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Reduction of hypervalent chromium in acidic media by alginic acid

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ABSTRACT

Selective oxidation of carboxylate groups present in alginic acid by Cr^{VI} affords CO_2, oxidized alginic acid, and Cr^{III} as final products. The redox reaction afforded first-order kinetics in [alginic acid], [Cr^{VI}], and [H^+], at fixed ionic strength and temperature. Kinetic studies showed that the redox reaction proceeds through a mechanism which combines $Cr^{VI} \rightarrow Cr^{IV} \rightarrow Cr^{II}$ and $Cr^{VI} \rightarrow Cr^{IV} \rightarrow Cr^{III}$ pathways. The mechanism was supported by the observation of free radicals, CrO_2^{2+} and Cr^V as reaction intermediates. The reduction of Cr^{IV} and Cr^V by alginic acid was independently studied and it was found to occur more than 10^3 times faster than alginic acid/Cr^{VI} reaction, in acid media. At pH 1–3, oxo-chromate(V)–alginic acid species remain in solution during several hours at 15 °C. The results showed that this abundant structural polysaccharide present on brown seaweeds is able to reduce $Cr^{VI/V/IV}$ or stabilize high-valent chromium depending on pH value.

1. Introduction

The major structural polysaccharide of brown seaweeds (*Phaeophyta*) is alginic acid, a linear copolymer of (1 → 4)-linked β-D-mannopyranuronic acid (M) and (1 → 4)-linked α-L-gulopyranuronic acid (G) residues, arranged in heteropolymeric and homopolymeric blocks (Scheme 1) (Larsen, Salem, Sallam, Misheikey, & Beltagy, 2003; Leal, Matsuhiro, Rossi, & Caruso, 2008). The content of uronic acids varies with species and tissues types, and partial acid hydrolysis of alginic acids allows the preparation of fractions enriched in hetero- and homopolymeric blocks (Craigie, Morris, Rees, & Thom, 1984). The presence of carboxylic acid groups in both monomeric units makes possible it interaction with different metal ions, and in this sense its complexation ability has been studied with heavy metal ions present in wastewaters for water purification. Several authors have proposed interaction models between alginic acid and specific metal ions (De Stefano, Gianguzza, Piazzese, & Sammartano, 2005; Emmerichs, Wingender, Flemming, & Mayer, 2004; Maureira & Rivas, 2009).

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

Polyoxygenated compounds, such as polyalcohols and hydroxycarboxylic acids, are effective as non-enzymatic reductants (at low pH) and can stabilize the labile oxidation states of chromium (Codd, Dillon, Levina, & Lay, 2001; Ciéslak-Golonka & Daszkiewicz, 2005). Due to the potential biological and ecological relevance of these kinds of biopolymers, the reduction and stabilization of hypervalent chromium by naturally occurring polysaccharides can provide useful information on the role that these polyoxygenated compounds play in the uptake and transport of chromium (Bellú, González, García, Signorella, & Sala, 2008). Although the reduction of hypervalent chromium by low molecular weight saccharides has been extensively studied (González et al., 2004; Mangiameli et al., 2010, 2011), little is known on the reaction of polysaccharides with Cr^{VI}. Kinetic and mechanistic studies of chromic acid oxidation onto kappa-karrageen; carboxymethyl cellulose and chondroitin-4-sulfate polysaccharides as natural polymers has been reported by Zaafarany, Khairou, and Hassan (2009), Hassan et al. (2010, 2013).

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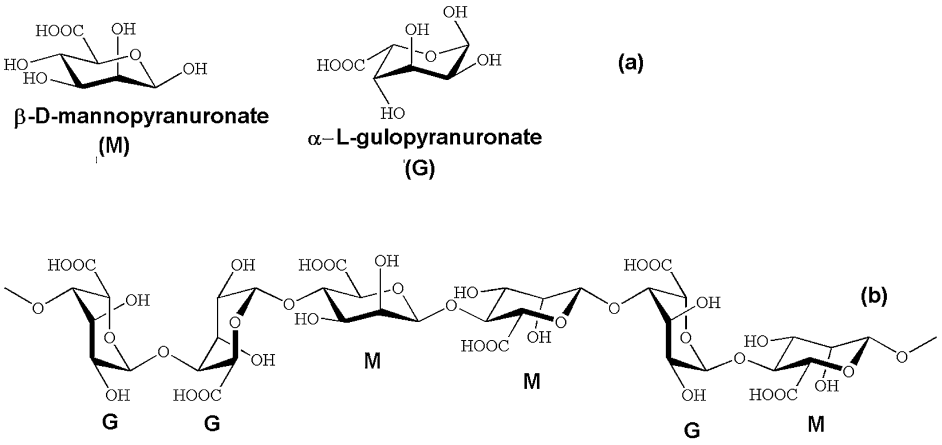

Scheme 1. Structure of alginic acid (a) monomers (b) polymeric chain.

