

**STUDY OF THE  
INFLUENCE OF  
CHLOROACETIC  
ACID CONTENT ON  
THE DEGREE OF  
CARBOXYMETHYLATION  
OF XANTHAN GUM FOR  
LEAD ADSORPTION**

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**Abstract:** Xanthan gum (GX) is a natural polysaccharide with adsorption capacity, with potential application for water decontamination. In this work, the GX was modified by carboxymethylation, testing the influence of the relative content of chloroacetic acid in relation to the gum. The FTIR and <sup>1</sup>H NMR results showed the insertion of carboxymethyl groups through the appearance of characteristic peaks in the respective spectra. The degree of substitution of the samples GXC 05:01 and GXC 07:01 were, respectively, 0.61 and 1.25. The adsorption tests revealed that the carboxymethylation resulted in greater adsorption of lead in relation to the unmodified gum, and the GXC 07:01 sample showed a higher adsorption rate in relation to the others, removing 90% of the metal ion in solution. Thus, carboxymethylated xanthan gum proved to be a promising material for adsorption of lead ions.

**Keywords:** Adsorption of metals, polysaccharides, structural modification, xanthan gum.

## INTRODUCTION

Xanthan gum is a polysaccharide produced by bacteria of the genus *Xanthomonas*, being a by-product of the fermentation of residues from dairy industries (Diniz, Druzian, Audibert, 2012, p. 278). According to Lima et al. (2001), xanthan gum is a poly-B-(1,4) -D-glucopyranose very similar to cellulose, has alternate branches at C-3 positions and has a high molecular weight, which reflects in a high viscosity even at low concentrations (Lima et al., 2001). It is a non-toxic polysaccharide, being widely used in the food industry to control the viscosity, retention of aromas and texture of foods due to its high stability at different pH's and different temperatures (Lima et al., 2001; Silva, Druzian, 2014), p. 5527).

Depending on the desired application of xanthan gum, structural modifications can be made in order to evidence or inhibit some of these properties (Vieira, 2012). The carboxymethylation reaction aims to obtain polysaccharide derivatives with greater solubility in a wide pH range, increase the interaction with several substances for the formation of polyelectrolytic complexes, form biocompatible derivatives that have low toxicity in human cells and increase the negative surface charge of the material, thus facilitating the interaction with toxic metal ions (Anitha et al., 2009, p. 672).

The modification of polysaccharides by carboxymethylation is a method widely used to obtain functional derivatives with different characteristics, as it has a great advantage in terms of low cost and for generating products with low toxicity (Abreu et al., 2009, p. 1267). The carboxymethylated derivatives have been extensively studied regarding their possible bactericidal and fungicidal action for application in agriculture, as well as in the bioremediation of contaminated systems, since the insertion of carboxylic groups with a negative charge can increase the adsorptive capacity of metals due to an increase in the capacity of interaction with ions in solution (Abreu, Campana-Filho, 2005, p.79; Pillai, Paul, Sharma, 2009, p.641; Wang et al., 2012, p.354; Yahoum, Moulai-Mostefa, Le Cerf, 2016, p. 267).

Toxic metals do not degrade easily and can accumulate in sediments and the aquatic environment. Its removal by adsorption can be a more attractive method, as it can be presented in a lower cost strategy, provided that alternative adsorbent materials are found that are efficient (Abreu et al., 2018, p.231). Among the most abundant toxic metal ions in industrial effluents, lead stands out, as the metal is present in automotive batteries, industrial pigments and roof coatings due

to its resistance to corrosion. Lead metal is poorly soluble in water, but at lower pH, with increasing acidity, there is an increase in its solubility, thus facilitating its dissipation in the aquatic environment (WHO, 2011). Once absorbed by the body, it bioaccumulates and has a low rate of excretion, thus preventing the metabolism of calcium, iron and zinc in the body, which increases the concentration of the metal in the blood, bones, liver and marrow (Wang et al, 2011, p.354).

The present work aimed to chemically modify the structure of xanthan gum by carboxymethylation, studying the influence of the relative content of chloroacetic acid on the degree of substitution of xanthan gum, to characterize the material in relation to its degree of substitution, infrared and NMR, and to evaluate its ability as a lead adsorbent at different pHs.

