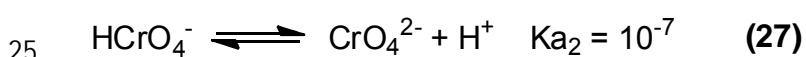
15 **Insert scheme 4 here**

16 The reduction of Cr^{VI} by alginate follows two pathways, one independent of
 17 [H⁺] and another dependent of [H⁺], because the acid base behavior of the
 18 polymer. The reactive species are alginate and chromate acid, both anionic
 19 species with charge = -1 as suggested by the dependence of k_{6exp} with the ionic
 20 strength.

21 In the [H⁺] range under study, Cr^{VI} exists predominantly as HCrO₄⁻ and in acidic
 22 medium Cr^{VI} presents dimerization equilibrium (Brasch, et al., 1996):



24 The value of the second acidic constant of chromic acid is very low:



26 Combining **eqn 26** and **27**, it is possible to calculate [HCrO₄⁻] and [Cr₂O₇²⁻]. This
 27 method was proposed by Sen Gupta and co workers (Sen Gupta et al., 1985) in
 28 order to identify the reactive chromium specie.

1 **Table 4** shows the dependence of $k_{6\text{exp}}$ with $[\text{HCrO}_4^-]$ and $[\text{Cr}_2\text{O}_7^{2-}]$.

2 **Table 4:** Identification of the chromium reactive specie^a

$[\text{Cr}^{\text{VI}}]_0$ (μM)	$[\text{Cr}_2\text{O}_7^{2-}]$ (μM)	$[\text{HCrO}_4^-]$ (μM)	$k_{6\text{exp}}^b$ $\times 10^2$	$k_{6\text{exp}}$ $\times A$	$k_{6\text{exp}}$ $B \times 100$
300	16	268	2.32 ± 0.04	1.16 ± 0.01	2.60 ± 0.10
500	20	459	2.33 ± 0.06	0.76 ± 0.01	2.54 ± 0.10
1000	55	889	2.27 ± 0.04	0.41 ± 0.01	2.55 ± 0.10
2000	125	1750	2.29 ± 0.08	0.24 ± 0.01	2.62 ± 0.10

3 ^a[alginate] = 9.13 g/L; $[\text{H}^+] = 0.30 \text{ M}$; $\mu = 0.50 \text{ M}$; $T = 60 \text{ }^\circ\text{C}$; $[\text{Cr}^{\text{VI}}]_0 = 0.30\text{-}$
 4 2.0 mM . ^b $k_{6\text{exp}}$ values are expressed in min^{-1} . $A = [\text{Cr}^{\text{VI}}]_0 / [\text{Cr}_2\text{O}_7^{2-}]$;
 5 $B = [\text{Cr}^{\text{VI}}]_0 / [\text{HCrO}_4^-]$

6 The values in **Table 4** shows a first- order dependence of $k_{6\text{exp}}$ with $[\text{HCrO}_4^-]$
 7 and not with $[\text{Cr}_2\text{O}_7^{2-}]$. This results together with the ionic strength effect
 8 supports that HCrO_4^- is the chromium reactive specie.

9 It is known that oxidation of polysaccharides by Cr^{VI} is preceded by the
 10 formation of a chromate ester (Bellú, et al., 2008; Zaafarany, et al., 2009;
 11 Hassan, et al., 2010; Lin & Wang, 2012; Hassan, et al., 2013). The observation
 12 of the absorbance bands characteristic of chromate oxy-esters around 375 nm,
 13 few minutes after mixing alginate and Cr^{VI} , under conditions where the redox
 14 reaction is slow, indicates that an intermediate Cr^{VI} complex is formed rapidly
 15 prior to the redox steps. Thus, the second and third step of the mechanism
 16 proposed in **Scheme 4** involved the formation of alginate- Cr^{VI} monochelate
 17 with alginate and alginate acting as bidentate ligands, which is also
 18 consistent with the first order dependence of the reaction on $[\text{Cr}^{\text{VI}}]$.

19 Oxidation rate of alginate by Cr^{V} and Cr^{IV} are faster than Cr^{VI} at the same
 20 experimental conditions. Therefore, Cr^{IV} and Cr^{V} , although formed in the Cr^{VI}
 21 /alginate reaction, should be involved in fast steps of the reaction pathway.

1 The slow redox step proposed in **Scheme 4** involves C—C bond cleavage
 2 through a two-electron redox process to yield Cr^{IV}, CO₂, and oxidized alginic
 3 acid (**eqn 17**). The initial two-electron reduction of Cr^{VI} by alginic acid is in
 4 agreement with previous reports on various acid saccharides that were
 5 selectively oxidized by Cr^{VI} to the lower homologous (Bellú, et al., 2008;
 6 González, et al., 2009; Mangiameli, et al., 2014).

7 The rate law for the Cr^{VI} consumption derived from **eqn 14-17** in **Scheme 4** is
 8 given by **eqn 26**, where [Cr^{VI}]_T refers to the total [Cr^{VI}] in the reaction mixture.

$$9 \quad -\frac{d[\text{Cr}^{\text{VI}}]}{dt} = \frac{(k_6 K_2 + k_6 K_3 K_1 [\text{H}^+])[\text{alginate}][\text{Cr}^{\text{VI}}]_{\text{T}}}{1 + K_2 [\text{alginate}] + K_3 [\text{alginic acid}]} \quad (26)$$

10 If $K_2[\text{alginate}] \ll 1$, and $K_3[\text{alginic acid}] \ll 1$ then **eqn 26** agrees perfectly
 11 with the experimental rate law, **eqn 2**.

