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Evaluation of a novel seriguela gum (*Spondias purpurea L.*) based flocculant aid for wastewater treatment: effect of carboxymethylation

Avaliação de um novo auxiliar de floculação à base de goma da seriguela (*Spondias purpúrea L.*) para tratamento de água contaminada: efeito da carboximetilação

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ABSTRACT

Seriguela gum is a barely explored polysaccharide, whose carboxymethylation reaction can expand its applications for water treatment by the increase of negative charges in the chain. This work aimed to produce carboxymethyl derivatives, under different reaction condition, to apply as a flocculation aid in water treatment. The derivatives were characterized by titration, Fourier transform infrared spectroscopy, nuclear magnetic resonance, and gel permeation chromatography techniques. The reaction condition parameters, sodium hydroxide concentration, and chloroacetic acid molar ratio significantly affected the degree of substitution, with values between 0.35 and 0.51. Optimal results were achieved using lower concentrations of sodium hydroxide and intermediate chloroacetic acid levels. The derivative produced with higher degree of substitution was used as flocculation aid combined with aluminum sulfate for the treatment of contaminated river water. The tests demonstrated that the use of 3 mg/L of carboxymethylated seriguela gum combined with 20 mg/L of aluminum sulfate removed 93.1% of turbidity, showing a 21.0% increase in efficiency and a 60.0% reduction in the use of aluminum sulfate alone. It also exhibited low toxicity to *Artemia salina* at high concentrations (100 mg/L) due to its biocompatibility. The study revealed that carboxymethylated seriguela gum with increased negative charges can be obtained with a high degree of substitution by a simple and high-yield process, and the tests showed high potential for application as a flocculation aid in water treatment processes.

Keywords: flocculation aid; natural gums; polysaccharides; water treatment.

RESUMO

A goma da seriguela é um polissacarídeo pouco explorado, cuja reação de carboximetilação pode ampliar suas aplicações para o tratamento de água pelo aumento de cargas negativas na cadeia. Este trabalho teve como objetivo produzir derivados carboximetílicos, sob diferentes condições reacionais, para aplicação como auxiliar de floculação no tratamento de água. Os derivados foram caracterizados por técnicas de titulação, espectroscopia de infravermelho com transformada de Fourier, ressonância magnética nuclear e cromatografia de permeação de gel. Os parâmetros da reação, concentração de hidróxido de sódio e razão molar de ácido cloroacético tiveram efeito significativo no grau de substituição, com valores entre 0,35 e 0,51. Resultados ótimos foram obtidos utilizando menores concentrações de hidróxido de sódio e níveis intermediários de ácido cloroacético. O derivado produzido com maior grau de substituição foi utilizado como auxiliar de floculação combinado com sulfato de alumínio para o tratamento de água contaminada de rio. Os testes demonstraram que, com o uso de 3 mg/L da goma carboximetil-seriguela associado a 20 mg/L de sulfato de alumínio, 93,1% da turbidez foi removida, constatando um aumento de 21.0% de eficiência e redução de 60.0% de sulfato de alumínio isolado, apresentando também baixa toxicidade em *Artemia salina* à altas concentrações (100 mg/L) devido a sua biocompatibilidade. O estudo revelou que a goma carboximetil-seriguela com cargas negativas elevadas pode ser obtida com alto grau de substituição por um processo simples e de alto rendimento, e os testes mostraram alto potencial para aplicação como auxiliar de floculação em processos de tratamento de água.

Palavras-chave: auxiliar de floculação; gomas naturais; polissacarídeos; tratamento de água.

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Introduction

Natural gums are substances that can be defined as polysaccharides soluble in different temperature ranges, which can form colloidal dispersions, high viscosity solutions, or gels at low concentrations (Barak et al., 2020). They can be extracted from various sources, such as exudates, seeds, or by microbiological fermentation processes (Reinoso et al., 2019; Salarbashi et al., 2019; Hasheminya and Dehghannya, 2023).

Seriguela (*Spondias purpurea L.*) is a plant of the Anacardiaceae family that can be found in several tropical regions of the world, especially in Latin America (Pinto, 2000). The gum of this plant can be extracted from its exudate, and the monosaccharide units are composed of galactose (59%), arabinose (9%), mannose (2%), xylose (2%), and rhamnose (2%). A fraction of uronic acids (26%) is represented by D-glucuronic acid, besides residual protein material (Martínez et al., 2008). Spectroscopic studies of the gum show that its structure is based on D-galactopyranose units linked by β 1→3 and 1→6 glycosidic bonds, as well as arabinose, rhamnose, β-D-glucuronic acid, and 4-O-methyl α-glucuronic acid as residual terminal chains (Gutiérrez et al., 2005).

Seriguela gum (SG) presents itself as a biopolymer with vast potential for applications, based on structural similarities with other polysaccharides extracted from exudates of plants of the same family, such as cashew gum (Azevedo et al., 2022). Among its properties, glucuronic acid in the branches of the chain provides anionic groups that allow the gum to interact with cations (Ribeiro et al., 2016). Teixeira et al. (2007) used cross-linked *S. purpurea* gum as a chromatographic affinity matrix for lectin isolation. However, this gum, although not an industrial residue, is little explored. Given its properties, it can be used to take advantage of the plant, since only its fruits are commercialized. Thus, it deserves attention regarding its applicability in bioremediation, adding value to its cultivation.

In the growing demand for ecologically sustainable alternatives to reduce impacts caused by mineral and synthetic flocculants used in water treatment, SG emerges as a promising alternative to be explored for this type of application. Seriguela gum, once natural, biodegradable and available on a large scale in tropical soil, presents desirable characteristics to be investigated as a flocculant in water treatment processes, providing a more sustainable solution in line with environmental concerns. However, it is crucial to conduct specific research to evaluate its effectiveness, optimal dosage, reaction conditions, and impacts on the coagulation and flocculation processes (Zhang et al., 2019).

For these types of applications, the existence of functional groups improves the adsorption capacity of the matrices, leading to better interaction with aluminum sulfate ($Al_2(SO_4)_3$), improving coagulation and flocculation processes. Structural modifications by inserting carboxymethyl groups have been applied to increase the electrical charge density in the polysaccharide structure (Xiong et al., 2020). Carboxymethylation is a commonly used chemical modification; one of its major advantages is the ease of synthesis, low-cost chemical reagents, non-toxicity, and biodegradability of the obtained derivatives (Chakka and Zhou, 2020).

The modification of polysaccharides via carboxymethylation comprises a bimolecular nucleophilic substitution reaction. In the first step, the deprotonation of the hydroxyl groups of the primary and secondary chains of the polysaccharide occurs, followed by the etherification of these chains, because of the replacement of the alcoholic groups by the carboxymethyl groups from chloroacetic acid (Chakka and Zhou, 2020). This reaction allows the polysaccharide to enhance its anionic character and interact more efficiently with particles destabilized by the positive charges of the mineral coagulant.

Water and effluents treatment aims to reduce the load of pollutants in water resources, making them safe for aquatic life and the general population. In coagulation flocculation, inorganic salts are used as coagulants such as aluminum sulfate and ferrous chloride; however, several studies point out to the danger of human exposure to these elements in treated water, especially aluminum, which is correlated with the neurodegenerative Alzheimer's disease (Alasfar and Isaifan, 2021).

The utilization of gums as flocculants presents environmental advantages such as the reduction of coagulant dosages, low required dosages, formation of dense flocs, and biodegradable sludge increasing the efficiency of the process and cost-effectiveness, reducing treatment costs (Lima Júnior et al., 2020). Studies involving biopolymers as flocculants show high efficiency in reducing the turbidity of treated water and wastewater samples, using different types of plant-based flocculants like *Aloe vera* mucilage (Figueiredo et al., 2022), okra gum (Mokhtar et al., 2021), and fenugreek and flaxseed gums (Venegas-Garcia and Wilson, 2022).