Cellullose, hemicellullose and chitin reactions with Cr^{VI} were also studied at acid media (Lin & Wang, 2012) but no redox mechanistic studies were performed in this case. In a previous work we report the mechanism of oxidation of apple pectin by Cr^{VI} in aqueous acid medium (Bellú et al., 2008). The determination of the ability of alginic acid to reduce or stabilize hypervalent chromium will contribute to understand the potential role of this polysaccharide in the biochemistry of this metal. In this work, we report the study of the redox reaction of alginic acid with Cr^{VI} providing information related to the relative reactivity of alginic acid toward Cr^{VI}, Cr^{V}, and Cr^{IV}, the influence of pH on the redox reactions, and the formation of long-lived oxo-Cr^{V}–alginic acid complexes, being characterized by paramagnetic electronic resonance.

2. Experimental

2.1. Materials

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

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

$Na[Cr^{V}O(ehba)_2]\cdot H_2O$, $[Cr^{IV}O(ehbaH)_2]$ and $K_3[Cr^{V}(O)(GSH)_2]$ were synthesized according to the method described in the literature (Krumpolc, Roček, Haight, & Merrill, 1980; Ghosh & Gould, 1991; Levina, Zhang, & Lay, 2003). For experiments performed in the 1–6 pH range, the pH of the solutions was adjusted by addition of $HClO_4$. In experiments performed at constant ionic strength (μ = 0.50 M) and different hydrogen ion concentrations; sodium perchlorate and perchloric acid solution mixtures were used. The concentration of stock solutions of perchloric acid was determined by titration employing standard analytical methods.

Caution: Cr^{VI}, $Na[Cr^{V}O(ehba)_2]\cdot H_2O$, $[Cr^{IV}O(ehbaH)_2]$ and dpph are human carcinogens. Contact with skin and inhalation must be avoided.

2.2. Alginic acid stability

Stability of polysaccharide in acidic conditions was studied by HPLC. The chromatograms were obtained on a Varian Polaris 200 chromatograph provided with a cc Star 9000 HPLC pump. The separation was carried out on an Aminex HPX-87X (300 × 7.8 mm^2, Bio-Rad Lab) HPLC column, using H_2SO_4 as eluent (pH 1.5) and a flow rate of 0.6 mL/min, at 30 °C. The samples were filtered through a 0.2 mm membrane prior to the injection into the chromatographic system. The effluent was monitored with a UV–vis detector (Prostar 325 UV–vis detector, λ = 220 nm). Chromatograms, recorded after incubation of the standard sample in 1.0 M $HClO_4$ (higher than the highest $[H^+]$ used in the kinetic measurements) at 60 °C during 3.0 h, showed only one peak (*tr*: 5.65 min) assigned to alginic acid. No others peaks were observed suggesting the stability of the polysaccharide under the present experimental conditions.

2.3. Measurement of free carboxylic groups of alginic acid

Measurements of free carboxylic groups of alginic acid were performed by acid base titration employing NaOH as titrant and phenolphthalein as visual indicator (Kolthoff, Sandell, Meehan, & Bruckenstein, 1969). Titration of 10.00 mL solution containing 20.00 g/L alginic acid with 0.08704 M NaOH until change color from colorless to pink afforded 10.75 mL of NaOH consumed which corresponds to 87.6 mM of free carboxylic groups. The employed polysaccharide contains an average of 4.38 mmol free carboxylic groups per gram of polymer.

2.4. Product analysis

Carbon dioxide was measured from a mixture of alginic acid (33.1 mg/mL), Cr^{VI} (5.0 mM) and $HClO_4$ (0.50 M). The temperature was kept constant at 60 °C and the reaction mixture was continuously stirred and flushed with pure nitrogen. The gaseous products were passed through three flasks containing NaOH (0.02 M). After reaction, in order to determine the yield of carbon dioxide, the NaOH solutions were titrated with standard HCl (0.0232 M). Aliquots of the reaction mixture of alginic acid/Cr^{VI} were analyzed by HPLC, using the same experimental conditions and column mentioned at Section 2.2. No peak corresponding to HCOOH (*tr*: 13.2 min) was observed.

2.5. Polymerization test

Detection of free organic radical generation, during the oxidation of alginic acid by hypervalent chromium, was tested employing