12 In the mechanism, we have included two competitive one- and two-electron
 13 reductions of Cr^{IV} by alginic acid. Thus, Cr^{IV} is proposed to react with excess
 14 alginic acid to yield Cr^{II}, CO₂, and oxidized alginic acid or Cr^{III} and alginic acid
 15 radical (R·), through two alternate fast steps, **eqns 19** and **20**. The first
 16 supposition was supported by the observation of CrO₂²⁺ (the product of the
 17 reaction of Cr^{II} with O₂), while the second one, by the observed polymerization
 18 of acrylamide when it is added to the Cr^{VI}- alginic acid reaction mixtures. Cr^V
 19 was generated by fast reaction of Cr^{II} with Cr^{VI}, **eqn 21**, and, alternatively, by
 20 rapid reaction of the alginic acid radical with Cr^{VI}, **eqn 22**. Cr^V can further
 21 oxidize alginic acid to yield Cr^{III}, CO₂, and oxidized alginic acid as final redox
 22 products, **eqn 23**.

23 In O₂-saturated solutions (1.26 mM) and [Cr^{VI}]₀ ≤ 0.06 mM, reactions **21** and **22**
 24 can be neglected because R· and Cr^{II} intermediates formed in reactions **19** and
 25 **20** should be rapidly trapped by O₂, **eqn 24** and **25** (Bakac, et al., 1995). The
 26 proposed mechanism is in accordance with the observation that O₂ has no
 27 kinetic effect on this reaction, because when [Cr^{VI}]₀ ≥ 0.06 mM (as employed in
 28 the kinetic measurements), both Cr^{II} and R· react with Cr^{VI} faster than they do
 29 with O₂, and therefore **eqn 24** and **25** could be neglected (Scott, et al., 1992;
 30 Lay & Levina, 1998).

1 Detection of free radicals and CrO_2^{2+} in the Cr^{VI} /alginic acid reaction, provided
2 information supporting that the reduction of Cr^{IV} by alginic acid took place
3 through **eqn 19** and **20**.

4 The reaction of Cr^{V} with alginic acid was also much faster than Cr^{VI} /alginic acid.
5 Only a few seconds were required to reduce Cr^{V} in acid solution, at 15°C . The
6 redox reaction involves two-electrons. At higher pH, the redox reaction was
7 slower, and oxo- Cr^{V} -alginic acid species remain in solution for hours. At pH
8 1.0-3.0, alginic acid is a good scavenger of oxo- Cr^{V} , and the EPR parameter,
9 g_{iso} values observed, suggests that the donor sites of alginic acid involved in
10 coordination to the metal are carboxylate and hydroxyl groups.

11 The overall reaction stoichiometry deduced from **eqn 14** to **23** of **Scheme 4**
12 agrees with the experimental 0.60:1 $\text{CO}_2/\text{Cr}^{\text{VI}}$ ratio found in mixtures of Cr^{VI} and
13 alginic acid.

14 The present results suggest that Cr^{VI} (as well as Cr^{IV} and Cr^{V}) selectively
15 oxidizes the free carboxylic groups of alginic acid through C—C bond break.
16 Hassan and Co-workers had reported the oxidation of similar polysaccharides
17 by this oxidant and they found that the oxidation processes led to the oxidation
18 of the hydroxyl groups on $\text{C}_2\text{-C}_3$ bonds to its corresponding keto forms without
19 the occurrence of any bond cleavage (Zaafarany et al., 2009; Hassan et al.,
20 2010; Hassan et al., 2013). The difference between our work and that of
21 Hassan and Co-workers is due principally by differences in the experimental
22 conditions. We work at higher temperature (60°C) and lower $[\text{H}^+]$ (lower than
23 0.5M), whereas Hassan and Co-workers use lower temperatures (around 40°C)
24 and higher $[\text{H}^+]$ (higher than 2.0 M). Experimental conditions employed in
25 our work increases the oxidant power of HCrO_4^- allowing the cleavage of C-C
26 bond with the release of CO_2 .

27 This pattern of selectivity distinguishes chromic oxidation of polyuronic acids
28 from that observed by others oxidizer agents. Thus, NaVO_3 oxidizes the
29 terminal unit of the polymeric chain (Gessa et al., 1983), KMnO_4 yields
30 ketoderivatives upon oxidation of vicinal hydroxyl groups (Abdel-Hamid et al.,
31 2003), and NaIO_4 oxidizes vicinal hydroxyl groups to yields aldehyde groups
32 (Gomez et al., 2007).

1

2 **4. Conclusions**

3 The reaction of alginic acid with Cr^{VI} strongly depends on pH. In acid media,
4 redox reaction occurs and reactive Cr^{V} , Cr^{II} , and Cr^{IV} intermediate species are
5 generated in the redox process, together with CO_2 , free radicals, and oxidized
6 forms of alginic acid. At pH 1- 3, alginic acid slowly reduces Cr^{VI} , and stabilizes
7 Cr^{V} yielding long-lived oxo- Cr^{V} - alginic acid species, that, if the medium
8 becomes acid, rapidly affords redox processes. The Cr-binding sites of alginic
9 acid are mainly the free carboxylic groups that can undergo redox processes
10 with $\text{Cr}^{\text{VI-IV}}$ in acid media or stabilize Cr^{V} together with hydroxo donor groups of
11 the polysaccharide. The present results evidence that alginic acid can act as
12 reducing agent of chromate acid (particularly at low pH), with formation of
13 highly toxic free radicals, CrO^{2+} and Cr^{V} intermediate species, or can be
14 involved in the transport of higher oxidation state of chromium at $\text{pH}>2$.

15

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22

23 **References**

24 Abdel-Hamid, M. I, Khairou, K. S., & Hassan, R. M. (2003). Kinetics and
25 mechanism of permanganate oxidation of pectin polysaccharide in acid
26 perchlorate media. *European Polymer Journal*, 39, 381- 387.