Given the growing demand for biodegradable and environmentally friendly materials, the use of low-cost natural gums can be a great option for replacing mineral flocculants, demonstrating the innovative potential of using a material abundant in the region that can be applied to local water treatment systems. Based on the literature review, there are no studies that apply SG or its derivatives in water treatment in coagulation or flocculation process or its toxicity, showing that it is a barely investigated material in this area. The objective of this work was to extract SG and study the effect of the reaction conditions used in carboxymethylation on the average degree of substitution, aiming to apply the material as a flocculation adjuvant in the treatment of water contaminated by mining activities and evaluate the toxicity of derivatives.

Materials and Methods

Materials

For extraction and purification of the gum, the following reagents were used: sodium chloride (NaCl) (Neon), ethanol 96% p.a. (Neon), methyl alcohol (Dinâmica), acetone p.a. (Neon), sodium hydroxide (NaOH) (Dinâmica), and potassium hydroxide (KOH) (Dinâmica). For modification via carboxymethylation, chloroacetic acid (Neon) was used.

Extraction and purification of *Spondias purpurea* L. gum

Initially, the exudate was extracted and obtained by mechanical shock from parts of the tree stem in Pacatuba, municipality of Ceará, Brazil. The liquid exudate was collected and dried at room temperature, and later crushed in a mortar. A fraction of 5 g of the ground exudate was solubilized in distilled water and kept under magnetic stirring for 24 hours. The first vacuum filtration was conducted in a number 1 porous plate funnel to remove large residues. Then, 2 g of NaCl powder was added to the mixture, followed by potential of hydrogen (pH) correction to 7 with 0.1 mol/L NaOH. Precipitation occurred in the mixture when a 1:4 solution/96% ethanol was added. Filtration of the precipitate was conducted through a number 3 porous plate funnel, followed by washing with methyl alcohol and acetone. The procedure was repeated two more times as a purification process. Finally, the extracted gum was dried in an oven at 50°C for 24 hours, weighed, and stored in a desiccator.

The acid content of the purified gum was determined by titration adapted from Yahoum et al. (2016). An amount of 4 g of the gum was dissolved in 100 mL of distilled water and titrated with KOH 0.1 mol/L in a pH meter Luca-210. The acid content was determined using Equation 1:

$$\%Acid: \frac{178\ x\ V_{KOH}\ x C_{KOH}}{C_{Gum}}\ \ x\ 100 \tag{1}$$

Where:
V_{KOH} = volume spent until inflection point (L);
C_{KOH} = concentration of base (mol/L);
C_{Gum} = concentration of gum (g/L); and
178 = molar mass of galacturonic acid in the chain.

Synthesis of carboxymethylated derivatives

For the structural modification, the methodology proposed by Silva et al. (2004) was employed with some adjustments. Initially, 2 g of the gum was added to 10 mL of distilled water until a paste was formed. Knowing that the process requires high concentrations of NaOH, two concentrations were selected (5 and 10 mol/L) and then added to the mixture at predetermined intervals under constant stirring. Subsequently, chloroacetic acid fractions based on molar ratios still poorly investigated, varying in 1:5, 1:9, 1:12, and 1:15, were slowly added to the alkalinized reaction medium. The solution was then heated at 60°C for approximately four hours. At the end of the reaction, the medium pH was neutralized with a NaOH 1.0 mol/L solution. The polymer was precipitated in 99% ethanol, followed by filtration and multiple washes with methyl alcohol and acetone to ensure purity.

The samples of carboxymethyl seriguela gum (CMSG) were dried in an oven at 50°C for approximately 24 hours and stored in a desiccator. With this material produced, eight experiments were conducted, varying two reaction parameters, the molar ratio between SG and chloroacetic acid and NaOH concentration.

Characterization of seriguela gum and its derivatives

SG and its derivatives were characterized by Fourier transform infrared (FTIR) spectroscopy on a Shimadzu IR-tracer-100 model spectrometer (Shimadzu, Kyoto, Japan) in the 4,000 to 400 cm^{-1} range, with 64 scans and a resolution of 4 cm^{-1}. Samples were also characterized by 1H nuclear magnetic resonance (NMR) on a 500 MHz advanced XRD spectrometer (Bruker), dissolving 20 mg of the sample in 0.5 mL of dimethylsulfoxide as a solvent. In total, 128 transients were performed, and the spectra were analyzed using TopSpin 3.6.2 software. The molar mass distribution was determined by gel permeation chromatography (GPC) on Viscotek GPX Max VE-2001 equipment at 35°C, using 2SB-807 HQ and 2SB-806M HQ columns in 0.1 mol/L NaNO3 solvent and a flow rate of 0.5 mL/min.

The absolute degree of substitution was determined and adapted from the modified method described by Yahoum et al. (2016), in which 0.2 g of CMSG was solubilized in 50 mL of 0.1 mol/L hydrogen chloride (HCl) and titrated with 0.1 mol/L KOH solution. The purified SG solution was also titrated by the same method in order to represent a blank sample. The SG value was calculated using Equations 2 and 3 below:

$$DS_{\text{abs}} = \frac{162\ \cdot A}{1000 - 58\ \cdot A} \tag{2}$$

$$A = \frac{(V_2 - V_1)_{KOH}\ \cdot\ C_{KOH}}{m_{CMSG}} \tag{3}$$

Where:
DS_{abs} = absolute degree of substitution;
162 = molar mass of the galactose unit;
58 = molar mass of the carboxymethyl groups;
A = general amount of ethanoic acid (CH_3COOH) and sodium acetate (CH_3COONa) groups/g of sample;
V_2 = volume of KOH (L) in titration of the CMSG samples;
V1 = volume of KOH (L) for the blank titration;
C_{KOH} = concentration of KOH (mol/L); and
m_{CMSG} = mass of dry sample (g).

The yield was determined through the ratio between the mass of the derivative obtained after the reaction and the molar mass of the galactose monosaccharide unit.

A study by Miyamoto (1996) alternatively suggested a method to determine the amount of carboxymethyl groups inserted into the polysaccharide using the infrared spectra of carboxymethyl gellan. The relative degree of substitution can be calculated by Equation 4:

$$DS_{rel} = \frac{A_{1608}}{A_{2933}}\ - B \tag{4}$$

Where:
DSrel = relative degree of substitution;

A_{1608} = stretch vibration absorbances of C=O (1,608 cm^{-1}) of the carboxymethylated derivatives;
A_{2933} = stretch vibration absorbances of C-H (2,933 cm^{-1}) of the carboxymethylated derivatives; and
B = constant corresponding to the $\frac{A_{1608}}{A_{2933}}$ ratio for the gum before modification.

Viscosity tests were performed according to the methodology described by Abreu et al. (2013). The specific viscosity of the pure gum and its derivatives was obtained by Equation 5, and the reduced viscosity, by Equation 6, using a Cannon-Feske viscometer, with various concentrations of the solution diluted in 0.2 mol/L NaCl at 30°C.

$$\eta_{spec.} = \left(\frac{t - t_o}{t_o}\right) \quad (5)$$

$$\eta_{spec._{red}} = \left(\frac{\eta_{spec.}}{c}\right) \quad (6)$$

Where:
$\eta_{spec.}$ = specific viscosity;
t = flow time of the solution;
t_0 = flow time of the solvent; and
c = concentration of the polymer in the solution (g/mL).

The intrinsic viscosity was obtained by the limit of the reduced specific viscosity, when the polymer concentration tends to zero, represented by Equation 7 and obtained graphically:

$$\eta_{intrisic} = [\eta] = \lim_{c \to 0} \left(\eta_{spec._{red}}\right) \quad (7)$$

Where:
$\eta intrisic$ = intrinsic viscosity;
[η] = viscosity;
$\lim_{c \to 0}$ = limit when the polymer concentration tends to zero; and
($\eta spec._{red}$) = reduced specific viscosity.

