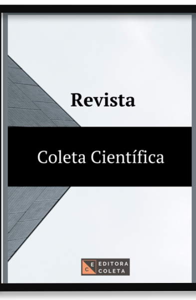

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COMPARISON OF CHITOSAN SULFATION METHODS FOR CU^{2} ADSORPTION^{+}

COMPARAÇÃO DE MÉTODOS DE SULFATAÇÃO DA QUITOSANA PARA ADSORÇÃO DE CU^{2+}

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ABSTRACT[1]

Chitosan is a polysaccharide that has free amine and hydroxyl groups, which is considered a good adsorbent material for heavy metals in contaminated water. In order to improve this property, some necessary modifications have been proposed in order to increase the adsorptive capacity of this polysaccharide. The objective of this work was to modify the structure of chitosan and carboxymethyl chitosan by sulfation, to characterize the materials synthesized through yield, by FT-IR and to analyze elementary and evaluate an adsorbent capacity of the materials against copper ions. The results attenuated that the reaction yield of the materials varied from 58% to 91%, and it was possible to identify through FT-IR the required groups C-O-S and S = O regarding the insertion of the sultate groups, identifying the presence of the sulfate groups in the structure. In adsorption tests, as sulphates sulphated over a percentage of adsorption above 90% copper, a performance superior to pure chitosan (%). The adsorptive capacity of 63 mg / g, in relation to the results found in the literature. Thus, it was observed that sulfation is a viable modification route for adsorption of metals.

KEYWORDS: *Adsorption. Sulfation. Copper.*

RESUMO

A quitosana é um polissacarídeo que possui grupamentos amina e hidroxila livre, sendo essa considerada um bom material adsorvente de metais pesados em águas contaminadas. Afim de melhorar essa propriedade algumas modificações estruturais têm sido propostas a fim de aumentar a capacidade adsortiva deste polissacarídeo. O objetivo deste trabalho foi modificar por sulfatação a estrutura da quitosana e da carboximetilquitosana, caracterizar os materiais sintetizados através de rendimento, por FT-IR e análise elementar e avaliar a capacidade adsorvente dos materiais frente a íons cobre. Os resultados mostraram que o rendimento reacional dos materiais variou de 58% a 91%, e foi possível identificar

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[1]Article from the Annals of the I Symposium on Environment and Energy (I SiMAE) – Fortaleza, CE

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através de FT-IR os grupos funcionais C-O-S e S=O referentes à inserção dos grupos sulfatos, identificando a presença dos grupos sulfato na estrutura. Nos ensaios de adsorção, as amostras sulfatadas apresentaram um percentual de adsorção acima de 90% de cobre, um desempenho superior à quitosana pura (%).A capacidade adsortiva foi de 63 mg/g, comparado aos resultados presentes na literatura. Desta forma, observou-se que a sulfatação é uma rota viável de modificação para a adsorção de metais.

PALAVRAS-CHAVE: Adsorção. Sulfatação. Cobre.

1. INTRODUCTION

Water is one of the most essential resources for life on earth, where studies and research on sustainable methods to increase freshwater quality through the decontamination of water beds have been reported (DESBRIERES; GUIBAL, 2018). Adsorption is one of the proposals that has several advantages, as it manages to remove both organic and inorganic pollutants and in addition to producing a low amount of waste (SPINELLI *et al.,* 2005). Among the adsorbent materials, polysaccharides have stood out, because in addition to having a high efficiency, they are also economically viable, biocompatible , biodegradable and non-toxic materials. (ARAMWIT; YAMDECH; AMPAWONG, 2016). Chitosan is a polysaccharide derived from chitin, found in great abundance in nature in crustacean shells that have good adsorptive potential (JIANG et *al.* , 2014). In recent years, modifications have been proposed in the structure of chitosan in order to increase its adsorptive capacity , as it has free amine and hydroxyl groups , which facilitates the entry of new groups (VAKILI *et al.* , 2014). Sulfation is a modification used that makes the structure of polysaccharides with a negative surface charge, which facilitates their adsorbing action through a complexation mechanism with metal ions that have a positive surface charge (SILVA, 2012). Copper is a heavy metal widely used in the electroplating industry due to its high conductivity and one of the components of some fungicides. Due to its applicability, due to improper handling or disposal, it can be found as a pollutant in high concentrations in soil and water (ANDREAZZA *et al.* , 2010). Thus, the objective of this work was to develop sulfated functional derivatives from chitosan and carboxymethylchitosan , in order to test their adsorptive capacity against copper.

