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COMMUNICATION

**CHEMICALLY CROSSLINKED POLYSACCHARIDE OF THE RED
MICROALGA *RHODELLA RETICULATA* - AN ION EXCHANGER
FOR TOXIC METAL IONS¹**

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The structure and physicochemical properties of the sulfated polysaccharides that encapsulate cells of the red microalgae have been studied in our laboratory for a number of years with the aim of evaluating their potential applications.²⁻⁶ Exploitation of the charged groups of these heteropolymers as chelating agents could provide an environmentally friendly means of disposing of toxic metals in industrial wastes. Ion exchangers and affinity absorbents may be prepared by crosslinking polysaccharides with epichlorhydrin, for example, mucopolysaccharides can bind polyvalent ions.⁷⁻⁹

In this work, we present the potential application of the extracellular polysaccharide of a species of red microalga *Rhodella reticulata* as an ion-exchanger for the removal of metal ions, such as Ni(II), Co(II), Cr(III), and Cd(II), from wastewater. The polysaccharide was crosslinked with epichlorohydrin to form an insoluble, chemically and mechanically stable system. Cp/mas ¹³C NMR spectra of the polysaccharide of *R. reticulata*¹⁰ before (Fig. 1A) and after (Fig. 1B) crosslinking were very broad and almost structureless. The presence of uronic acid and methylated sugars in the native and crosslinked polysaccharides (Fig. 1), as was previously determined,⁴⁻⁶ was confirmed. After crosslinking, the resonance peak of the C-6 carbon was broader and shifted to a lower field, buried in the somewhat nonsymmetrical broad peak at 72 ppm. The new peak