Experimental design and variance statistical analysis

The effect of two independent variables—NaOH concentration and chloroacetic acid/silver gum molar ratio—was investigated in relation to the dependent variable degree of substitution (DS). The independent variables were studied at different levels and defined as:

- Factor A: NaOH concentration (mol/L). Two levels: high level (10M) and low level (5M);
- Factor B: seriguela gum/chloroacetic acid molar ratio. Four levels: highest level: 1/15; medium-high level: 1/12; medium-low level: 1/9; lowest level: 1/5.

Eight runs were performed in duplicate, in groups of four experiments randomLy chosen. The statistical treatment was performed through analysis of variance (ANOVA) in the program Microsoft Excel® (2022). ANOVA analysis was applied to emphasize the calculated effects using a statistical reliability of 95%.

River water parameters

River water was gathered from the Poti river at Quiterianópolis, Ceará, Brazil. The water used as study material was collected approximately 10 km downstream from a mining company along the river course. The collection was performed using 10 L plastic gallons and tested according to the Standard Methods for the Examination of Water and Wastewater, immediately to obtain physicochemical interruptions before treatment (APHA, 2023).

The river water sample collected had a large amount of suspended material. Table 1 shows some physical-chemical parameters of this water. The sample analyzed contained a significant amount of turbidity, probably originating from industrial mining activities close to the course of the river. The other parameters analyzed presented values characteristic of this type of water body, demonstrating that this water had a low amount of ionic pollutants. However, the amount of iron found in the sample indicated the presence of the metal associated with the suspended material.

Coagulation and flocculation tests

To perform the tests, a jar test device (Milan brand, model JTC) was used, with three graduated acrylic vats with a capacity of 1 L and stainless-steel straws. Tests were made using 500 mL of the collected water. The coagulant was added to the system, which was then subjected to rapid mixing at 200 rpm for two minutes and slow mixing at 40 rpm for two minutes. After this period, the system was kept at rest for 40 min and the supernatant was carefully removed 2 cm below the surface with the aid of a peristaltic pump. This aliquot was subsequently analyzed in a turbidimeter (Del Lab, DLI 2500). These are the standard operating conditions of the system. The turbidity removal efficiency was calculated from Equation 8 below:

$$\%Removal_{Turbidity} = \left(\frac{T_{initial} - T_{final}}{T_{initial}}\right) x\ 100 \quad (8)$$

Based on these conditions, the effect of pH on the coagulation process was first tested, and 50 mg/L of $Al_2(SO_4)_3$ was added to the system, varying the pH from 4.0 to 8.0, and using HCl and NaOH solutions at 0.1 mol/L to regulate the pH. After determining the ideal pH, the dosage of $Al_2(SO_4)_3$ at this pH was studied, altering the coagulant concentration in a range from 20 to 70 mg/L. Then, with the same concentrations of $Al_2(SO_4)_3$, the influence of the addition of pure and CMSG with a higher DS as a flocculant was evaluated, varying in concentrations of 1, 3, and 5 mg/L of gum.

Toxicity testing by *Artemia salina*

Dried *Artemia salina* eggs were placed in a bottle containing artificial seawater that was prepared by dissolving 35 g NaCl, 1.390 g

magnesium chloride ($MgCl_2$), 0.652 g calcium chloride ($CaCl_2$), 0.414 g KCl, 1.888 g magnesium sulfate ($MgSO_4$), and 0.116 g sodium bicarbonate ($NaHCO_3$) in 1 L of distilled water. After 24 hours of incubation at room temperature (28–30°C) under strong aeration and continuous illumination conditions, the larvae (nauplii) hatched. The cytotoxicity evaluation of CMSG5A and SG *A. salina* was performed according to the method described by Rajabi et al. (2015) with adaptations. A stock solution of 1,000 mg/L of SG and CMSG5A was prepared. Next, serial dilutions of 100, 10, 1, and 0.1 mg/L were made in tubes, totaling 5 mL, using artificial seawater as diluent. After that, 10 nauplii per tube were added and incubated at room temperature for 24 hours. The number of surviving nauplii in each well was counted after 24 hours. The experiments were conducted in triplicate for each concentration. Negative control tubes contained 10 nauplii and artificial seawater only, and positive control tubes contained potassium dichromate ($K_2Cr_2O_7$) at the same concentrations. The percentages of deaths were calculated by comparing the number of survivors in the test and control tubes. Lethality was calculated using the following formula: %Lethality=[(Test–Control)/Control]×100.

Results and Discussions

Purified SG was obtained successfully, with an average yield of 63.83 standard deviation (±) 0.09% from the brute exudate. The glucuronic acid content in SG was determined by titration and indicated an average acid content of 6.67±0.02%. The study of the reaction conditions effect on the DS will be addressed, as well a comparative study between the properties of CMSG derivatives and SG.

Effect of reaction parameters on the absolute degree of substitution

Carboxymethylated seriguela derivatives had the DS_{abs} determined, with results presented in Table 2. The carboxymethyl reaction of SG using 5 mol/L NaOH showed a higher DS, with an average value of 0.38±0.11. By using 10 mol/L of NaOH, there was an average value of 0.14±0.03. The molar ratio SG:chloroacetic acid also showed some variation in the DS.

The DS_{abs} decreased significantly as the concentration of NaOH increased from 5 to 10 mol/L. A study by Kaity and Ghosh (2013) revealed that the carboxymethylation of *Parkia biglobosa* gum (locust bean) presented an increase in the DS with increasing volume until a certain volume (14 mL of NaOH 10 mol/L). Above this volume, the authors showed that the increase in OH^- ions caused a progressive reduction in DS, associated with the secondary reaction of formation of sodium glycolate, predominating in the reaction medium instead of carboxymethylated derivatives. Thus, the excess of NaOH caused a decrease in DS_{abs} for CMSG samples, corroborating Kaity and Ghosh's findings.

Table 1 – Physicochemical parameters of river water at the collection point.

Parameters	Results
pH	7.63±0.11
Turbidity (NTU)	810.33±2.52
Electrical Conductivity (uS.cm^{-1})	258.33±0.58
Total Dissolved Solids (mg/L)	129.33±0.58
Alkalinity (mg/L)	8.25±0.23
Iron	61.42±2.59

Table 2 – Reaction parameters, absolute degree of substitution obtained by titration, and yields of the carboxymethyl seriguela gum derivatives produced.

Sample	Molar ratio SG:CA	NaOH concentration (mol/L)	DS_{abs}	Yield (%)
CMSG3A	1:5	5	0.35±0.01^a	66.5
CMSG5A	1:9	5	0.51±0.02^b	67.2
CMSG7A	1:12	5	0.38±0.06^a	62.9
CMSG9A	1:15	5	0.23±0.05^{a,c}	62.6
CMSG3B	1:5	10	0.11±0.02^c	87.8
CMSG5B	1:9	10	0.18±0.04^c	86.9
CMSG7B	1:12	10	0.12±0.02^c	72.4
CMSG9B	1:15	10	0.15±0.06^c	69.4

NaOH: sodium hydroxide; SG: seriguela gum; CA: chloroacetic acid; DS_{abs}: absolute degree of substitution. Identical superscript alphabetical letters indicate that there is no statistical difference between averages with 95% confidence intervals.

From a ratio of 1:5 to 1:9, the DS_{abs} exhibited an upward trend as the acid content increased; on the other hand, they decreased with higher acid content. In other studies, intermediate levels of acid provided a greater availability of carboxymethyl ions to react with the polysaccharide chains of the gum (Pushpamalar et al., 2006; Patra et al., 2020). Nevertheless, increased acid levels may promote glycolate production and reduce carboxymethylation efficiency.

