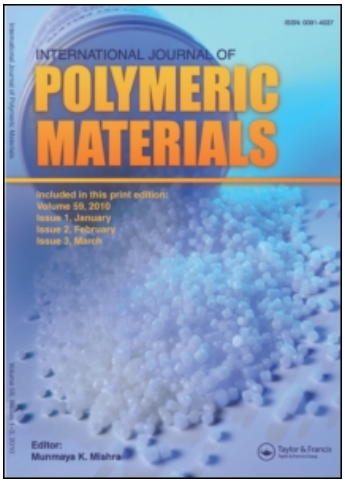

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ALGINATES DECOLORATION BY HYPOCHLORITE

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The isolation and purification of alginates from seaweeds -decoloring with hypochlorite- has been discussed by different authors, but a study about the influence of hypochlorite treatment on alginate properties was not found. The aim of this work has been the research of hypochlorite decoloration in order to obtain highly decolored alginates that have suffered minimal degradation during isolation.

Preliminary experiments were carried out varying the hypochlorite dose from 1,5 to 25,0 percentage on dry weight alga basis. Alginate yield was determined, while hypochlorite consumption and pH changes in time were measured. Infrared and UV-Visible spectra of alginates were recorded. Hypochlorite consumption was complete from the very beginning of the reaction for all experiments where an hypochlorite dose of 10% or less was applied, meanwhile low yields were obtained when the dosage was 15% or higher. Alginate absortivity ($g^{-1}Lcm^{-1}$) in UV-Visible spectra decreases when hypochlorite dose increases, but no differences were found for doses of 15 and 25%, which cause a deep degradation as confirmed IR spectra.

Hypochlorite dose (6 to 12%) and initial reaction pH (9,5 to 10,5) were varied in a 2^2 factorial design where an additional experiment was conducted at 9% hypochlorite and pH 10. Viscosimetric molecular weights were measured in addition to the responses determined for preliminary experiments. For those experiments at 12% hypochlorite the consumption was not complete, even at a reaction time of 45 minutes, but residual hypochlorite and pH reached stationery values at 30 minutes. This fact indicates that hypochlorite consumption must be monitored during decoloration and that this reaction must not exceed 30 minutes, when used the procedure here described. A dosage of 6% hypochlorite produces highly colored alginates, while 12% causes excessive degradation. Hypochlorite dose of 9% assures good decoloration and keeps, at the same time, degradation as controlled as possible.

Keywords: alginates, alga, seaweed, decoloration, bleaching, hypochlorite, viscosity, degradation

I. INTRODUCTION

Algae are structurally supported by alginates, polysaccharides which constitute 80–85% of the total weight of algae intercellular material [1, 2].

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The main characteristics of alginates, from a practical and economical viewpoint, lie on the high viscosity of their solutions, even at low concentrations. Accordingly, alginates are used in the manufacture of paintings, ceramics, detergents and polishes. In the food industry, alginates are utilized as gelifying agents and icecream stabilizers while in pharmaceutics they are used as emulsion stabilizers, desintegrant agents for tablets and others. Since 1991, the Center of Biomaterials at the University of Havana has begun the study of seaweeds, mainly brown algae, that arrive to cuban coasts [3, 4] with the aim of using alginates for pharmaceutical and medical purposes.

Many of the above mentioned uses require not only adequate viscosity but also a highly decolored alginate. Different authors [4–6] have studied the factors that influence alginate color, like specie of alga and methods for removing color. During alginate isolation a pre-extraction treatment is carried out, trying to remove colored components through an extraction with a solvent. These colored components and the pre-extraction itself could be connected in some way with viscosity losses during isolation and purification of alginate [5]. However, pre-extraction is not totally successful in decoloring alginates and a decoloration treatment with a bleaching chemical, like hypochlorite, may be needed. In that case, a strict control is recommended [6] in order to avoid an excessive and undesired degradation.

The main goal of this work has been the study of hypochlorite decoloration, trying to obtain highly decolored alginates which have suffered only minimal degradation, analyzing in particular the influence of the hypochlorite dose and pH on alginate properties.

II. EXPERIMENTAL

Alga used in this work was collected along the eastern beaches of Havana in January, 2000, then washed with plenty water and air-dried 48 hours. All experiments were performed by the procedure outlined in Figure 1 [3, 4, 7]. Hypochlorite decoloration was carried out at $(40,0 \pm 0,2)^{\circ}C$ with continuous stirring during 45 minutes unless hypochlorite total consumption occurred, in which case decoloration was concluded and began next stage.