27

- 1 Al-Ajlouni, A., Bakac, A., & Espenson, J. (1994). Hydride Abstraction from 1,2-
2 Diols by the Pentaqua(oxo)chromium(IV) Ion. *Inorganic Chemistry*, 33, 1011-
3 1014.
- 4
- 5 Bakac, A., Scott, S. L., Espenson, J. H., & Rodgers, K. R. (1995). Interaction of
6 Chromium(II) Complexes with Molecular Oxygen. Spectroscopic and Kinetic
7 Evidence for η^1 -Superoxo Complex Formation. *Journal of the American*
8 *Chemical Society*, 117, 6483- 6488.
- 9
- 10 Barr-David, G., Charara, M., Codd, R., Farell, R. P., Irwin, J. A., Lay, P. A.,
11 Ramley, R., Brumby, S., Ji, J. Y., & Hanson, G. R. (1995). EPR
12 characterisation of the Cr^{V} intermediates in the Cr^{VI} oxidations of organic
13 substrates and of relevance to Cr-induced cancers. *Journal of Chemistry*
14 *Society Faraday Transaction*, 91, 1207- 12016.
- 15
- 16 Bellú, S.E., González, J. C., García, S. I., Signorella, S. R., & Sala, L. F.
17 (2008). Kinetics and mechanism of oxidation of apple pectin by CrVI in aqueous
18 acid medium. *Journal of Physical Organic Chemistry*, 21, 1- 10.
- 19
- 20 Brasch, N. E., Buckingham, D. A., Evans, A. B., & Clark, C. R. (1996). ^{17}O NMR
21 Study of Chromium(VI) Ions in Water. *Journal of American Chemical Society*,
22 118, 7969- 7980.
- 23
- 24 Ciésłak-Golonka, M., & Daszkiewicz, M. (2005). Coordination geometry of
25 Cr(VI) species: Structural and spectroscopic characteristics. *Coordination*
26 *Chemistry Reviews*, 249, 2391- 2407.
- 27

- 1 Clesceri, L., Greenberg, A., & Eaton, A. (1998). Standard Methods for the
2 Examination of Water and Wastewater, 20th Ed., American Public Health
3 Association, American Water Association, and Water Environment Federation,
4 Washington, D.C., p. 366.
- 5
- 6 Codd, R., Dillon, C. T., Levina, A., & Lay, P. A. (2001). Studies on the
7 genotoxicity of chromium: from the test tube to the cell. *Coordination Chemistry*
8 *Reviews*, 216-217, 537- 582.
- 9
- 10 Cood, R., Irwin, J. A., & Lay, P. A. (2003). Sialoglycoprotein and carbohydrate
11 complexes in chromium toxicity. *Current Opinion in Chemical Biology*, 7, 213-
12 219.
- 13
- 14 Craigie, J. S., Morris, E. R., Rees, D. A., & Thom, D. (1984). Alginate block
15 structure in phaeophyceae from Nova Scotia: Variation with species,
16 environment and tissue-type. *Carbohydrate Polymers*, 4, 237- 252.
- 17
- 18 De Stefano, C., Gianguzza, A., Piazzese, D., & Sammartano, S. (2005).
19 Modelling of proton and metal exchange in the alginate biopolymer. *Analytical*
20 *Bioanalysis Chemistry*, 383, 587- 596.
- 21
- 22 Diehl, H., & Smith, G. F. (1959). Wet oxidation of organic matter employing
23 mixed perchloric and sulphuric acids at controlled temperatures and graded
24 high potentials. *Talanta*, 2, 209- 219.
- 25
- 26 Eckert, J.M., Judd, R.J., Lay, P.A., & Symons, A.D. (1991). Response of
27 chromium(V) to the diphenylcarbazide spectrophotometric method for the
28 determination of chromium(VI). *Analytica Chimica Acta*, 255, 31- 33.

1

2 Emmerichs, N., Wingender, J., Flemming, H-C., & Mayer, C. (2004). Interaction
3 between alginates and manganese cations: identification of preferred cation
4 binding sites. *International Journal of Biological Macromolecules*, 34, 73- 79.

5

6 Espenson, J.H. (2002). *Chemical Kinetics and Reactions Mechanism*, Mc Graw
7 Hill, New York, 2nd edn., pp 206- 214.

8

9 Gessa, C., De Cherchi, M. L., Dessi, A., Deiana, S., & Micera, G. (1983). The
10 reduction of Fe(III) to Fe(II) and V(V) to V(IV) by polygalacturonic acid: A
11 reduction and complexation mechanism of biochemical significance. *Inorganica
12 Chimica Acta*, 80, L53- L55.

13

14 Gheju, M., Iovi, A. (2006). Kinetics of hexavalent chromium reduction by scrap
15 iron. *Journal of Hazardous Materials*, B135, 66- 73.

16

17 Ghosh, M. C., & Gould, E. S. (1991). Electron transfer. 106. Stabilized aqueous
18 chromium(IV), as prepared from the chromium(VI)-arsenic(III) reaction.
19 *Inorganic Chemistry*, 30, 491- 494.

20

21 Gomez, C. G., Rinaudo, M., & Villar, M. A. (2007). Oxidation of sodium alginate
22 and characterization of the oxidized derivatives. *Carbohydrate Polymers*, 67,
23 296- 304.

24

- 1 González, J. C., Daier, V., García, S., Goodman, B. A., Sala, L. F., & Signorella,
2 S. (2004). Redox and Complexation Chemistry of the Cr^{VI}/Cr^V-D-galacturonic
3 acid system. Dalton Transaction, 2288- 2296.
- 4
- 5 González, J. C., García, S. I., Bellú, S., Atria, A. M., Salas- Peregrín, J. M.,
6 Rockenbauer, A., Korecz, L., Signorella, S., & Sala, L. (2009). Oligo and
7 polyuronic acids interactions with hypervalent chromium. Polyhedron, 28, 2719-
8 2729.
- 9
- 10 González, J. C., García, S., Bellú, S., Salas Peregrín, J. M., Atria, A. M., Sala,
11 L. F., & Signorella, S. (2010). Redox and complexation chemistry of the
12 Cr^{VI}/Cr^V/Cr^{IV}-D-glucuronic acid system. Dalton Transaction, 39, 2204- 2217.
- 13
- 14 Hassan, R. M., Ahmed, S. A., Fawzy, A., Abdel-Kader, D. A., Ikeda, Y., &
15 Takagi, H. D. (2010). Acid-catalyzed oxidation of carboxymethyl cellulose
16 polysaccharide by chromic acid in aqueous perchlorate solutions. A kinetics
17 study. Catalysis Communications, 11, 611- 615.
- 18
- 19 Hassan, R., Ibrahim, S., Dahy, A. R., Zaafarany, I., Tirkistani, F., & Takagi, H.
20 (2013). Kinetics and mechanism of oxidation of chondroitin-4-sulfate
21 polysaccharide by chromic acid in aqueous perchlorate solutions. Carbohydrate
22 Polymers, 92, 2321- 2326.
- 23
- 24 Ibáñez, J. P., Umetsu, Y. (2004) Uptake of trivalent chromium from aqueous
25 solutions using protonated dry alginate beads. Hydrometallurgy, 72, 327- 334.
- 26