Therefore, for application in adsorption of metals, the derivatives with the highest DS may present a high potential for electrostatic interaction between the charges of the inserted carboxymethyl groups, with the charges of polluting metallic ions (Rahmatpour and Alijani, 2023). Guan et al. (2021) reported that the distribution of negative charges in the carboxymethylated material can also be beneficial in the treatment of textile effluents containing high amounts of color from cationic dyes, potentially enabling a simultaneous effect in the removal of various types of contaminants.

Infrared analysis (Fourier transform infrared)

FTIR was used to evaluate SG with various degrees of carboxymethylation (Figure 1).

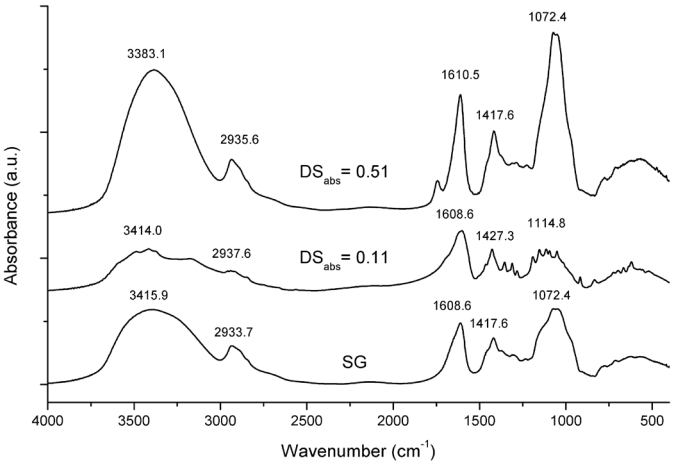


Figure 1 – Fourier transform infrared spectra of seriguela gum and its carboxymethylated derivatives, CMSG3B and CMSG3A, with respective absolute degree of substitution values (DSabs) of 0.11 and 0.51.

SG and its derivatives had significant variations in the vibrational groups. These are primarily linked to the varying presence of carboxymethyl groups, which is determined by the degree of carboxymethylation. SG and CMSG derivatives showed bands close to 3,300 cm^{-1}, attributed to the O-H stretch, besides a band near 2,933 cm^{-1}, referring to the C-H stretch (Cai et al., 2020). According to the literature, the absorption peaks at 1,608 and 1,417 cm^{-1} in SG are attributed to the symmetrical and asymmetrical stretching of C=O groups of carboxylic acid in the glucuronic acid of terminal chains (Chen et al., 2014; Santos et al., 2019). However, in the CMSG derivatives spectra, there is a considerable increase in the intensity of these peaks caused by the introduction of new carboxymethyl groups. Derivatives with higher intensity on the C=O stretching peaks are associated with higher DS_{abs}.

Applying Miyamoto's equation to CMSG samples, we noted that the value of constant B reported in Equation 8 is equal to 1.57 obtained for SG. Figure 2A shows the relationship between these values and the DS_{abs} determined by titration and DS_{rel} determined by FTIR. A linear correlation can be observed for the carboxymethylated products with DS_{abs} up to 0.38, following Equation 9:

$$DS_{abs} = DS_{rel}18.291 - 1.4119 \quad (9)$$

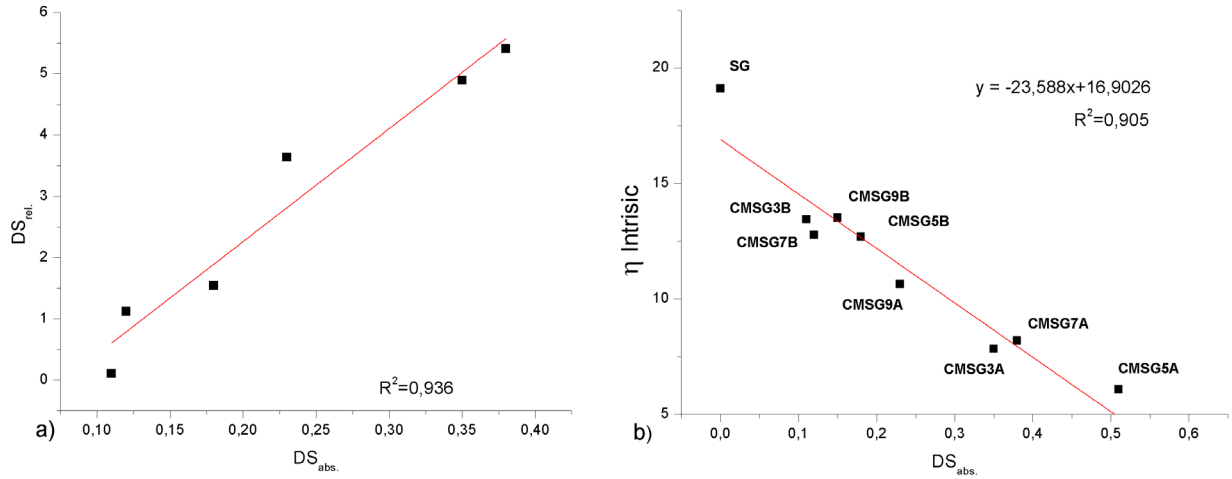
Based on the Miyamoto equation, the B constant found for SG demonstrates that the amount of carboxymethyl groups is higher than other polysaccharides; previous studies reported that gellan (Miyamoto, 1996) and cashew tree gum (Silva et al., 2004) have values of 0.23 and 1.0, respectively. These studies on carboxymethylation of polysaccharides found limited correlation between the two methods. DS_{rel} and DS_{abs} values, obtained for carboxymethyl cashew tree gum and carboxymethyl gellan, presented a correlation value limited to DS_{abs} of 0.20. In this work, a correlation was achieved up to a value of 0.38, as shown in Figure 2A. These linearity deviations, when in samples with a high content of –COOH groups (i.e., more substituted), can be attributed to the high absorption and/or formation of ionic pairs, arising from a higher density charge of the polyelectrolyte. This phenomenon was also observed in carrageenan sulfate, analyzing the relationship between DS and 1,250/2,920 cm^{-1}, where linearity was obtained up to a value of DS=0.5 (Rochas et al., 1986; Miyamoto, 1996).

Viscosimetric analysis and molar mass distribution

The intrinsic viscosity of the isolated SG and the CMSG derivatives as a function of DS is depicted in Figure 2B. Isolated SG presented a value of 19.12 mL/g, which is much higher than the corresponding derivatives obtained after carboxymethylation.

Considering that the Williamson etherification reaction is conducted at high concentrations of NaOH and chloroacetic acid and high temperature, degradation processes can occur in the major polysaccharide units, which can lead to a reduction in the viscosity of the carboxymethylated material. In addition, some gums may end up generating saccharide acids, which have greater solubility in aqueous media, reducing the viscosity of the products (Mudri et al., 2021). In our study, samples produced using 10 mol/L NaOH, with low DS_{abs} results, obtained an average intrinsic viscosity value of 13.10 mL/g. Derivatives with higher DS_{abs} values, ranging from 0.23 to 0.51, showed a significant decrease in viscosity. This may be associated with a decrease in intermolecular forces between the polysaccharide chains and the solvent due to the insertion of carboxymethyl groups, or even a reduction in molecular weight due to the degradation of the polymeric chain (Goyal et al., 2007). The decrease in intrinsic viscosity when DS_{abs} increases was also observed for carboxymethyl scleroglucan in the study performed by de Nooy et al. (2000).