## MATERIALS AND METHODS

Xanthan gum was used for the carboxymethylation reaction (scientific exodus, purity 91%), acid monochloroacetic (dynamics), Sodium hydroxide (cromoline), hydrochloric acid (cromoline), álcool Etilíco 96% (neon) e Methyl alcohol (neon).

## SYNTHESIS OF DERIVATIVES CARBOXYMETHYLATED

The carboxymethylated derivatives were modified using the methodology proposed by Abreu et al. (2009), with few adaptations (Abreu et al., 2009, 1267). In a 250 mL beaker, 5.6 g of xanthan gum were suspended in 100 mL of ethyl alcohol, keeping the system under stirring, where 25 mL of 5 mols. L-1 NaOH were gradually added and the system was kept under stirring for 30 minutes. After this period, monochloroacetic acid was added in 5:1 and 7:1 acid:gum proportions and the reaction mixture was heated at 50 °C for 4 hours. Subsequently, the reaction system

was filtered, the polysaccharide was washed with methyl alcohol and dried in an oven at 60°C. Considering the repetitive unit of xanthan gum as the glucose (180g/mol) and chloroacetic acid (94.5g/mol).

## SPECTROSCOPY IN THE INFRARED REGION

Infrared spectra were obtained using a Thermo Scientific spectrometer, model Nicolet is5. The samples were prepared with KBr pellets in the proportion 1:20 (m/m) (Sample:KBr) and the spectra were recorded in the range of 4000 to 400 cm<sup>-1</sup> with a resolution of 32 scans.

## NUCLEAR MAGNETIC RESONANCE (RMN)

<sup>1</sup>H NMR analysis was performed to verify the modification of the xanthan gum sample. Were dissolved 3 mg gives sample in D<sub>2</sub>O and subsequently analyzed in a 400MHz Bruker Ascend NMR spectrometer.

## POTENTIOMETRIC TITRATION

To determine the degree of substitution (GS) by potentiometric titration, the methodology adapted from Somensi (2014) and Abreu et al. (2009) was used (Somensi, 2014; Abreu et al., 2009, p.1267). About 0.2000 g of GXC was solubilized in 100 mL of water. The mixture was acidified with 0.1 mol.L<sup>-1</sup> HCl until pH equal to 2. Then, the mixture was titrated with 0.1 mol. L<sup>-1</sup> NaOH, recording the addition of base volume as a function of pH using A pH meter with glass electrode model Luca-210 is used. The GS was calculated based on equations 1 and 2 (Abreu et al., 2009, p. 1267):

$$A = \frac{C_{NaOH} \cdot 58 \cdot (V_2 - V_1)_{NaOH} \cdot 100}{m_{CGX}} \quad (1)$$

$$DS = \frac{A \cdot 180}{(180 - A) \cdot 58} \quad (2)$$

Being:  $C_{\text{NaOH}}$  is the concentration of NaOH (mol/L);  $V_1$  is the volume of NaOH expense to own the GX;  $V_2$  is the spent volume of NaOH spent to titrate the GXC;  $m_{\text{CGX}}$  is the mass of the sample; 180 and 58g/mol are respectively, the molar mass of xanthan gum and the molar mass of the carboxymethyl group.

## STUDIES OF ADSORPTION

The effect of contact time and adsorption kinetics were evaluated for the carboxymethylated samples and the pure gum in acidic medium (pH=5). For this, 100 mg of the samples were added to 100 mL of lead nitrate solution at concentrations of 100 and 200 ppm. The solution was kept under continuous stirring on a magnetic stirrer where 2mL aliquots were taken in duplicate and filtered through a syringe filter at time intervals of 5, 10, 20, 30, 40, 50, and 60 minutes. The residual concentration of lead ions was determined using a flame atomic absorption spectrophotometer. The calculations were performed using the calibration curve shown in equation 3.

$$y = 0.0239x + 0.0007 \quad R^2 = 0.9986 \quad (3)$$

To verify the adequacy of the reaction kinetics, the pseudo-first order (equation 4), pseudo-second order (equation 5) and intraparticle diffusion (equation 6) models were evaluated, which are represented below:

$$(q_e - q_t) = \ln q_e - K_1 t \quad (4)$$

And:  $K_1$  ( $\text{min}^{-1}$ ) the pseudo-first order kinetic constant;  $q_e$  e  $q_t$  ( $\text{mg.g}^{-1}$ ) represent the amount of adsorbate adsorbed at equilibrium and in a given time, respectively. To evaluate the model, a graph of  $\ln(q_e - q_t)$  is plotted as a function of time.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \quad (5)$$

And:  $K_2$  ( $\text{g}^{-1} \cdot \text{min}^{-1}$ ) the pseudo second order kinetic constant. The evaluation of the model is carried out by the construction of a graph of  $t/q_t$  as a function of time.

$$q_t = K_{id} t^{0.5} + C \quad (6)$$

Sendo  $K_{id}$ : the intraparticle diffusion constant and  $C$  a constant that can be determined by constructing a graph of  $q_t$  versus time.