No information was found about the operating conditions for hypochlorite decoloration, so preliminary experiments were carried out, varying the dose from 1, 5 to 25% (25, 15, 10, 5 and 1, 5%) on dry weight alga basis. A "blank" experiment was performed according to the same procedure but without decoloration stage. The following results were determined for these experiments: alginate yield, hypochlorite consumption and pH changes *versus* time and IR and UV-Visible spectra of alginates.

Based on the results of these preliminary experiments, a 2^2 factorial design was planned for the study of the influence of varying hypochlorite

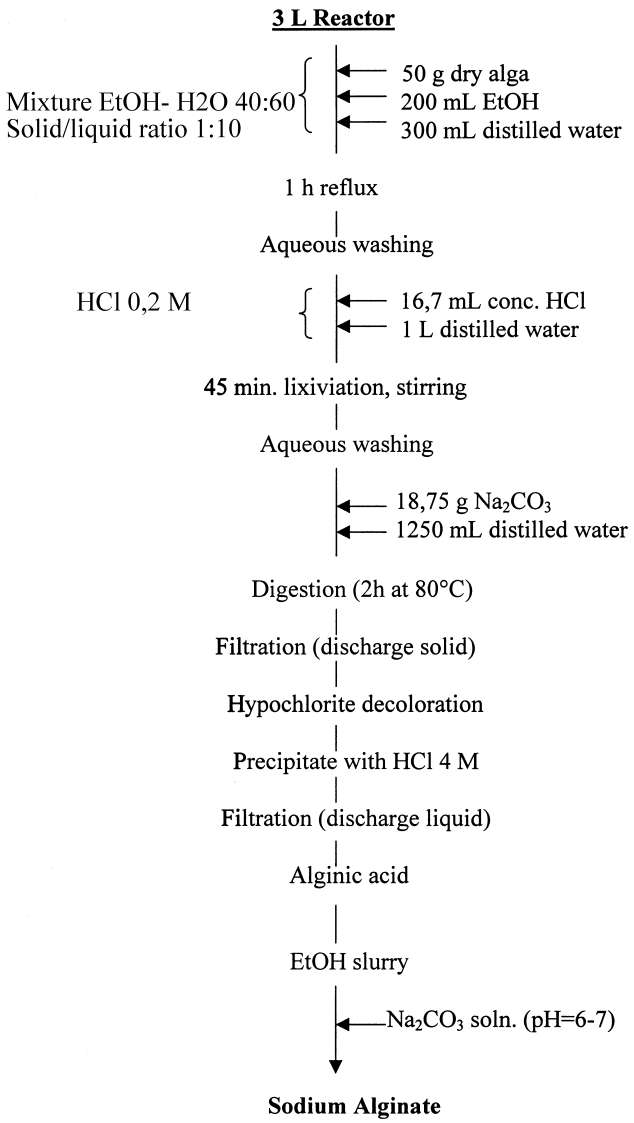

FIGURE 1 Alginate isolation procedure.

dose (6 to 12%) and pH (9, 5 to 10, 5), as well as an additional experiment was conducted at 9% hypochlorite and pH 10. Table 1 shows the independent variables and Table 2 the experimental matrix for this factorial design. Additionally to the results determined for preliminary experiments, viscosimetric molecular weights were measured for these experiments.

TABLE 1 Independent variables of the factorial design

		Level		
Variables	*Symbol*	−1	0	+1
Hypochlorite dose, (% alga)	H (X_1)	6	9	12
Initial pH	pH (X_2)	9, 5	10, 0	10, 5

TABLE 2 Experimental matrix of the factorial design

	Coded		*Decoded*	
Exp.	X_1	X_2	*H* (%)	*pH*
1	−1	−1	6	9,5
2	1	−1	12	9,5
3	−1	1	6	10,5
4	1	1	12	10,5
5	0	0	9	10,0

Hypochlorite concentration was determined as available chlorine by reaction with potassium iodide in acidic medium and titration with sodium thiosulfate. Residual hypochlorite was similarly determined and referred to initial hypochlorite and alga weights. A digital pH meter WPA Scientific Instruments model CD 500 was used for pH measurements with automatic temperature compensation. UV-Visible spectra of 0,1% w/v aqueous alginate solutions were recorded using a Pharmacia Ultrospec III spectrophotometer, while IR spectra were determined in KBr pellets at a concentration of 2 mg alginate/100 mg KBr using a FTIR ATI Matson spectrometer. Relative intensity of carboxylate stretching ($1616-1621\,cm^{-1}$) was referred to the signal at $1030-1050\,cm^{-1}$, typical of pyranosic structures. Viscosity was measured to alginate solutions in NaCl 0,2 M at $(25{,}0 \pm 0{,}1)^{\circ}C$ using an Ostwald viscosimeter.