Table 3 shows the molecular chain mass distribution for the SG and the carboxymethylated samples. The SG polydispersity value is high (20.02), suggesting chain size heterogeneity, whereas the carboxymethylated samples, CMSG5A and CMSG7A, have values of 1.63 and 1.31, respectively, indicating greater chain size uniformity (Scopel et al., 2020). The peaks corresponding to molecular weight indicate that the SG sample has an average molar mass value of 77.5 Kda, whereas the carboxymethylated products showed an average reduction of 66.52% in this value. Due to its branched structure and few long chains, the SG has a high molar mass. The reaction causes chain breakage, leading to the formation of smaller chains. The decline in molecular weight values of the samples that underwent carboxymethylation could be due to polymeric chain degradation caused by excess base or residual chloroacetic acid, resulting in the breakdown of SG chain aggregates and the formation of smaller chains with lower molecular mass (Kim et al., 2018). The decrease in molecular mass due to chain degradation corroborates the intrinsic viscosity decay for the CMSG samples (Silva et al., 2004).



DS_{rel}: relative degree of substitution; DS_{abs}: absolute degree of substitution; η*intrisic*: intrinsic viscosity; R^2: coefficient of determination; FTIR: Fourier transform infrared; CMSG: carboxymethyl seriguela gum.

Figure 2 – (A) Correlation between the degree of substitution determined from the titration method (DS_{abs}) in comparison with the degree of substitution determined from FTIR (DS_{rel}); (B) Correlation between the intrinsic viscosity and their corresponding degree of substitution for CMSG samples.

Table 3 – Molecular masses obtained by gel permeation chromatography for seriguela gum, CMSG5A and CMSG7A.

	SG	CMSG5A	CMSG7A
Mn (Kda)	3.869	18.399	16.704
Mw (Kda)	77.459	29.922	21.954
Mz (Kda)	263.807	48.791	29.175
Mw/Mn	20.016	1.626	1.314

SG: seriguela gum; Mn: number average molecular weight; Mw: weight-average molecular weight; Mz: z-average molecular weight.

Nuclear magnetic resonance analysis (1H NMR and 13C NMR)

In the literature, the purified SG showed chemical shifts in the region of 4.34 to 6.00 ppm, indicating the presence of -D-glucose, -l-rhamnose, -d-galactose (1→3), and -d-glucuronic acid. Furthermore, there is a distinctive signal at 1.31 ppm that represents the methyl group of rhamnose (Lima et al., 2018; Vasconcelos et al., 2019). Figure 3 displays the spectra of the carboxymethylated samples, revealing the confirmation of the reaction through the emergence of new proton peaks at 3.40, 3.68, and 4.75 ppm. These peaks are attributed to the methylene protons of the carboxyl group (Dodi et al., 2016). Other peaks characteristic of the insertion of carboxymethyl groups in the region of 3.40 to 4.10 ppm correspond to the methylene proton of the CH2-O-CH2 group (Maity and Sa, 2014).

The use of 13C NMR can enhance the understanding of polysaccharide chain structure modifications. Figure 4 illustrates the characteristic signs of carbons arranged in the structure. In a spectrum, it is possible to observe signs of strong intensity of the carbon atoms of the repeating units of the polysaccharide. The chemical shifts agree with the values given in the literature (León de Pinto et al., 1996; Zhang et al., 2013). New signals can be detected in the CMSG spectra (Figure 4, spectrum b), corroborating the new absorption bands of the FTIR spectra. The prominent peaks at 175.8 ppm in b and 178.3 ppm in c are attributed to the carboxylate anion (–COO–) of the inserted carboxymethyl group. The other peaks in this same range can be attributed to different positions of the carboxymethyl substituent in the polymeric chain (Chaves et al., 2024). Because it is an etherification, the methylene carbon atom (–CH2-) of the substituents generates peaks at 72.48 and 73.02 ppm, as can be seen in spectrum b. These values are found in the literature (Lawal et al., 2008; Xu et al., 2009).

The other peaks result from the arrangement of carbon atoms in the chain of saccharide units. Unlike other gums, SG exhibits low-intensity peaks at 170–180 ppm, indicating a significant presence of carboxylate ions in the branches. This information is verified through potentiometric titration and FTIR analysis of pure gum. However, these ions indicate the presence of repetitive units of β-glucuronic acid. The spectrum, within the range 70 to 100 ppm, supports this finding (Chaves et al., 2024). Table 4 displays peaks corresponding to carbons 1, 2, and 3, while other peaks may have been suppressed by carbons from different units.

Coagulation and flocculation tests

Although coagulation with $Al_2(SO_4)_3$ at a concentration of 50 mg/L effectively reduced turbidity to 15.45 NTU, it did not meet the potability standards required by Brazilian legislation of 5 NTU. Figure 5A presents a bar graph that illustrates the residual turbidity as a function of pH and a line graph showing the corresponding efficiency of turbidity removal as a function of pH. In this test, efficiencies of 97.9 and 98.1% were obtained at pH 5 and 6, respectively, with final turbidity of 17.3 and 15.6 NTU.

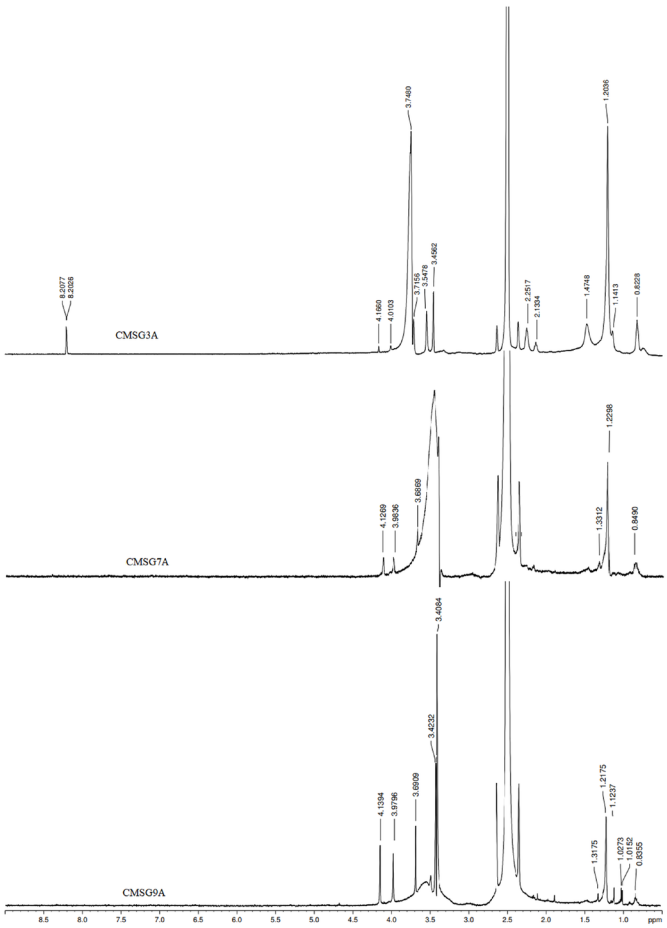


Figure 3 – 1H nuclear magnetic resonance spectrum of carboxymethylated samples with different degree of substitution CMSG3A, CMSG7A, and CMSG9A.

The lower efficiency observed for $Al_2(SO_4)_3$ outside this pH range, compared to the maximum permitted value established by legislation, may be related to its chemical behavior in solution. When dissolved in water, $Al_2(SO_4)_3$ acts as a strong acid because of successive hydrolysis reactions, resulting in the generation of H_3O^+ cations and a consequent decrease in pH, besides consuming the alkalinity of the medium, considering a low river alkalinity of 8.25 mg/L. These changes directly affect the coagulation process, which, for $Al_2(SO_4)_3$, ideally occurs in the pH range 5.5 to 6.5 (Sillanpää et al., 2018).

Based on the results of the pH test, pH 6.0 was selected as a fixed study parameter in the addition of the polymer produced as a flocculation aid in the treatment of contaminated water. Based on the characterization results of the carboxymethylated derivatives obtained, the sample CMSG5A was selected to perform flocculation and coagulation tests, due to its high DS_{abs}; in addition, the use of SG was tested for comparison purposes.