- 1 Kolthoff, I. M., Sandell, E. B., Meehan, & E. J., Bruckenstein, S. (1969).
2 Quantitative Chemical Analysis, 4th Ed., The Macmillan Company Collier-
3 Macmillan Limited, London, p. 777- 794.
- 4
- 5 Krumpolc, M., Roček, J., Haight Jr., G. P., & Merrill, P. (1980). Sodium Bis[2-
6 Ethyl-2-Hydroxybutyrato(2-)]-Oxochromate(V). *Inorganic Synthesis*, 20, 63- 65.
- 7
- 8 Larsen, B., Salem, D. M. S. A., Sallam, M. A. E., Misheiky, M. M., & Beltagy,
9 A. I. (2003). Characterization of the alginates from algae harvested at the
10 Egyptian Red Sea coast. *Carbohydrate Research*, 338, 2325- 2336.
- 11
- 12 Lay, P. A., & Levina, A. (1998). Activation of Molecular Oxygen during the
13 Reactions of Chromium(VI/V/IV) with Biological Reductants: Implications for
14 Chromium-Induced Genotoxicities. *Journal of the American Chemical Society*,
15 120, 6704- 6714.
- 16
- 17 Leal, D., Matsuhiro, B., Rossi, M., & Caruso, F. (2008). FT-IR spectra of alginic
18 acid block fractions in three species of brown seaweeds. *Carbohydrate*
19 *Research*, 343, 308- 316.
- 20
- 21 Levina, A., Zhang, L., & Lay, P. A. (2003). Structure and Reactivity of a
22 Chromium(V) Glutathione Complex. *Inorganic Chemistry*, 42, 767- 784.
- 23

- 1 Levina, A., & Lay, P. A. (2005). Mechanistic studies of relevance to the
2 biological activities of chromium. *Coordination Chemistry Reviews*, 249, 281-
3 298.
- 4
- 5 Levina, A., Zhang, L., & Lay, P. A. (2010). Formation and Reactivity of
6 Chromium(V)-Thiolato Complexes: A Model for the Intracellular Reactions of
7 Carcinogenic Chromium(VI) with Biological Thiols. *Journal of American*
8 *Chemical Society*, 132, 8720- 8731.
- 9
- 10 Lin, Y., & Wang, S. (2012). Chromium(VI) reactions of polysaccharide
11 biopolymers. *Chemical Engineering Journal*, 181-182, 479- 485.
- 12
- 13 Mangiameli, M. F., González, J. C., Bellú, S., Bertoni, F., & Sala, L. F. (2014).
14 Redox and complexation chemistry of the Cr^{VI}/Cr^V- D-glucaric acid system.
15 *Dalton Transactions*, 43, 9242- 9254.
- 16
- 17 Mangiameli, M. F., González, J. C., García, S. I., Bellú, S., Santoro, M.,
18 Caffaratti, E., Frascaroli, M. I., Salas- Peregrín, J. M., Atria, A. M., & Sala, L. F.
19 (2010). Redox, kinetics, and complexation chemistry of the
20 Cr^{VI}/Cr^V/Cr^{IV}-D-glycero-D-gulo-heptono-1,4-lactone System. *Journal of Physical*
21 *Organic Chemistry*, 23, 960- 971.
- 22
- 23 Mangiameli, M. F., González, J. C., García, S. I., Frascaroli, M. I., Van
24 Doorslaer, S., Salas Peregrín, J. M., & Sala, L. F. (2011). New insights on the

- 1 mechanism of oxidation of D-galacturonic acid by hypervalent chromium. Dalton
2 Transaction, 40, 7033- 7045.
- 3
- 4 Maureira, A., & Rivas, B. L. (2009). Metal ions recovery with alginic acid
5 coupled to ultrafiltration membrane. European Polymer Journal, 45, 573- 581.
- 6
- 7 Mitewa, M., & Bontchev, P. (1985). Chromium(V) coordination chemistry.
8 Coordination Chemistry Reviews, 61, 241- 272.
- 9
- 10 Pérez Benito, J., & Arias, C. (1993). A kinetic-study on the reactivity of
11 chromium(IV). Canadian Journal of Chemistry, 71, 649- 655.
- 12
- 13 Pérez Benito, J., Arias, C., & Lamrhari, D. (1994). Chromium(II) is an
14 intermediate in the reduction of carcinogenic chromate with biological thiols.
15 New Journal of Chemistry, 18, 663- 666.
- 16
- 17 Roldán, V., Daier, V., Goodman, B., Santoro, M., González, J. C., Calisto, N.,
18 Signorella, S., & Sala, L. (2000). Kinetics and mechanism of the reduction of
19 chromium(VI) and chromium(V) by D-glucitol and D-mannitol. Helvetica Chimica
20 Acta, 83, 3211- 3228.
- 21
- 22 Sala, L. F., González, J. C., García, S. I., Frascaroli, M. I., & Van Doorslaer, S.
23 (2011). Detection and structural characterization of oxo-chromium(V)-sugar
24 complexes by electron paramagnetic resonance. Advances Carbohydrate
25 Chemistry Biochemistry, 66, 69- 120.
- 26