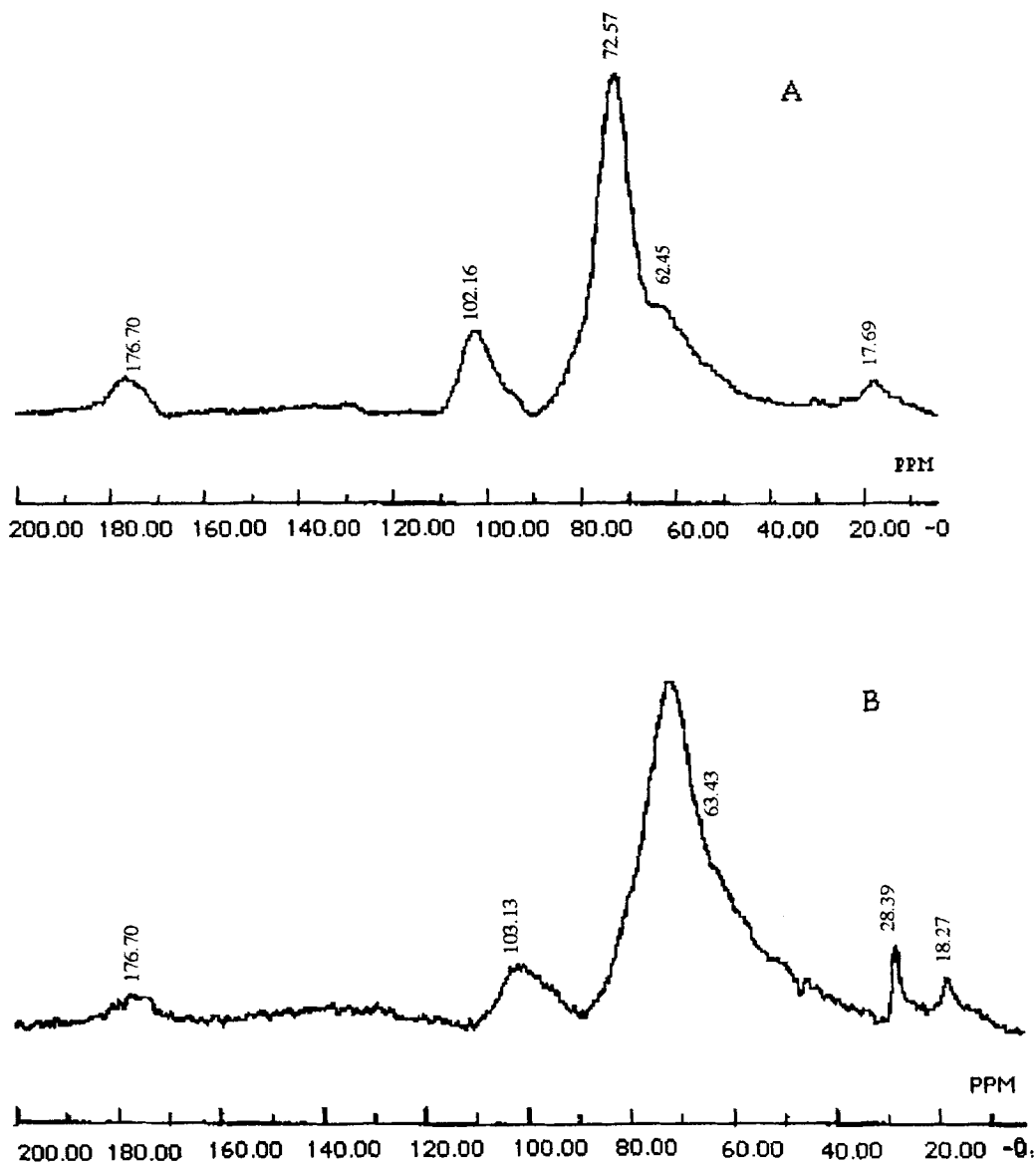


Figure 1. Representative cross-polarization magic-angle-spinning ^{13}C NMR spectrum of A) the native polysaccharide and B) the crosslinked polysaccharide.

at 28 ppm corresponded to a carbon in the vicinity of a halogen atom; chemical analysis of chlorine before and after crosslinking showed an increase in chlorine content from 0.5 to 3.5 wt %. It seems that a monofunctional side reaction occurred by the epoxidation of hydroxyl groups to form glycol chloride functional groups.¹¹

To optimize the conditions of crosslinking,¹² the stoichiometric ratio of epichlorohydrin to polysaccharide was changed while keeping the unit weight of the polymer constant (usually 1 g). By changing the volume of epichlorohydrin for crosslinking, the volume of acetic acid required for neutralization also changed (Table 1), since different amounts of hydrochloric acid were released as a result of the reaction conditions. When a large excess of epichlorohydrin was added, at a ratio of 4:1 (v/w) to the polymer, less than 0.5 mL acetic acid 7% (v/v) was needed to obtain a pH of 5.0, indicating that at high concentrations of epichlorohydrin, the environment of the crosslinking process was far from the basic conditions achieved with the addition of 5 M NaOH. The conditions of the procedure finally chosen to crosslink the polysaccharide were similar to those described for Entry 4, Table 1. Swelling was evaluated from the increase in volume after 24 h in a sample of dry material or gel placed in water in a graduated cylinder.

To determine the capacity of the crosslinked polysaccharide for metal ions, a column (10 × 0.5 cm) was loaded with the crosslinked polysaccharide, and solutions of salts (NiCl₂, CoCl₂, CrCl₃, CdCl₂) were passed through the column. After loading, the column was washed with water (×4 the column volume) to remove non-attached ions. A solution of 1 M potassium chloride was used to elute the attached ions, and the concentration of toxic ions in the eluate was determined. Analysis of the Ni²⁺, Co²⁺, Cr³⁺ ions before and after absorption was performed by measuring their absorption at the wavelength of maximum absorption using an LKB NOVASPEC spectrometer. The absorption values obtained were translated into concentrations by means of calibration curves, and the efficiency of ion retention or ion recovery was determined. The concentration of Cd²⁺ was determined with a Varian Atomic Absorption Spectrophotometer AA-375.

The extent of retention of salt solutions of toxic Ni²⁺, Co²⁺, Cr³⁺, Cd²⁺ ions at the same concentration was determined per unit weight (0.5 g) of crosslinked polysaccharide (Table 2). This preliminary data showed that about 50% cations remained on the column, but that the polysaccharide was not selective for any particular cation.