According to the flocculation tests using SG, the outcomes were promising and close to the results obtained when using the modified derivatives. Previous studies have shown that other raw gums, such as guar gum (Cheng et al., 2020), were used as flocculation aids and presented good results. However, the polymeric solutions produced with carboxymethylated gum presented greater solubility and stability. This may represent benefits in relation to operating parameters in flocculation systems, being able to increase the pH range and coagulant concentration (Loganathan and Sankaran, 2021). Regarding the turbidity removal percentage, a significant difference was observed in the treatment system when carboxymethylated gum was incorporated, compared to the use of $Al_2(SO_4)_3$. Figure 5B shows the results generated using three polymer concentrations. The difference between the outcomes derived by the concentrations of modified polysaccharide added is quite subtle. However, the addition of a minimum applied dosage of the polymer (3 ppm) with 40 ppm of $Al_2(SO_4)_3$ was sufficient to reduce turbidity by 99.32%, obtaining 5.52 NTU of final turbidity, increasing efficiency, and reducing the amount of salt required at 20%, for the water samples to reach ideal conditions.

Studies showed that the reactivity of coagulant with polymer occurs through adsorption and neutralization, promoting the formation of larger and stable flocs with the probability of faster sedimentation (Dwari and Mishra, 2019). This finding suggests that the formation of large flocs is caused by the ability of the negative charges of the polymer to neutralize the charges of $Al_2(SO_4)_3$, allowing faster and more efficient sedimentation (Hu et al., 2013). Figure 6 exemplifies the effect of floc formation when carboxymethylated gum is used.

In the Jar Test analyses, a visual difference was noticed in the floc formation. Faster flocculation was observed with the addition of the modified polymer and with the formation of large flocs right after the slow agitation period. In contrast, when only $Al_2(SO_4)_3$ was used, visual flocculation occurred only at the final stage of the test. This difference in time may represent a reduction in energy costs in real treatment plants. However, further studies are needed to evaluate the efficiency resulting from the increased sedimentation rate.

Figure 7 shows this difference; in the first 30 seconds of sedimentation after slow agitation, the test containing the carboxymethylated gum already showed evidence of larger and denser flocs, indicating a rapid water clarification effect.

This notable improvement in flocculation effectiveness came from the considerable hydrodynamic volume of the polymer. The longer polymer chain allows for a larger interaction zone between the interface of the particles destabilized by $Al_2(SO_4)_3$ with the interface of the negative charges of the carboxymethylated polysaccharide (Banerjee et al., 2013).

Chua et al. (2020) studied the efficiency of sesbania seed gum (SSD) as a flocculant in the treatment of river water. The ideal conditions for application were 10.2 mg/L of coagulant and 4.25 mg/L of SSD as a flocculant. Despite that, the SSD extraction required several steps, such as acid extraction and heating at elevated temperatures. Mishra and Kundu (2019) extracted fenugreek gum and synthesized a polyacrylamide grafted derivative. The studies showed that only 1 mg/L is necessary to led a high efficiency in the process, which reduces the turbidity by 76.2%. The findings of Mishra and Kundu showed that the derivative does not present significantly efficient results in the treatment of river water, and the gum modification process is very expensive due to the various steps and the consumption of reagents, such as acrylamide, which is potentially carcinogenic.

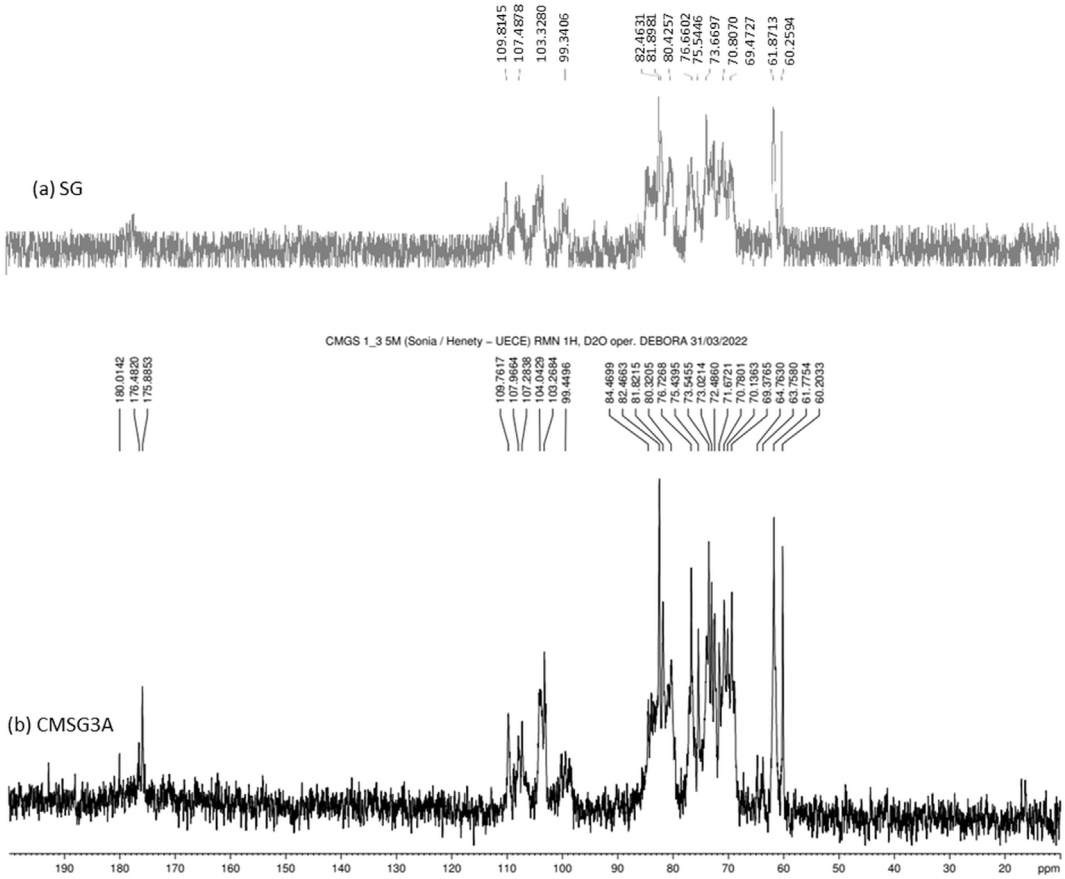


Figure 4 – 13C nuclear magnetic resonance spectrum of carboxymethylated samples with different degree of substitution, seriguela gum and CMSG3A.

Table 4 – Displacement values (ppm) for the carbons of the polysaccharide repeating units for the seriguela gum and carboxymethylated samples.

Unit	Carbon	SG	CMSG3A
β-Galactose	C-1	103.33	103.26
	C-2	70.81	70.78
	C-3	82.46	82.46
	C-4	69.47	69.37
	C-5	73.67	73.54
	C-6	61.87	61.77
β-Glucuronic acid (4-O-methyl-glucuronic acid)	C-1	99.34	99.44
	C-2	75.54	75.43
	C-3	76.66	76.72
	C-4	-	-
	C-5	-	-
	C-6	-	-
Carboxymethyl group	-COO-	-	175.8/176.5/ 180.01
	-CH2-	-	72.48/73.02

SG: seriguela gum; CMSG: carboxymethyl seriguela gum.

In summary, SG derivatives demonstrated high efficiency in turbidity reduction when combined with aluminum sulfate. They required fewer purification and synthesis steps compared to other gum-based flocculants and demonstrated efficacy at lower dosages, highlighting their potential as a cost-effective flocculant. In addition, although SG is a less investigated material, it has high potential to develop new other derivatives with different functional groups and molecular weights to make the process more efficient. Other studies presented carboxymethylated materials as flocculants, also aiding in the removal of metals (Zhang et al., 2024) and dyes (Guan et al., 2021; Zhang et al., 2023).