## RESULTS AND DISCUSSION

### DEGREE OF SUBSTITUTION

The degree of substitution represents the average number of carboxymethyl functional groups that were introduced into the monomeric unit of the polysaccharide, being an important factor for evaluating the influence of the studied reaction conditions. The degree of substitution was determined by potentiometric titration of the carboxymethylation gums and the pure gum, used as a blank (Somensi, 2014).

It was observed that the degree of substitution of the GXC 05:01 sample was 0.61, thus the substitution occurred in about 61% of a hydroxyl site present in the xanthan gum structure. In the GXC 07:01 sample, a GS of 1.25 was obtained, constituting the highest degree of substitution. In this case, it is assumed that there was a complete replacement of a hydroxyl site present in the repeating unit of the gum, and still 25% replacement in another hydroxyl site of the polysaccharide structure. The degree of carboxymethylation found for xanthan gum was higher than previous studies that used another type of polysaccharide (Somensi, 2014; Heinze, Koschiella, 2005, p.13; Stojanovic et al., 2005, p. 79; Liu et al., 2014, p. 42). In the work by Somensi (2014), a reaction time of 8 hours was used at a temperature of 50 °C with an acid:polysaccharide ratio of

12:1 (m:m) and the DS obtained was 1.27, comparable to the GXC7 sample, however, requiring a much larger amount of acid (Somensi, 2014).

### SPECTRUM OF INFRA-RED

Fourier transform infrared spectroscopy (FTIR) analysis was performed in order to prove the modification of xanthan gum by carboxymethylation through the appearance of characteristic bands of the carboxymethyl groups. The spectra are shown in figure 1.

In pure xanthan gum (GX), it is possible to observe the characteristic peaks: in the region of  $1080\text{ cm}^{-1}$ , referring to the asymmetric stretching of the C-O-C bond, the peak at approximately  $1700\text{ cm}^{-1}$  referring

to the stretching of the COO- and CO bond of esters alkyl and at  $3300\text{ cm}^{-1}$  there is the O-H stretch. The carboxymethylated gum samples show a peak broadening in the region at approximately  $1100\text{ cm}^{-1}$  referring to the C-O-C stretching of the ether that was inserted in the structure as a function of the carboxymethylation reaction, as well as the peak at  $1320\text{ cm}^{-1}$  which is attributed to the stretching C-O, as well as at  $1600\text{ cm}^{-1}$  referring to the C=O stretching of the inserted carboxymethyl groups. It is also observed in the GXC 07:01 sample the decrease in the intensity of the peak referring to the O-H stretch and the increase in the intensity of the peaks referring to the C=O and C-O stretch, which corroborates the indication of