Nickel chloride was used further as a model system to test the behavior of the crosslinked polysaccharide as an ion exchanger. In the first experiment, different volumes of nickel chloride solution of the same concentration were passed through a column loaded with 0.5 g of crosslinked polysaccharide (Table 3). Since the amount of cation held on the column decreased as the amount of salt loaded on the column increased, a more dilute

Table 1. Changes in Reagents and Conditions used for Crosslinking, Expressed in Wet and Dry Weight of the Products.^a

Entry	Epichlorohydrin (ml)	Volume HOAc (ml)	Wet weight (g)	Dry weight (g)	Conditions (temperature, time)
1	1	3.5	13.5	0.89	RT ^b , 20 h
2	2	2.1	12.5	0.94	RT, 20 h
3	1	3.5	12.8	0.95	RT, ON ^c
4	2	2.1	11.3	0.93	RT, 4 h, then 70 °C, 4 h

a. Crosslinking was performed on a 1g sample polysaccharide; the results are from two repetitions to confirm the reproducibility of the method. b. RT = room temperature. c. ON = overnight.

Table 2. Percent of Absorption of Toxic Ions from their Salt Solution by Crosslinked Polysaccharide.^a

Salt ^b	Absorption, % ^c
NiCl ₂	51
CoCl ₂	45
CdCl ₂ ^d	46
CrCl ₃	54
K ₂ Cr ₂ O ₇	0

a. A 0.5g sample of crosslinked polysaccharide was used in this experiment. b. Solutions of 1.0 ml (0.2 M) were used, and then water was passed (x 4 column volume) to wash out excess salt. c. Percent absorption was calculated using calibration curves of the respective salt solutions. d. Cd²⁺ was determined by atomic absorption spectrophotometry.

solution (0.05 M, 16 mL) was used (Table 3). In this case, 89% of the salt was retained by the column. When a larger column (20 × 3 cm) was loaded with the crosslinked polysaccharide (4.0 g dry weight), similar results were observed: passing a larger volume at a low concentration resulted in a higher absorption of NiCl₂ and hence better retention of the ion on the column. In the case of the most dilute solution, almost full capacity of the ion exchanger was achieved (Table 3).

Since the polysaccharide has carboxylic and half sulfate groups,^{3,4} which are likely to confer ion-exchange properties on it, the H⁺ capacity was determined and compared to that of Amberlite IRC-50, a weak acid cation exchanger. The crosslinked polysaccharide had a capacity of 2.9 meq H⁺/g, whereas that for Amberlite was 8.9 meq H⁺/g (the value

Table 3. Percent of Retained Ni²⁺ Ions as a Function of Salt Concentration and Solution Volume in Two Columns with Different Amounts of Crosslinked Polysaccharide.^a

NiCl ₂			Retained Ni ²⁺ (%)
Weight (mg)	Volume (mL)	M	
Small column (0.5 g polysaccharide)			
47.4	1	0.2	51
237.7	5	0.2	15
189.6	16	0.05	89
Larger column (4.0 g polysaccharide)			
237.6	5	0.2	73
237.6 ¹	5	0.2	76
237.6	20	0.05	92
178.1	1	0.75	81

a. Second application after regenerating the column with dilute HCl.

Table 4. Binding of Ni²⁺ and Cr³⁺ from their Salt Solutions by the Epichlorohydrin-Crosslinked Polysaccharide of *R. reticulata* and Amberlite IRC-50.^a

Ion exchanger	Dry weight (g)	% retained ions	
		Ni ²⁺	Cr ³⁺
<i>R. reticulata</i> crosslinked polysaccharide	4	76	75
Amberlite IRC-50	25	27	0

a. Samples of 5 mL of 0.2 M NiCl₂ solution, and 0.087 M CrCl₃ solution were applied.

supplied by the manufacturer, Sigma, was 10 meq H⁺/g). The lower capacity of our crosslinked polysaccharide system means that it is a weaker ion exchanger than Amberlite. However, when both ion exchangers were tested for their ability to bind Ni²⁺ and Cr³⁺ ions, the crosslinked polysaccharide proved to be superior (Table 4). Since about 75% of the ions were retained (0.75 mmol Ni²⁺ and 0.33 mmol Cr³⁺) by 4 g of polysaccharide, the capacity for each ion is 0.19/2 and 0.08/3 meq/g, respectively. The data seem to indicate that both ionic interaction and absorption are involved in the mechanism of cation binding by the crosslinked polysaccharide.

The potential of the *R. reticulata* polysaccharide crosslinked with epichlorohydrin as an effective cation exchanger for the removal of toxic ions has thus been demonstrated. The results from our model system will be used to design efficient ion exchangers for wastewaters from industrial locations.

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