- 1 Sala, L., Palopoli, C., Alba, V., Signorella, S. (1993). A secondary reaction in
2 the oxidation of L-methionine by chromium(VI) in acidic medium. *Polyhedron*,
3 12, 2227- 2234.
- 4
- 5 Santoro, M., Caffaratti, E., Salas-Peregrin, J.M., Korecz, L., Rockenbauer, A.,
6 Sala, L.F., & Signorella, S. (2007). Kinetics and mechanism of the chromic
7 oxidation of *myo*-inositol. *Polyhedron*, 26, 169- 177.
- 8
- 9 Scott, S., Bakac, A., & Espenson, J. (1991). Preparation and reactivity of the
10 aquachromium(IV) ion. *Journal of American Chemical Society*, 113, 7787- 7788.
- 11
- 12 Scott, S., Bakac, A., & Espenson, J. (1992). Oxidation of alcohols, aldehydes,
13 and carboxylates by the aquachromium(IV) ion. *Journal of American Chemical*
14 *Society*, 114, 4205- 4213.
- 15
- 16 Sen Gupta, K. K., Samanta, T., & Samanendra, N. B. (1985). Kinetics of
17 oxidation of methanol and mono-deutero-methanol by chromium(VI) in
18 perchloric acid medium. *Tetrahedron*, 41, 205- 208.
- 19
- 20 Signorella, S., Daier, V., García, S., Cargnello, R., González, J.C., Rizzotto, M.,
21 & Sala, L.F. (1999). The relative ability of aldoses and deoxyaldoses to reduce
22 Cr^{VI} and Cr^{V} . A comparative kinetic and mechanistic study. *Carbohydrate*
23 *Research*, 316, 14- 25.
- 24
- 25 Signorella, S., Frascaroli, M.I., García, S., Santoro, M., González, J.C., Palopoli,
26 C., Casado, N., & Sala, L.F. (2000). Kinetics and mechanism of the
27 chromium(VI) oxidation of methyl- α -D-glucopyranoside and methyl- α -D-

1 mannopyranoside. Journal of Chemical Society Dalton Transaction, 1617-
2 1623.

3

4 Zaafarany, I. A., Khairou, K. S., & Hassan, R. M. (2009). Acid-catalysis of
5 chromic acid oxidation of kappa-carrageenan polysaccharide in aqueous
6 perchlorate solutions. Journal of Molecular Catalysis, 302, 112- 118.

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Highlights

Alginic acid reduces hypervalent chromium to Cr^{III}.

The mechanism combines Cr^{VI}→Cr^{IV}→Cr^{II} and Cr^{VI}→Cr^{IV}→Cr^{III} pathways.

Oxo-chromate(V)–alginic acid species are stable at pH 3- 5 for several hours.

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Figure Captions

Fig. 1 Effect of [alginate] on $k_{6\text{exp}}$. $T = 60\text{ }^{\circ}\text{C}$, $\mu = 0.50\text{ M}$ and $[\text{H}^+] = 0.10$, (b) 0.20, (c) 0.30, (d) 0.40, (e) 0.50 M. Inset: dependence of $k_{6\text{S}}$ on $[\text{H}^+]$.

Fig. 2 UV-vis differential spectra of alginate/ Cr^{VI} mixtures at pH 6.0, showing the increasing band at 375 nm with increasing [alginate]. (a) [alginate] = 0.228 g/L, (b) [alginate] = 0.457 g/L. $[\text{Cr}^{\text{VI}}] = 0.5\text{ mM}$, $\mu = 0.50\text{ M}$, $T = 25\text{ }^{\circ}\text{C}$.

Fig. 3 Experimental and simulated X-band EPR spectra of oxo- Cr^{V} -alginate species. $T = 15\text{ }^{\circ}\text{C}$; [alginate] = 4.57 g/L; $[\text{Cr}^{\text{VI}}] = 1.0\text{ mM}$; $\mu = 0.50\text{ M}$; pH = 2; Center Field = 3410 G ; Modulation amplitude = 2.0 G ; resolution = 1024 points ; Frequency = 9.4312 GHz. Spectra were collected after 1 hour of mixing reactants.

Fig. 4 CrO_2^{2+} formation from the reaction between alginate and Cr^{VI} . [alginate] = 0.78 g/L, $[\text{HClO}_4] = 3.0\text{ M}$, $[\text{O}_2] = 1.26\text{ mM}$, $[\text{Cr}^{\text{VI}}] = 0.0797\text{ mM}$, $\mu = 3.0\text{ M}$, $T = 25\text{ }^{\circ}\text{C}$. Spectra were recorded every 3.0 min. Inset: differential spectrum after addition of Fe^{II} .

Fig. 5 Formation of CrO_2^{2+} from the reaction 2.28 g/L alginate, $[\text{H}^+] = 0.30\text{ M}$, $[\text{O}_2] = 1.26\text{ mM}$, $\mu = 0.50\text{ M}$, $T = 25\text{ }^{\circ}\text{C}$, $[\text{Cr}^{\text{VI}}] = 0.207\text{ mM}$. Inset: absorbance at 290 vs. time. Fitted lines were calculated using eqn (4) and SigmaPlot 11.0 program.