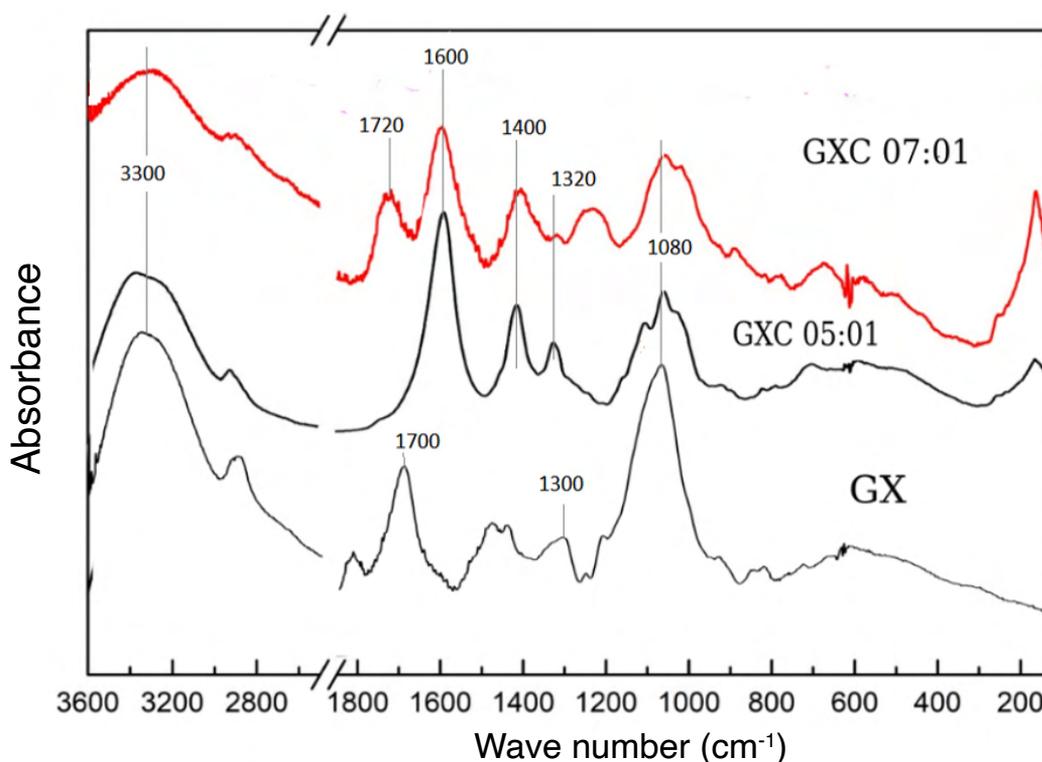


Figure 1: Infrared spectra of pure xanthan gum (GX), and 5:1 (GXC5) and 7:1 (GXC7) carboxymethylated xanthan gum.

Legenda: GX se refere a goma xantana; GXC 05:01 a goma xantana carboximetilada na proporção 05:01, acido:goma e GXC 07:01 a goma xantana carboximetilada na proporção 07:01, acido:goma.

Fonte: Elaborado pelo autor.

a higher degree of than that obtained for the sample GXC 05:01 (Matos, 2020).

### SPECTRA OF RMN OF $^1\text{H}$

The spectra obtained for the pure gum and for the carboxymethylated gums are shown in figure 2.

In the GX spectrum, it is possible to observe the characteristic peaks of its structure in the region 4.90 ppm attributed to the hydrogen bonded to the C1 of the polymeric chain, a peak at 3.88 ppm that refers to the methylene proton of the group  $\text{CH}_2\text{-COOH}$  of the glucuronic acid present. The peaks in the region between 1.18 and 2.0 ppm can be attributed respectively to the presence of acetate and pyruvate groups. (Makhado *et al.*, 2017, p. 315; Hu *et al.*, 2019, p. 730). for the samples GX5 and GX7 it is possible to observe the characteristic peaks of the insertion of carboxymethyl groups in the region of 3.83-389 ppm, which corresponds to the methylene proton of the group  $\text{CH}_2\text{-O-CH}_2$ . It is also observed in the region of 4.00 ppm the peak that is attributed to the methylene proton of the group  $\text{CH}_2\text{-COOH}$  from the insertion of the carboxymethyl group (Maity; Sa, 2014, p.78). In the spectra of all samples, it is possible to observe the presence of the peak in the region of 4.70 ppm, which is attributed to the peak of the anomeric proton superimposed on the peak of the solvent ( $\text{D}_2\text{O}$ ) used in the analysis (Maity; Sa, 2014, p.78; Hu *et al.*, 2019, p.730).

### CONTACT TIME EFFECT

Figure 3 shows the results obtained in the adsorption tests using the modified samples and the pure gum, where it is possible to observe the profile of the adsorption rate of lead ions as a function of time. For this test, samples of GXC5 and GXC7 were selected because they have, respectively, the lowest and highest GS.