III. DISCUSSION OF RESULTS

III.1. Preliminary Experiments

Results obtained for these experiments are shown in Table 3, where can be appreciated that final pH was between 9,15 and 9,30 in all cases, independent of hypochlorite dose. As initial pH was close to 9,5 for all these experiments, it is evident that pH did not suffer significant changes. Nevertheless, taking into consideration the known influence of pH on the degradation caused by hypochlorite [6], it seemed appropriate to include pH as an independent variable in the factorial design to be carried out.

TABLE 3 Results of preliminary experiments

	Experiment				
Parameters	1	2	3	4	5
NaClO dose (% alga)	25	15	10	5	1,5
Final pH	9,27	9,15	9,25	9,30	9,25
Residual hypochlorite (% on initial)	19,12	11,47	–	–	–
Residual hypochlorite (% on alga)	4,78	1,72	–	–	–
NaClO consumption, %	20,22	13,28	10	5	1,5
Time, min	45	45	5	5	5
Alginate yield, %	3,2	8,44	15,5	16,7	16,97

Notes: Temperature: 40°C; Alginate yield (%) of "blank" experiment: 22.86%.

Hypochlorite consumption was complete from the very beginning of the reaction for those experiments where a hypochlorite dose of 10% or less was applied. On the other hand, there was a non null residual hypochlorite at the end of decoloration (45 min) only when the dose was over 10% (15 and 25%), where also low alginate yields were obtained.

Figure 2 shows UV-Visible spectra for preliminary experiments. Alginate absortivity ($g^{-1}\,Lcm^{-1}$) decreases when hypochlorite dose increases, but no differences were found for 15 and 25%. This fact could mean that 15%

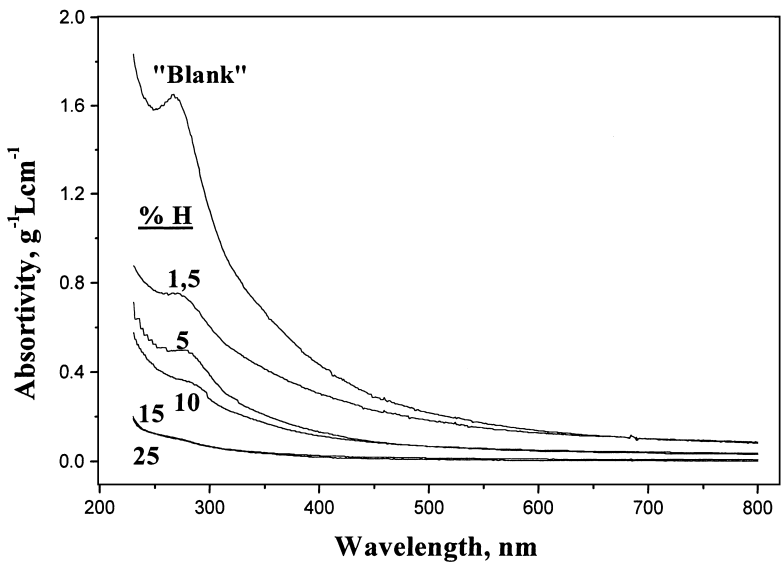

FIGURE 2 UV-Visible spectra of preliminary experiments.

hypochlorite is quite enough for decoloring all colored components in alginate.

Infrared spectra are shown in Figure 3, while the assignment of the signals is in Table 4. Figure 4 is a plot of the relative intensity of the signal dues to carboxylate groups (1616 – 1621 cm^{-1}), referred to the corresponding to pyranosic structure, *versus* the applied hypochlorite dose.

The variation of the relative intensity of carboxylate groups agrees with the mechanism of polysaccharide oxidation [8]. When hypochlorite dose