Fig. 1

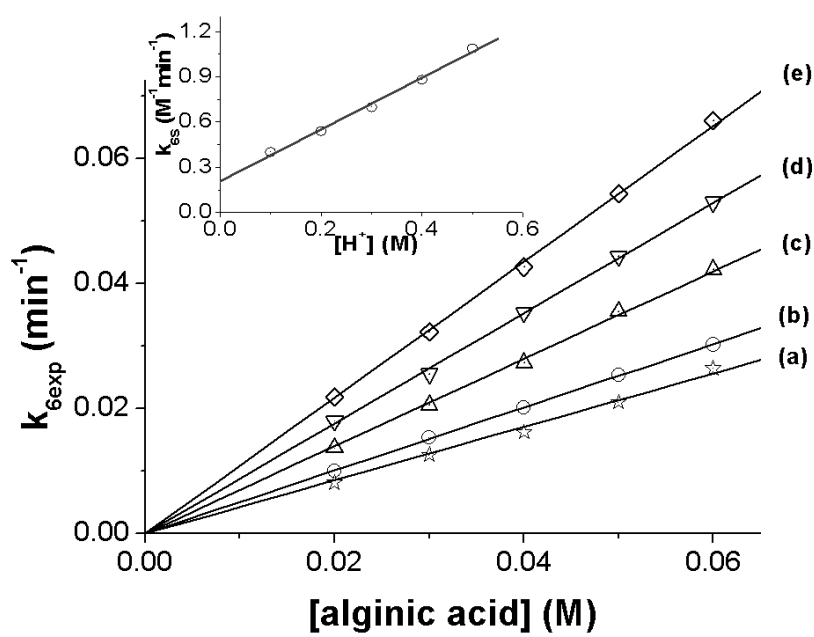
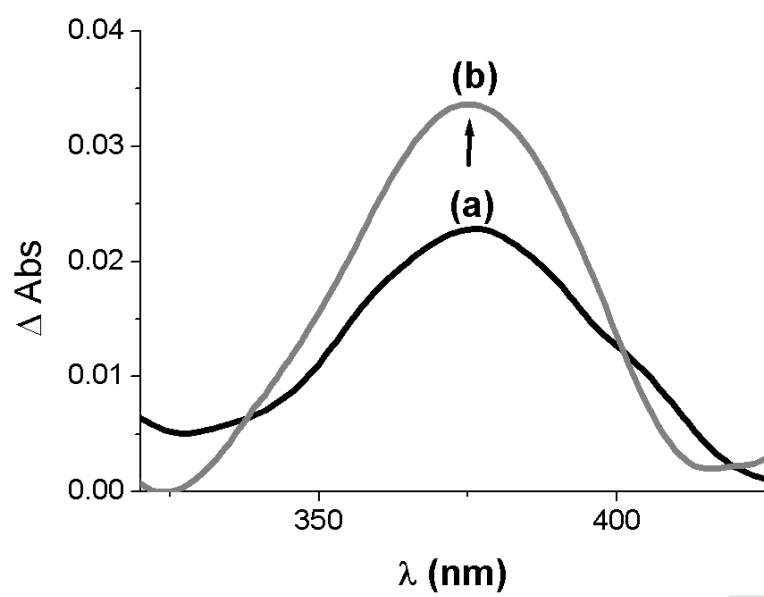
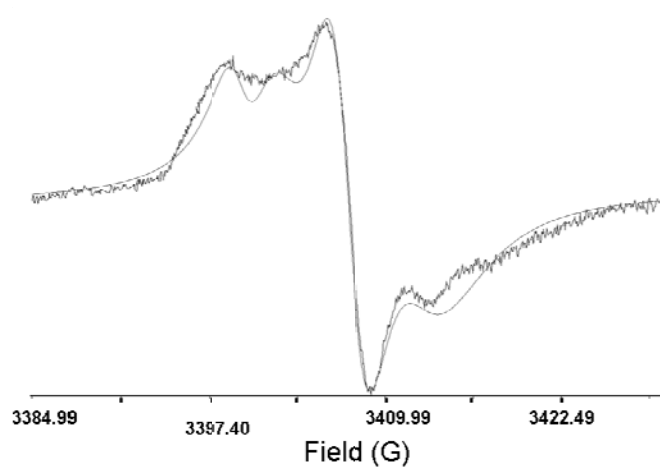