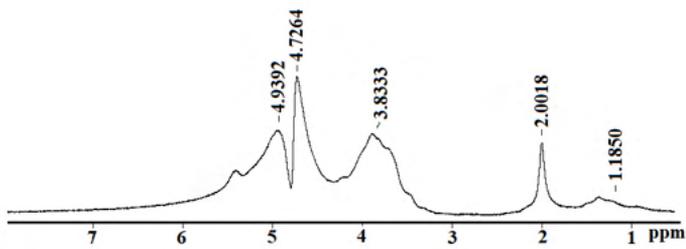
Analyzing the figure, it is observed that there is a tendency for an increase in the adsorption capacity when the carboxymethyl groups are inserted into the polymer chain, as observed for the GXC7 sample, which obtained a maximum adsorption of about 90%, while for in the GXC5 sample, the maximum adsorption was on the order of 35%. Both samples showed a low equilibrium time, which was around 20 minutes. In the studies carried out by Almeida *et al.* (2020), using carboxymethylated chitosan for the adsorption of cadmium ions, it was also possible to observe this tendency to increase the removal of ions with GS, since the increase in the amount of carboxymethyl groups in the polymer chain increases the number of sites that can adsorb metal ions (Borsagli *et al.*, 2015, p. 34).

The equilibrium time obtained was shorter than that presented by other materials present in the literature that involved several steps of synthesis, as is the case of chitosan spheres with polyvinyl alcohol that required 500 minutes to reach equilibrium (Jin, Bai, 2002), p. 9765), of carboxymethyl chitosan cross-linked with glutaraldehyde which required 15 hours to reach equilibrium (Sun, Wang, Wang, 2006, p. 930).

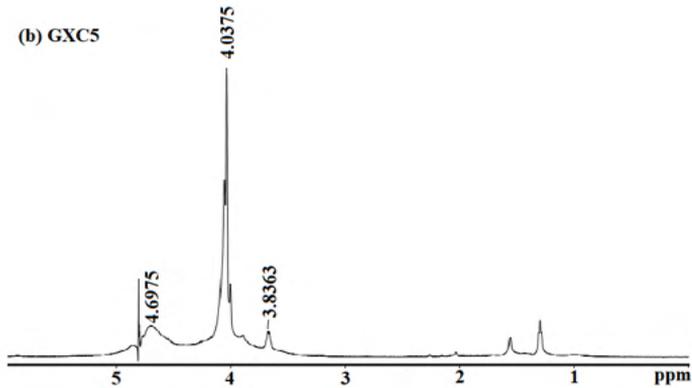
In a complementary study, the  $\text{Pb}^{+2}$  ion adsorption test at pH 5 was performed for the GXC 07:01 samples and the unmodified Xanthan Gum, in order to compare the performance at two different analyte concentrations (100ppm and 200ppm). The results are shown in figure 4.

Xanthan gum had a similar adsorption percentage for concentrations of 100 and 200 ppm with some fluctuations in adsorbed concentrations, with an average adsorption of 40%. The GXC 07:01 sample showed adsorption superior to xanthan gum and dependent on the concentration of  $\text{Pb}^{+2}$  ions in the solution. The GXC 7:1 sample had a

(a) GX



(b) GXC5



(c) GXC7

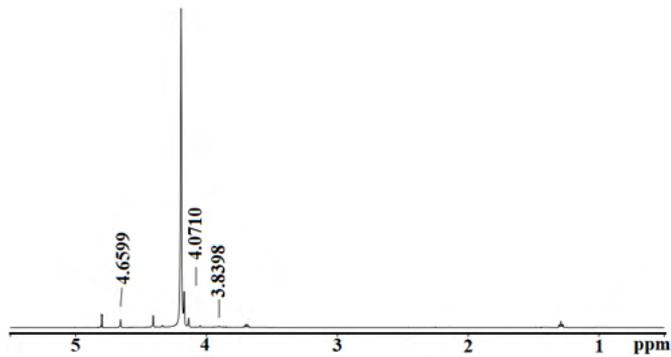


Figure 2: Spectra of RMN of the samples of (a) GX, (b) GXC5 e (c) GXC7.

Subtitle: GX refers to xanthan gum; GXC 05:01 to carboxymethylated xanthan gum in the ratio 05:01, acid:gum and GXC 07:01 to carboxymethylated xanthan gum in the ratio 07:01, acid:gum

Source: Prepared by the author.