Toxicity testing

The toxicity test indicated promising results regarding the biocompatibility of CMSG. The resistance of *A. salina* was evaluated by the positive control, in which none survived in contact with potassium dichromate ($K_2Cr_3O_7$). In the negative control, all 10 *A. salina* survived, obtaining a lethality rate of 0%. In the test, there was no significant increase in the toxicity of saline water with the concentrations of SG and CMSG5A. This behavior demonstrates that the use of a biodegradable bioflocculant does not provide a toxic effect in the system to be treated. The observed lethality did not exceed 50% for any of the samples, with maximum values of 16.0% for SG and 13.3% for CMSG5A, only at concentrations of 100 mg/L. Considering that this concentration is not necessary for the efficiency of the process and that a large part of the biopolymer is sedimented in the flocculation step, we can state that

SG does not present any risk of ecotoxicity in aquatic environments that use this material as a flocculant. Furthermore, studies show that applying a natural flocculant associated with $Al_2(SO_4)_3$ reduces toxicity in models of brine shrimp (Freitas et al., 2016).

Assessment of operating costs

To evaluate the operational costs of the studied processes, commercial values from Brazilian e-commerce were used, following Schmitt at al.'s (2021) comparison methodology. Since SG is not a commercially

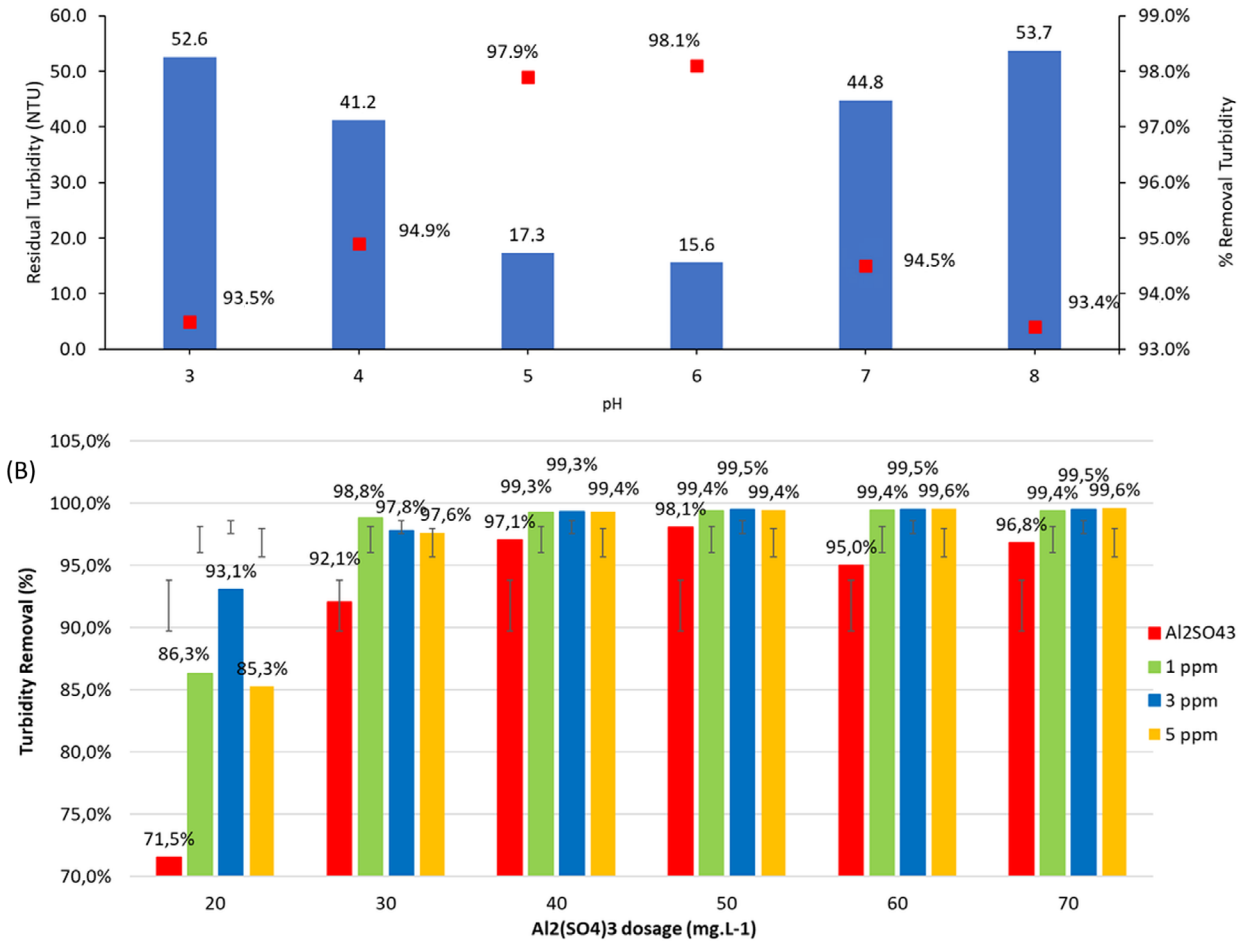


Figure 5 – (A) Residual turbidity and %turbidity removal from contaminated water as a function of pH using aluminum sulfate (50 mg/L); (B) Residual turbidity as a function of aluminum sulfate dosage and effect of CMSG5A addition as an aid flocculant.

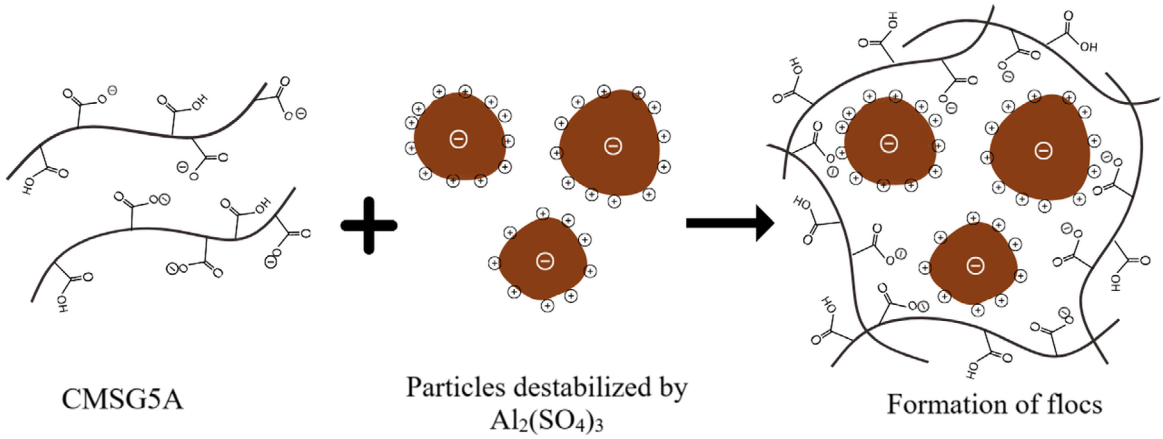


Figure 6 – Process of formation of flocs from the addition of carboxymethylated gum to particles destabilized by aluminum sulfate ($Al_2(SO_4)_3$).

consolidated material, a reference value of R$97.08 was used for guar gum, which is a biopolymer with similar process, and for $Al_2(SO_4)_3$, a value of R$58.80 was considered. Figure 8 shows a flowchart of the processes employed in the synthesis of this biopolymer. It is important to consider that the laboratory-scale process presents a higher cost than $Al_2(SO_4)_3$ alone. However, modified polysaccharides are already widely commercialized at prices similar to that of guar gum, demonstrating that the industry has established processes that reduce the manufacturing cost of this type of material.