Fig. 2



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Fig. 3



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Fig. 4

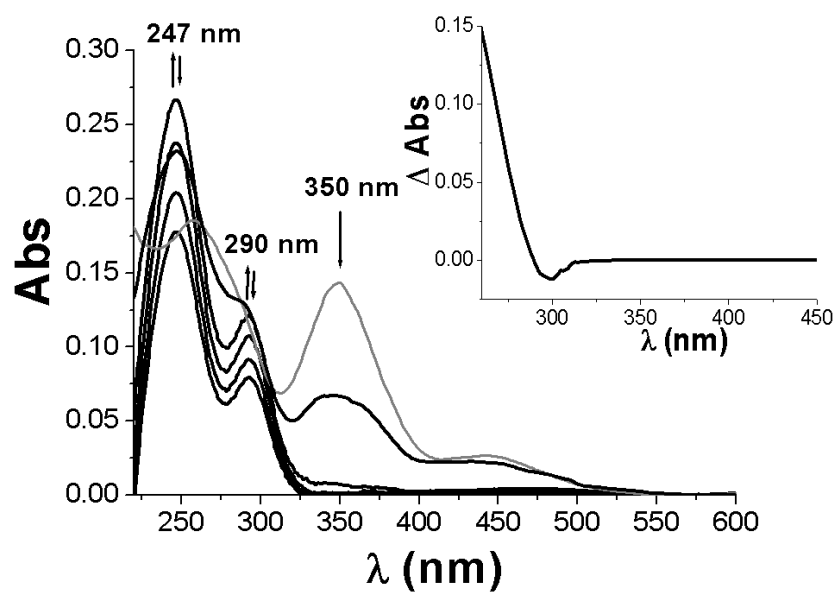
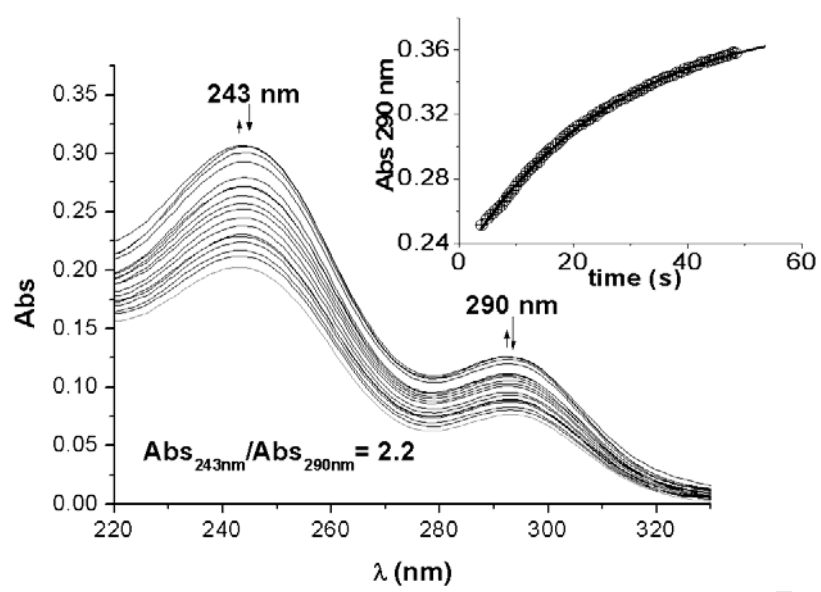
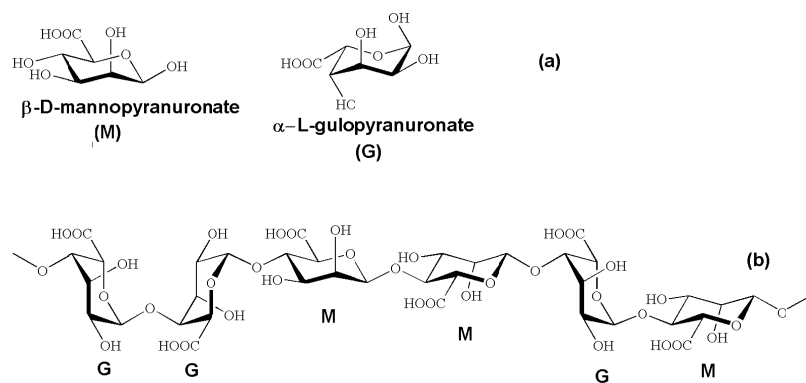
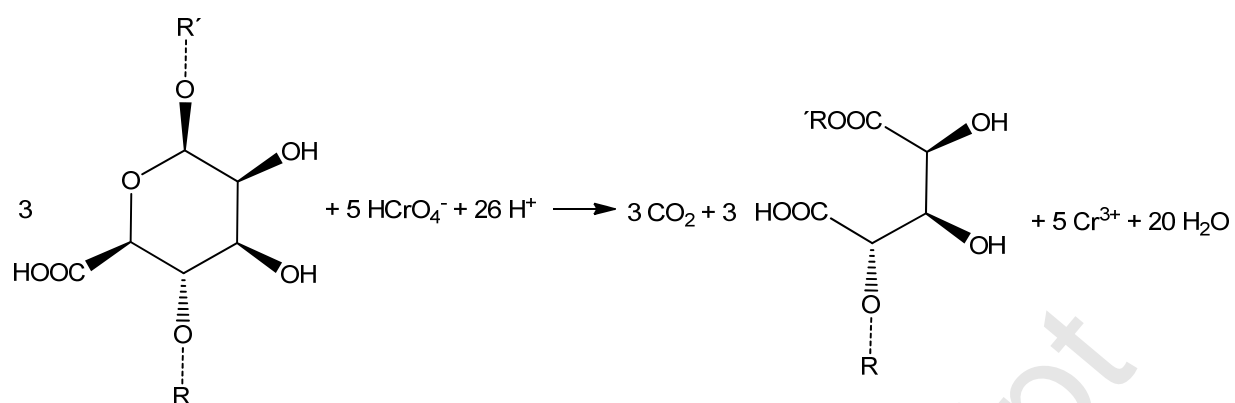


Fig. 5

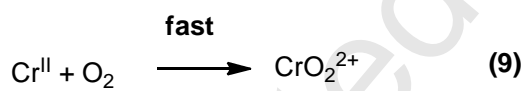
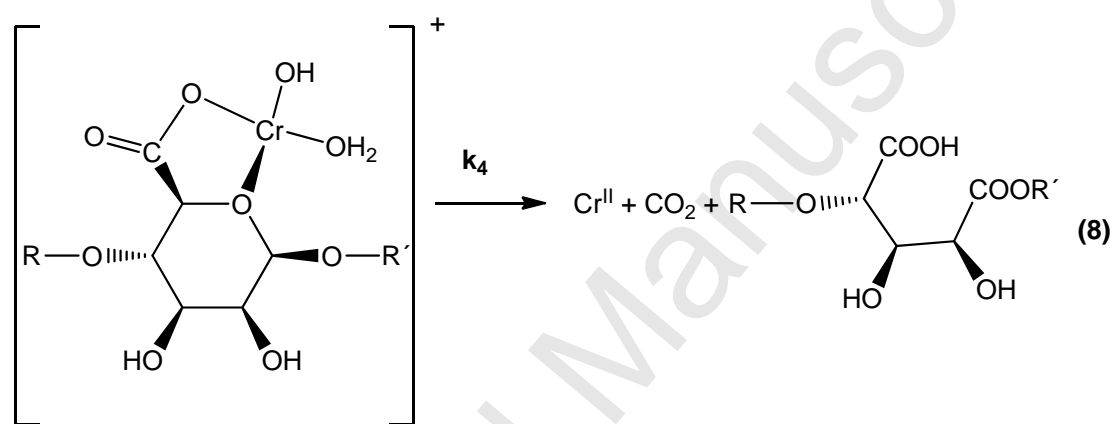
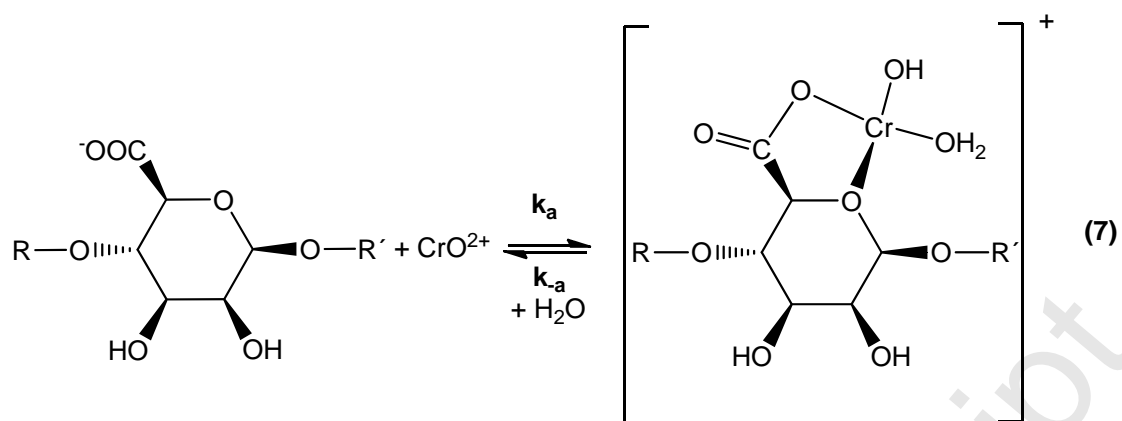