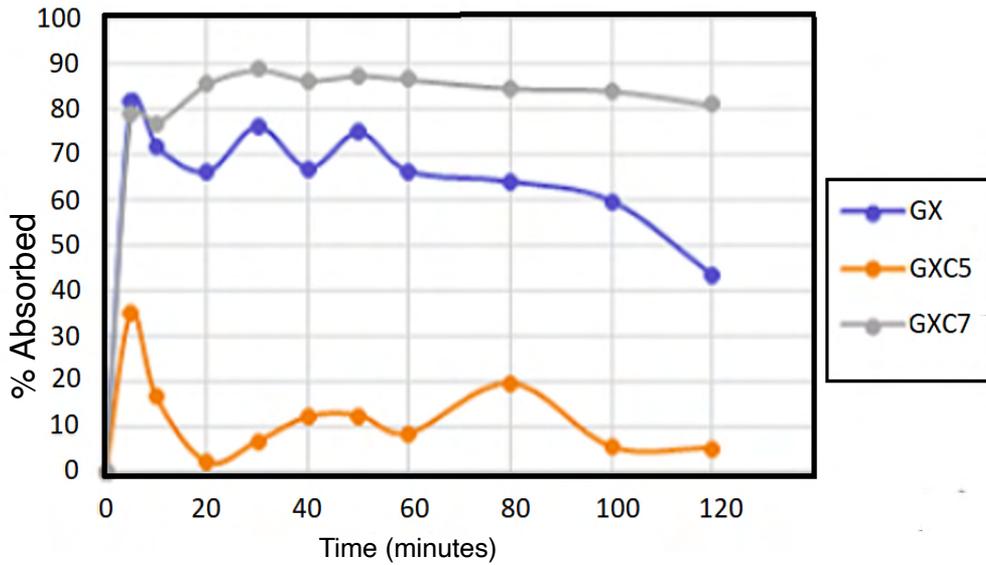
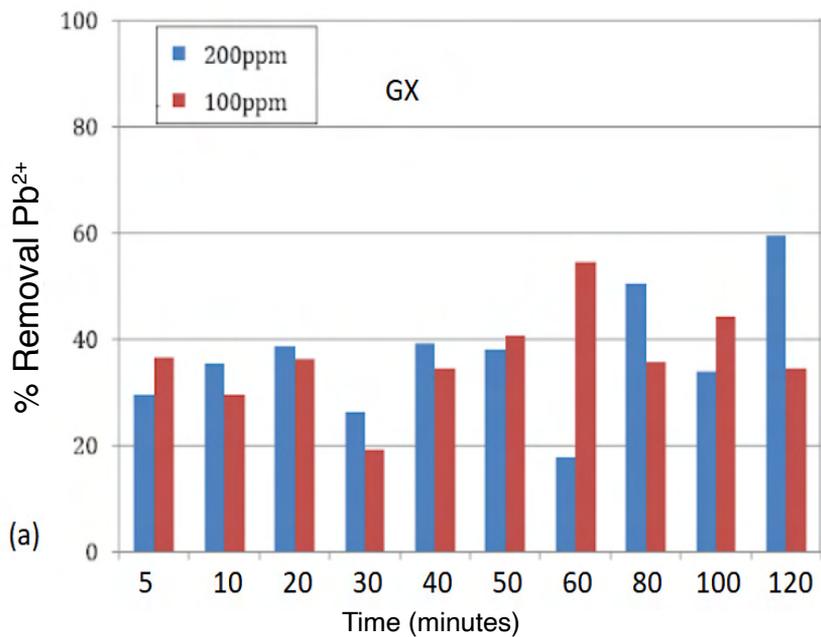


Figure 3 – Percentage of adsorption as a function of time at pH 5 for samples (a) GX, (b) GXC5 e (c) GXC7  
 Subtitle: GX refers to xanthan gum; GXC 05:01 to carboxymethylated xanthan gum in the ratio 05:01, acid:gum and GXC 07:01 to carboxymethylated xanthan gum in the ratio 07:01, acid:gum.

Source: Prepared by the author.