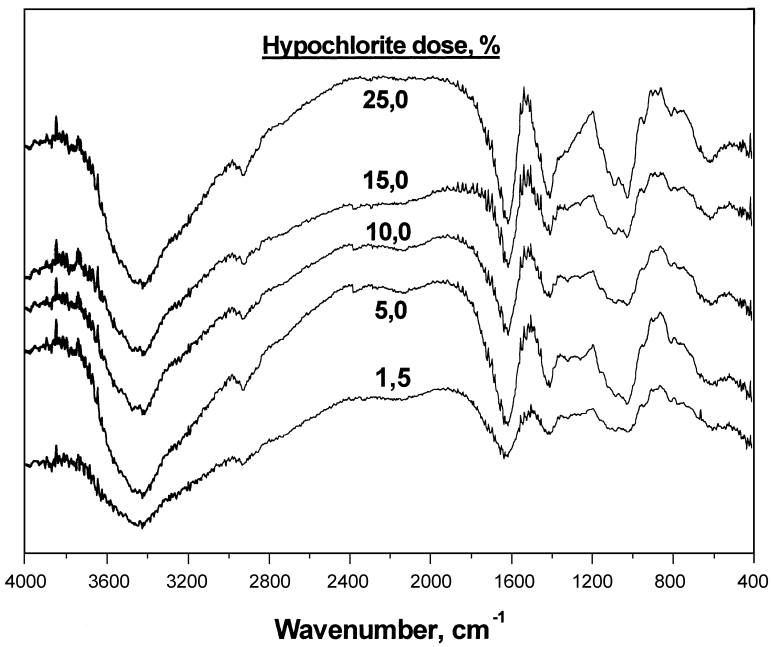

FIGURE 3 IR spectra of preliminary experiments.

TABLE 4 Assignment of IR signals

Signal, cm^{-1}	*Assignment*
3412 – 3478	O—H stretching (ν)
2923 – 2932	C_{sp3}-H stretching (ν)
1616 – 1621	Carboxylate C—O stretching (ν)
1409 – 1424	Asymmetric C—O stretching (ν^{as})
1260 – 1264	C—O—C stretching (ν)
1025 – 1031	C—O and C—O* stretching (ν)

*In pyranosic structure.

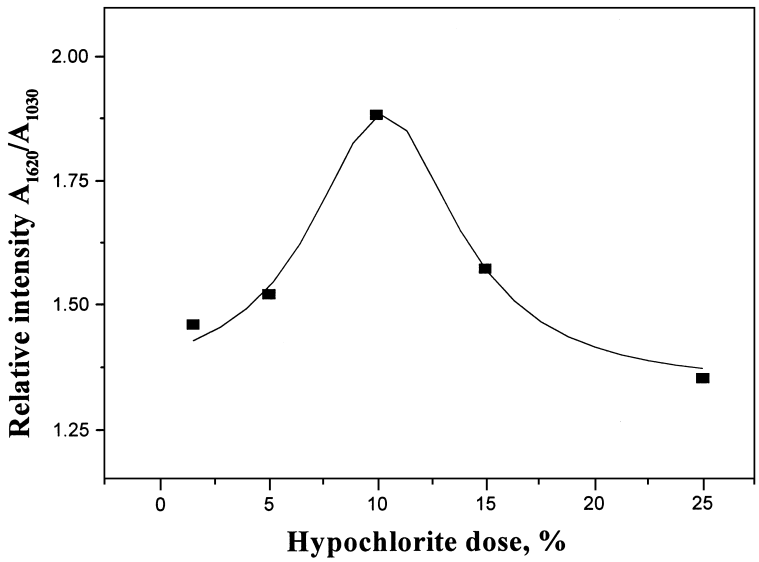

FIGURE 4 Influence of hypochlorite dosage on IR relative intensity.

increases up to 10%, the relative intensity rises to a maximum because oxidation produces carboxylate groups, but a further increment causes a remarkable degradation of alginate and the relative intensity logically decreases. It means that around 10% hypochlorite is the maximal recommended dose because higher dosage will cause an excessive degradation, in agreement with the obtained low yields for 15 and 25% hypochlorite. According to these results, the 2^2 factorial design was planned for an hypochlorite dose from 6 to 12%, with a central value of 9%.

III.2. Factorial Design

Same as for preliminary experiments, hypochlorite consumption was complete from the very beginning of the reaction for those experiments where a dose of 10% or less (6 and 9%) was applied. A non null residual hypochlorite was obtained even at a reaction time of 45 min, only when the dose was superior to 10%, but at 30 min it reached a stationary value of approximately 99% consumption, as can be seen in Figure 5.