Then, by conducting a comparative cost analysis based on price per kilogram, it was observed that for the same amount of $Al_2(SO_4)_3$ (30 mg/L), there was an increase in turbidity removal efficiency of approximately 7.0% when 1 mg/L of CMSG5A was used. This represents a cost-effective option, as a small amount of polymer can maintain the overall cost while increasing efficiency. Furthermore, an eco-friendly alternative was achieved by using 3 mg/L of CMSG5A and 20 mg/L of $Al_2(SO_4)_3$, since this not only reduces the cost but also decreases the amount of residual aluminum in the water and in the sludge generated by the flocculation process. Figure 5 shows that to achieve a removal efficiency of 98.0%, corresponding to the ideal $Al_2(SO_4)_3$ concentration of 50, 30 and 1 mg/L of CMSG5A are required. Thus, Table 5 presents the prices that justify the savings caused by the polymer, where a small amount of gum can provide the treatment process with a 36.4% reduction in input costs. Furthermore, the reduction in aluminum concentration and the increase in biodegradable organic load in the sludge can help reduce treatment plant costs, in addition to positively impacting the disposal of waste from these facilities.

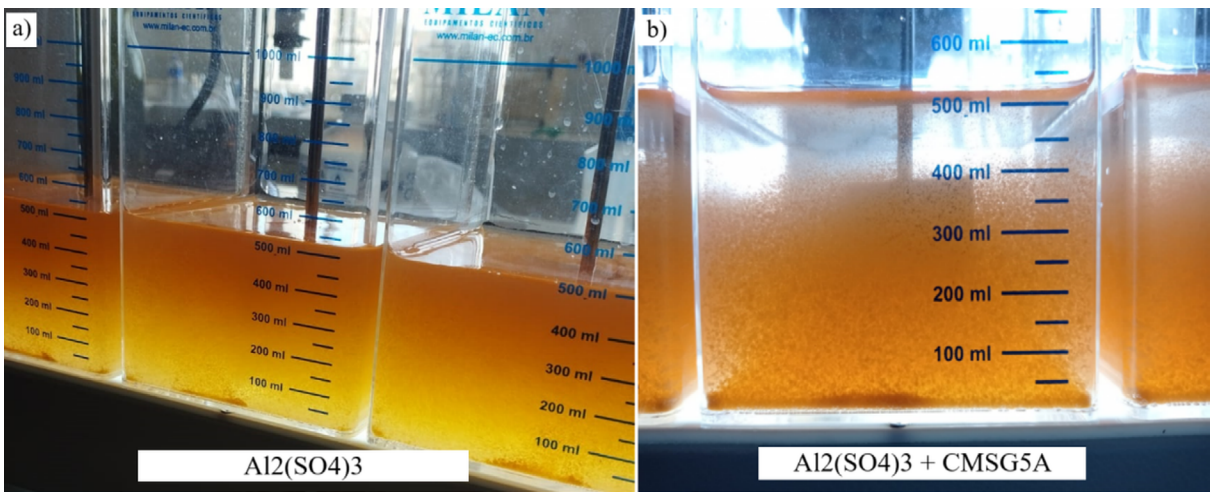


Figure 7 – Comparison of floc formation in the sedimentation process between the treatment using only aluminum sulfate (A) and that with the addition of CMSG5A (B).

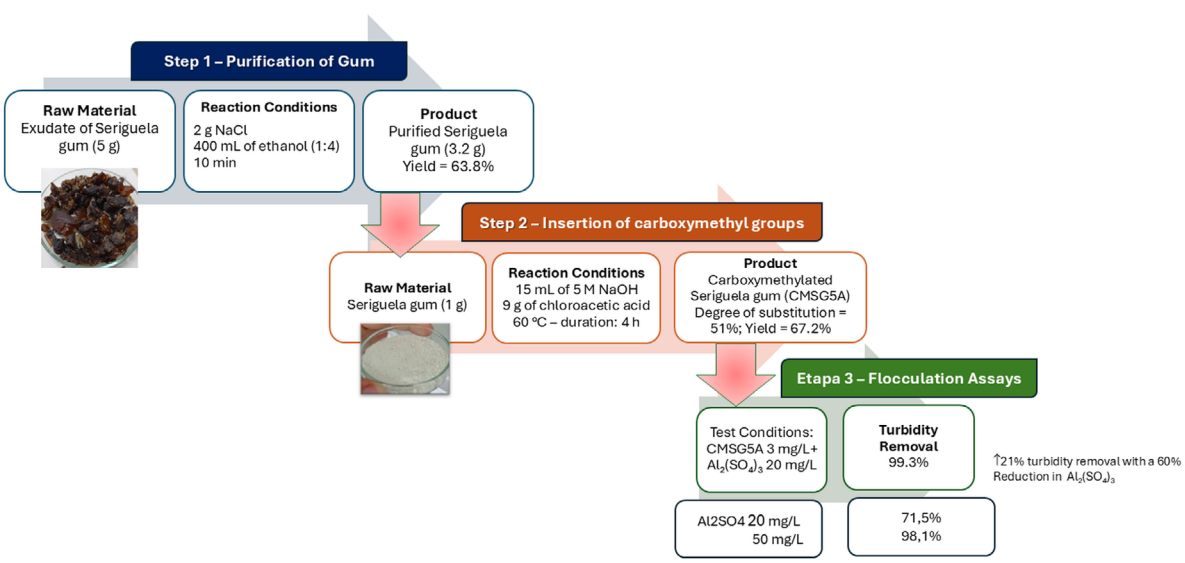


Figure 8 – Flowchart of the process containing operating parameters and results obtained in the production of the flocculation aid.

Table 5 – Comparison of costs associated with the treatment process using CMSG5A as a flocculation aid.

	$Al_2(SO_4)_3$		30 mg/L $Al_2(SO_4)_3$ + 1 mg/L CMSG5A
	30 mg/L	50 mg/L	
Removal turbidity (%)	92.00	98.10	98.78
Price/kg (R$)	1.76	2.94	1.87
Cost/m^3	0.053	0.147	0.057

$Al_2(SO_4)_3$; aluminum sulfate; CMSG: carboxymethyl seriguela gum.

Conclusions

Extraction and purification of *S. purpurea* exudate was successfully achieved in a simple high-yield process, being a viable alternative polysaccharide. Carboxymethylation of the gum was increased using lower levels of NaOH and intermediate-low levels of chloroacetic acid, resulting in a higher DS. Carboxymethylated gums had reduced molecular weight and greater solubility, making them more versatile for pH range and coagulant concentration in flocculation systems. The addition of 3 mg/L of CMSG combined with $Al_2(SO_4)_3$ was able to significantly reduce (in 60.0%) the required dosage of $Al_2(SO_4)_3$ for the flocculation process, without water filtration. The study also showed that the material could also reduce residual turbidity reaching an efficiency of up to 99.6%, achieving acceptable levels of the Brazilian, Chilean, Canadian, and American legislation (5.0 NTU, considering a system without filtration) compared to only the metallic coagulant. The toxicity tests showed that derivatives have low toxicity in *A. salina*—an advantage due to its low toxicity and eco-friendly properties—which leads to the capacity to reduce the pollutant charge in this step of water treatment. In this way, reducing inputs and operational costs by around 36.0%, and adding commercial value to the native species of Brazil, whose application was not previously published in studies, the material obtained appears innovative and promising for application as a flocculation aid in water treatment plants.

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Authors' contributions:

Abreu, F.: conceptualization, resources, formal analysis, software, writing – review & editing, supervision. **Pinheiro**, H. N.: conceptualization, data curation, formal analysis, investigation, methodology, project administration, resources, software, validation, visualization, writing – original draft. **Almeida**, J. L. I. O.: methodology, writing – review & editing. **Veloso**, F. F.: data curation, investigation.

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