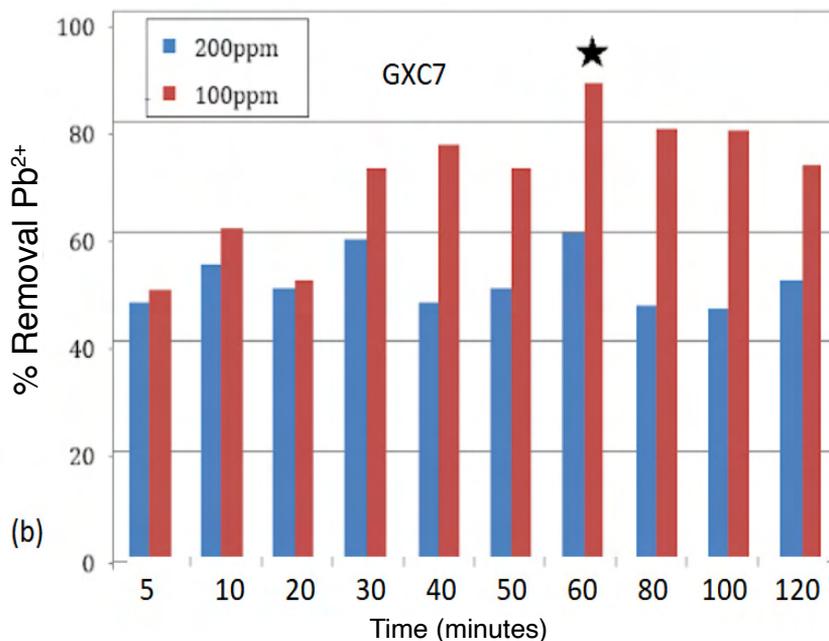


Figure 4 – Effect of ion concentration Pb<sup>2+</sup> in the adsorption capacity in pH 5 for the samples GX e GXC7  
 Subtitle: GX refers to xanthan gum; GXC 05:01 and GXC 07:01 the carboxymethylated xanthan gum in the ratio 07:01, acid:gum.

Source: Prepared by the author.

Kinetic Model	Parameters	Values
Pseudo 1 <sup>a</sup> order	$q_e$ (mg.g <sup>-1</sup> )	1,733
	$K_1$ (min <sup>-1</sup> )	0,0032
	$R^2$	0,0574
Pseudo 2nd order	$q_e$ (mg.g <sup>-1</sup> )	97,08
	$K_2$ (g.mg <sup>-1</sup> min <sup>-1</sup> )	1,06.10 <sup>-4</sup>
	$R^2$	0,9843
Intraparticle Diffusion	C	104,69
	$K_{id}$ (mg.(g.min <sup>-0.5</sup> ) <sup>-1</sup> )	-0,4098
	$R^2$	0,0139

Table1 – Kinetic parameters of adsorption of Pb<sup>2+</sup>

Source: Prepared by the author.

maximum adsorption of 85% of ions  $Pb^{+2}$  at a concentration of 100 ppm after 1 hour of testing, while at a concentration of 200 ppm its maximum was 60%. The carboxymethylated material proved to be more effective than xanthan gum at the two tested concentrations of ions  $Pb^{+2}$ .

### KINETICS OF ADSORPTION

The GXC7 sample was selected for evaluation of the kinetic model, as it showed the highest percentage of lead ion removal when compared to the others. Table 2 shows the  $R_2$  values for the models analyzed for the three samples.

For the analyzed sample, it is possible to observe that the pseudo second order model was the best suited to describe the kinetics of the process, as it has a value of  $R^2$  above 0.98, which suggests that the rate-determining step occurs by chemisorption, which occurs through the interaction of the different functional groups present in the polysaccharide with the residual metal ions. Other studies using carboxymethylated polysaccharides also found pseudo-second order kinetics to be the best fit (Almeida et al., 2020, p. 53657; Sun, Wang, Wang, 2006, p. 930).

### CONCLUSIONS

Carboxymethylation of xanthan gum was performed with different proportions of monochloroacetic acid to enable its use as adsorbent for lead ions. The materials were successfully synthesized, being confirmed by the degree of substitution of the material, particularly the GXC7 sample whose value was greater than 1.0, corroborated by the appearance of peaks in the region of 1320 and  $1600\text{cm}^{-1}$  referring to the presence of carboxymethyl groups. The appearance of peaks in the region of 3.80 ppm and 4.00 ppm in the  $^1\text{H}$  NMR spectra also

corroborate the confirmation of the insertion of carboxymethyl groups. The GX obtained an adsorption percentage of 35%, partially adapting to the pseudo first order and pseudo second order model, and it is noteworthy that under the same conditions, the GXC7 sample presented a remarkable performance, adsorbing 90% on the metal ion in solution in pH 5, which may be associated with an increase in the percentage of adsorption by chemisorption, due to pseudo-second order kinetics, between the carboxymethylated sites with lead ions, in addition to the fact that the samples showed a higher rate of adsorption at the initial concentration of ions of 100 ppm. Therefore, it is concluded that the insertion of carboxymethyl groups in the polymer chain increases the adsorption capacity of polysaccharides that can act as excellent adsorbents of metals in water treatment.

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