During the reaction, pH behaves similarly. It decreases from the initial pH to a stationary value that is reached also at 30 min. This means that decoloration reaction was over at a maximum time of 30 min and it does not make sense to prolong this stage after that time. However, as reaction is

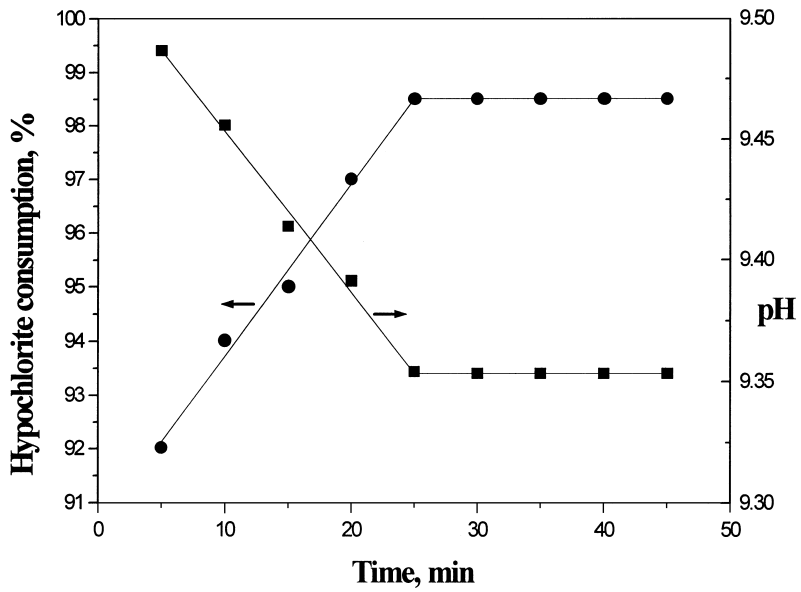

FIGURE 5 Hypochlorite consumption and pH changes in time.

finished from the very beginning, when dose is 10% or less, it is recommended to check hypochlorite consumption and pH during the reaction, in order to avoid an unnecessary longer time that would increase alginate degradation.

UV-Visible spectra of experiments from factorial design are shown in Figure 6. A minimal color removal (maximum absortivity) characterized the experiment 3 (6% H and pH 10,5). This low dose does not assure a satisfactory decoloration.

Maximum decoloration was obtained for experiment 4 (12% H at pH 10,5) but other experiments of the factorial design cause similar color removal, except experiment 3. Experiments 2 (12% H at pH 9,5) and 5 (9% H at pH 10) remove colored components so similarly that it was difficult to clearly identify them in the figure, so it was preferred not to do. The very similar color removal caused by Exp. 4 (12% at pH 10,5) and Exp. 5 (9% at pH 10) is shown in Figure 7 through the difference absortivity spectra of both experiments referred to the "blank".

A more detailed approach to chromophoric structures in alginate samples was obtained by derivative spectroscopy [9]. Figure 8 plots first derivative spectra of "blank" experiment, while Figure 9 shows second derivative of difference spectra Δ4-b and fourth derivative of difference spectra Δ5-b is shown in Figure 10. These results are summarized in Table 5.

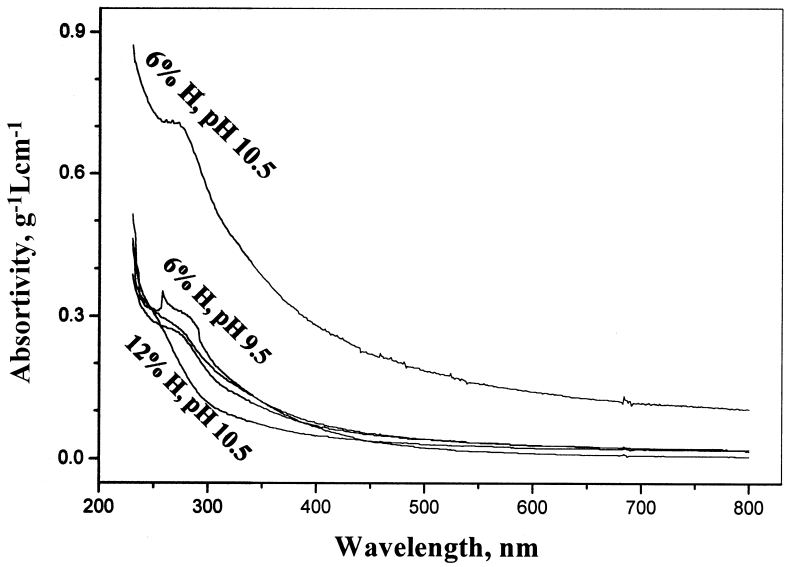

FIGURE 6 UV-Visible spectra of experiments from factorial design.