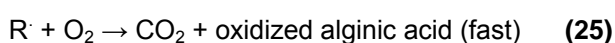
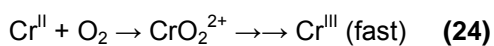
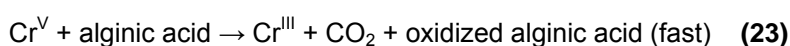
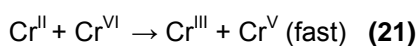
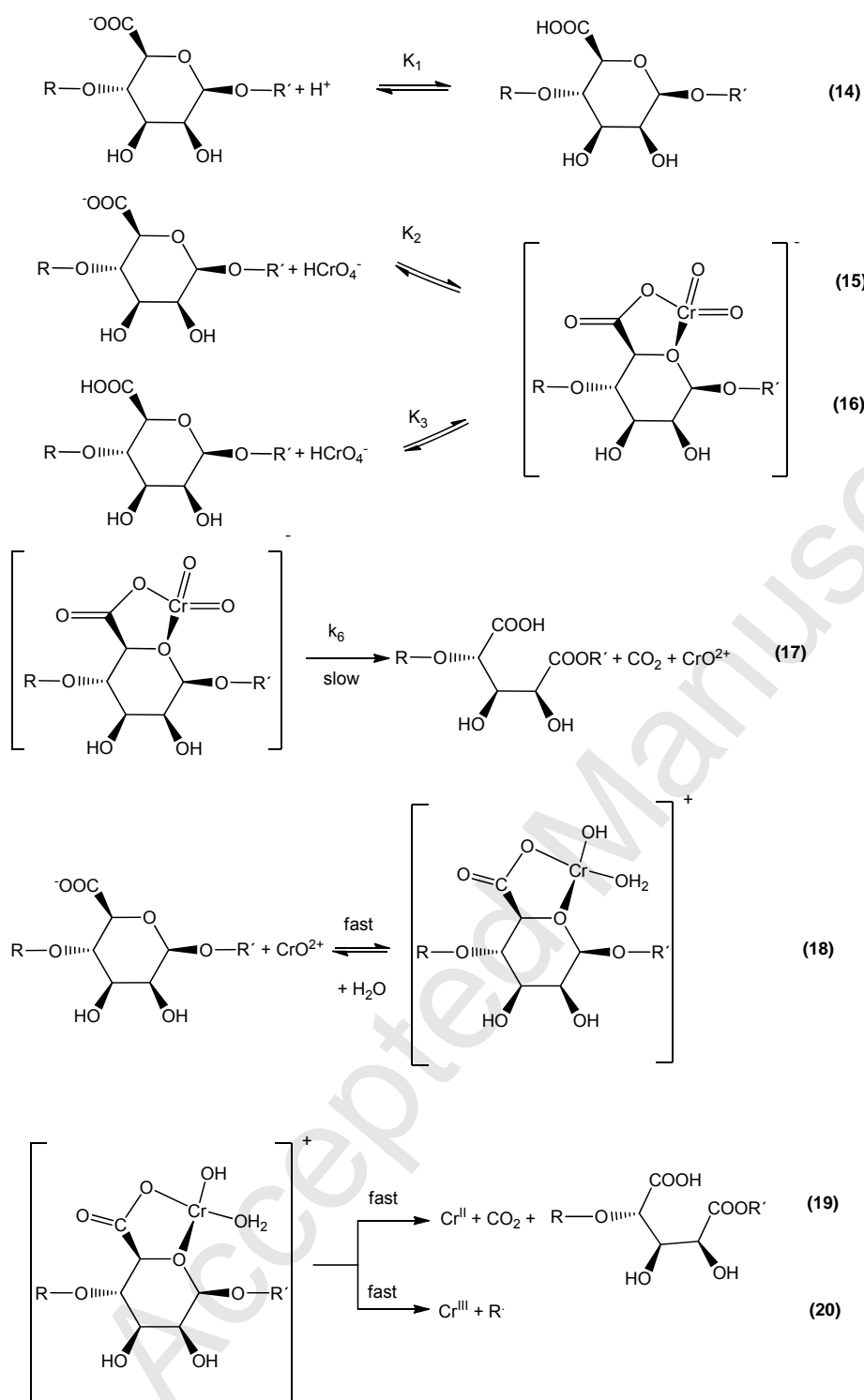
Scheme 1: Structure of alginic acid (a) monomers (b) polymeric chain



Scheme 2: Stoichiometry of the redox reaction between alginic acid and Cr^{VI} in acid media



Scheme 3: Proposed mechanism for the oxidation of alginic acid by CrO_2^{2+}



Scheme 4: Proposed mechanism for the oxidation of alginate by Cr^{VI}