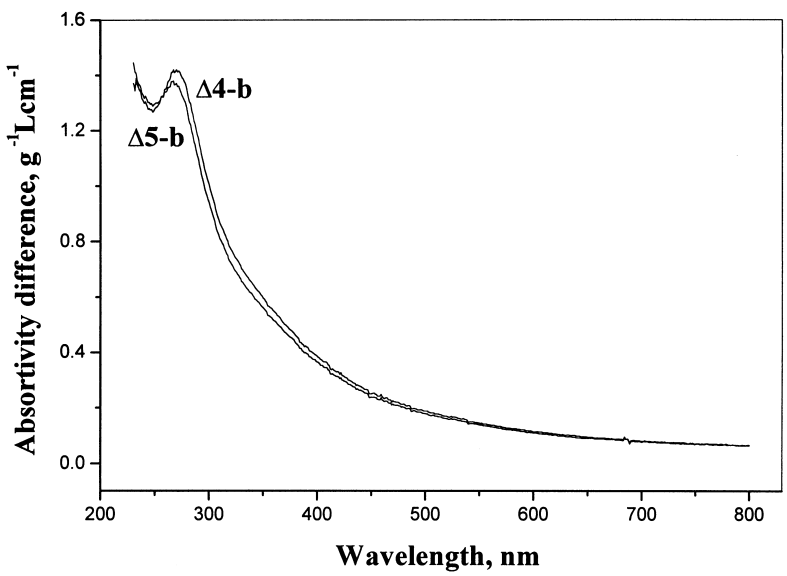

FIGURE 7 Difference spectra of experiments 4 and 5 referred to "blank".

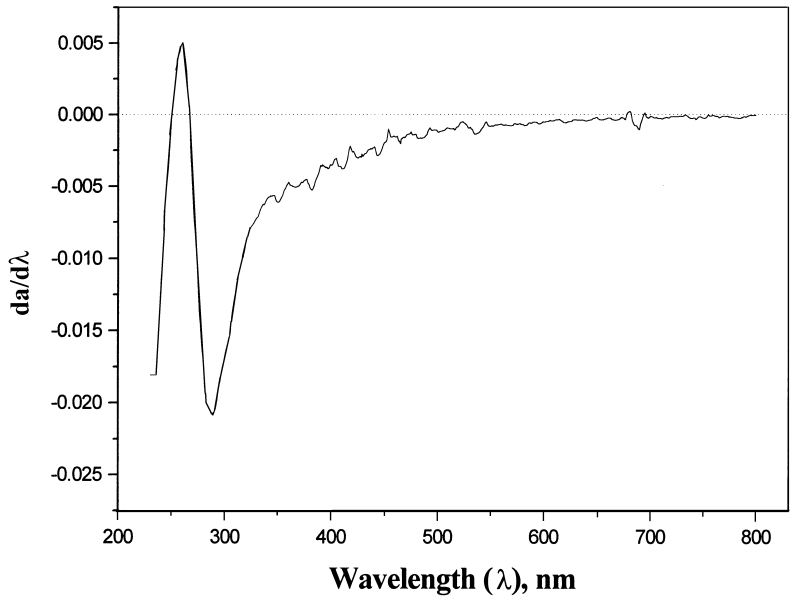

FIGURE 8 First derivative (da/dλ) of "blank" alginate UV-Visible spectrum.

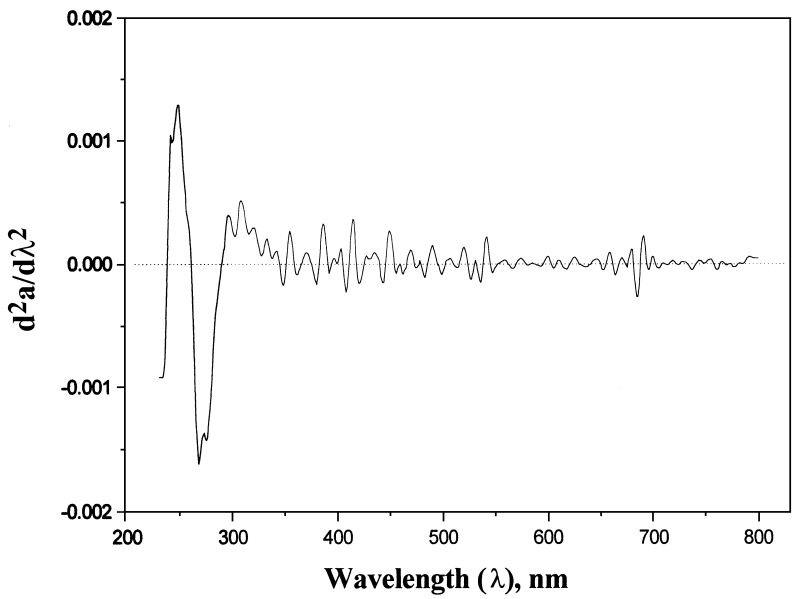

FIGURE 9 Second derivative ($d^2a/d\lambda^2$) of difference spectra Δ4-b.

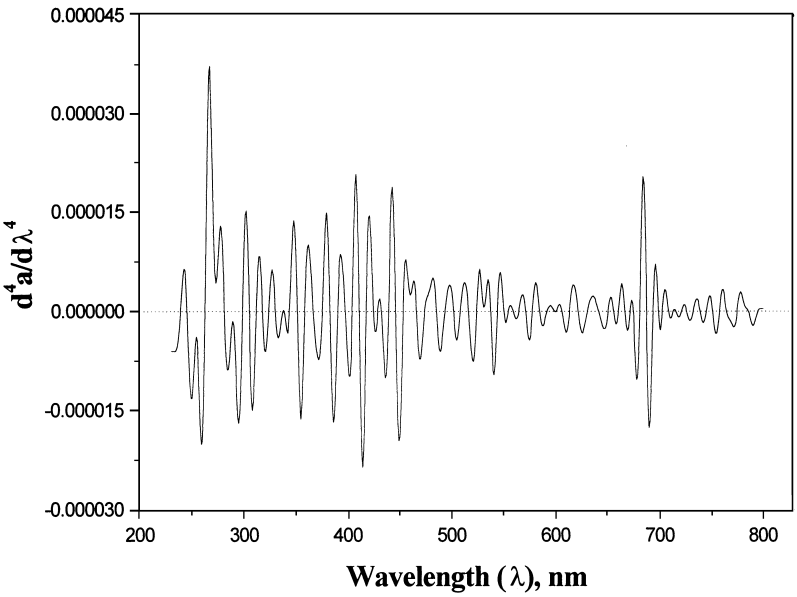

FIGURE 10 Fourth derivative ($d^4a/d\lambda^4$) of difference spectra Δ5-b.

TABLE 5 Results of UV-Visible derivative spectroscopy

Wavelength (nm)								
"Blank" spectrum			*Δ4-b spectrum*			*Δ5-b spectrum*		
$da/d\lambda$	$d^2a/d\lambda^2$	$d^4a/d\lambda^4$	$da/d\lambda$	$d^2a/d\lambda^2$	$d^4a/d\lambda^4$	$da/d\lambda$	$d^2a/d\lambda^2$	$d^4a/d\lambda^4$
266	268	266	270	269	269	268	268	268
–	–	301	–	–	301	–	–	302
–	348	348	–	349	350	–	349	349
–	380	380	–	380	380	–	380	380
–	408	409	–	408	409	–	408	408
–	420	421	–	420	420	–	420	–
–	443	442	–	444	444	–	444	444
–	527	–	–	528	525	–	526	–
–	535	–	–	536	536	–	536	–
682	684	685	682	685	684	682	685	685

Results from derivative spectroscopy pointed out the following:

- It was practically confirmed that detection sensitivity increases when the order of derivative is higher. First derivative spectra detects only very few signals and therefore next remarks are concerned only to second and fourth derivative.

- For all samples, coincident signals were detected in 266–270 nm, 348–350 nm, 380 nm, 408–409 nm, 420–421 nm, 442–444 nm and 682–685 nm.
- There are low intensity signals that are not present in all derivative spectra and could be results of derivation, without additional meaning, as the ones in 525–528 nm, 535–536 nm and 301 nm.
- The signal at 682–685 nm could be responsible of alginate color.

UV-Visible spectra for most experiments (preliminary and factorial design) can be seen in Figure 11. For all experiments, alginate absortivity decreases when hypochlorite dose increases, same as outlined for preliminary experiments alone. The lower absortivity of experiment 5 (9% H at pH 10) in comparison with experiment at 10% H (pH 9,5) could only be explained by the influence of pH, rather than the difference of dose.

Degradation of decolored alginates was evidenced not only by viscosity measurements but also by solubility increases of alginate when hypochlorite dose raises, although solubility may also increase because the removal of colored hydrophobic components. Experiment 3, the less decolored alginate, did not dissolve adequately and therefore its viscosimetric molecular weight could not be determined.

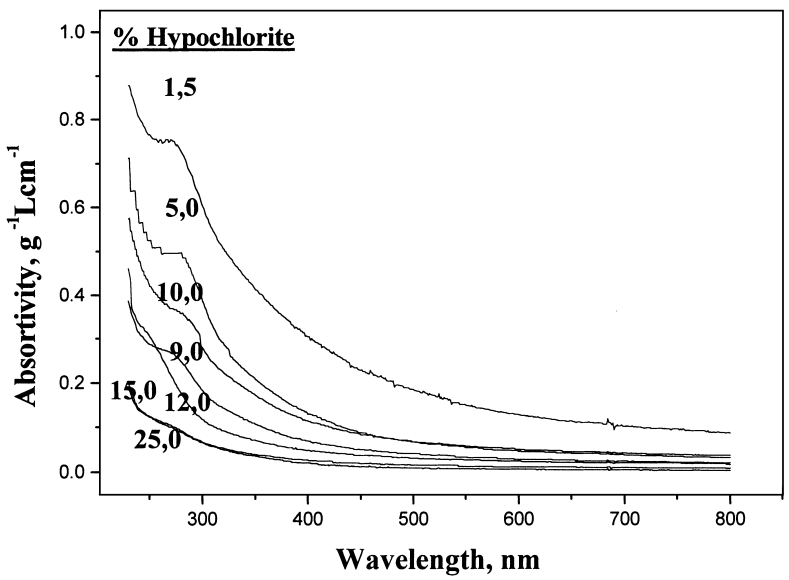

FIGURE 11 Hypochlorite dose effect on UV-Visible spectra for all experiments (preliminary and factorial design).

Figure 12 shows the plot for determining the intrinsic viscosity of experiment 5 (9% H at pH 10) and Table 6 summarizes viscosimetric results. Experiment 4 was the most decolored alginate and therefore had the lowest molecular weight, which means that the most pronounced degradation of factorial experiments occurred at 12% hypochlorite and pH 10,5. The highest molecular weight was obtained for experiment 1 (6% H at pH 9,5) but this alginate was still highly colored. Best experimental conditions were 9% hypochlorite and pH 10 (Exp. 5) that produce satisfactory molecular weight and decoloration.

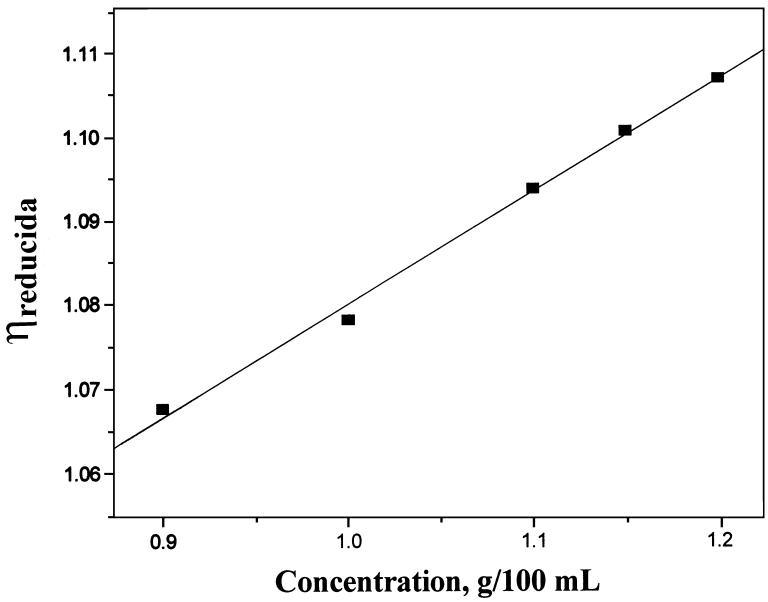

FIGURE 12 Determination of intrinsic viscosity for experiment 5 (9% H, pH 10).

TABLE 6 Statistical fit for intrinsic viscosity determination

	Experiment			
Parameter	1	2	4	5
Correlation coefficient (R)	0,9416	0,9851	0,9981	0,9976
Critical correlation coefficient (R_c)	0,934	0,959	0,992	0,992
Confidence level (α)	0,98	0,99	0,999	0,999
Intrinsic viscosity [η] g/100 mL	2,276	0,668	0,334	0,946
Average viscosimetric molecular weight Mv	28 560	8 630	4 190	11 870

IV. CONCLUSIONS

Increases of hypochlorite dose in alginate decoloration produces not only a more pronounced removal of colored structures but also a more pronounced degradation. Doses of 12% or higher (based on alga dry weight) are not recommended because of degradation, while 6% hypochlorite or less does not satisfactorily remove colored structures and therefore alginate is not well decolored. The best conditions for hypochlorite decoloration, established in this work, are a dose of 9% and an initial pH of 10. Alginates obtained under these conditions are characterized by satisfactory molecular weight and low color, while decoloration reaction is almost instantaneous. Decoloration could be evaluated by UV-Visible spectroscopy of alginate solutions, while derivative spectroscopy pointed out the signals associated with the main chromophoric structures. Relative intensity methodology, applied to IR signals corresponding to carboxylate groups, is capable of estimating alginate degradation.

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