2. Materials and methods

2.1 - Materials

Chitosan (Polymar), acetic acid (dynamic), monochloroacetic acid (dynamic), sodium hydroxide (cromoline), isopropyl alcohol (neon), methyl alcohol (neon), sodium bisulfite (synth), sodium (synth) and sodium sulfate (vetec .

2.2 Synthesis of sulfated chitosan

Two types of sulfation reaction were carried out on the original chitosan and on the chitosan carboxymethylated ; The carboxymethyl chitosan was synthesized in a previous work according to the methodology described in ABREU, 2008. In the first sulfation method, a sulfating agent was used where 10 mL of a 3.1% m/v $NaHSO_3$ solution $_3$ was added to a solution of 3.1% $_m$/v. The mixture, which acts as a surfactant,

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was stirred for 90 min at 60°C. The pH of the solution was corrected to 9.0 with NaOH or HCl . Then , 0.5 g of pure QT or carboxymethyl chitosan was added to the sulfating agent , leaving it under magnetic stirring for 4 h at 40°C. Finally, the supernatant was centrifuged and discarded and the precipitate was washed with distilled water and dried at 60°C in an oven. in the second method of sulfation sodium sulfate was used. 3 g of chitosan or carboxymethyl chitosan were added to 100 ml of 3% acetic acid and allowed to stir until homogenized. 100mL of 4 % sodium sulfate was added to the solution under stirring for 90 min. The precipitate was then centrifuged at 4000 RPM, washed and lyophilized.

2.3 - Characterizations

Four types of bioadsorbent materials were synthesized and these functional derivatives were characterized by infrared spectroscopy (Thermo Scientific with KBr tablets) to evaluate functional groups, as well as to indicate the synthesis reaction, an elemental analysis was also carried out to prove the presence of sulfur in the modified polysaccharide structure and to calculate the degree of substitution through the equation 1. (PAIVA JUNIOR, 2020)

$$GS = \frac{\left(\frac{S\%}{massa\ atômica\ do\ S}\right)}{\left(\frac{C\%}{massa\ atômica\ do\ C}\right)6} \qquad (1)$$

To calculate the yield where the initial mass of chitosan and the mass after the reactions were weighed, it was possible to observe the reaction yield

2.4 - Adsorption tests

For the adsorption studies, approximately 0.3 g of samples were weighed each and immersed in 40 mL of 0.3 mol/L copper sulfate solution. After 24 h, an aliquot was taken and the remaining copper was determined using EDTA - 0.01001 Mol/L. The remaining Cu +2 ion concentration was calculated by the equation below:

$$q = (ni - nf) / m \quad (2)$$

Where q is the adsorptive capacity , ni is the initial number of moles, nf the final number of moles in the mass of sample used.

3. Results and discussion

Two sulfated derivatives of chitosan were produced , chitosan sulfated with sulfating agent (QTS) and sulfated with sodium sulfate (QTSNa). Sulfated derivatives of carboxymethyl-chitosan were also produced , carboxymethyl chitosan sulfated with sulfating agent (QTCS) and sulfated with sodium sulfate (QTCSNa). The percentage yield by mass of the functional derivatives was determined in order to analyze the feasibility of each process and its cost-benefit ratio, whose values are shown in table 2. It is observed that the direct derivatives of chitosan obtained a higher yield in relation to the derivatives of carboxymethylchitosan , in which QTS and QTSNa had a yield greater than 89%, indicating that they are viable processes and that they have an excellent cost-benefit ratio, as it is a process carried out in fewer steps, therefore with lower cost and high yield . The sulfated derivatives of carboxymethylchitosan obtained yields of 68% for QTCS and 58% for QTCSNa , where losses occur due to the process

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involving several steps, susceptible to more losses in each washing and purification step.

3.1 Infrared Spectroscopy

In the QT spectrum, it is possible to observe the characteristic peaks of chitosan , where a broad band is observed in the region of 3426 cm-1 referring to the OH stretch and in the same region the peak referring to the NH stretch is superimposed, there are also peaks in the region of 1656 cm-1 referring to the C=O bond and in 1080 referring to the CO stretch. In the sulphated derivatives of chitosan and carboxymethylchitosan , it is possible to observe the characteristic peaks of chitosan , it is also possible to observe the existence of bands referring to the entrance of the sulphate groups, where they are present in all derivatives at approximately 617 cm $^{-1}$, referring to for the COS stretch and in the QTCS and QTCSNa , there is a peak in the region of approximately 1254 cm $^{-1}$ referring to the S=O stretch, whereas in the QTS and QTSNa it was not possible to observe it due to the overlapping of bands. It is possible to observe the peaks of all the samples in Fig 1. Thus, it was confirmed that the sulfate groups were successfully inserted into the chitosan structure .

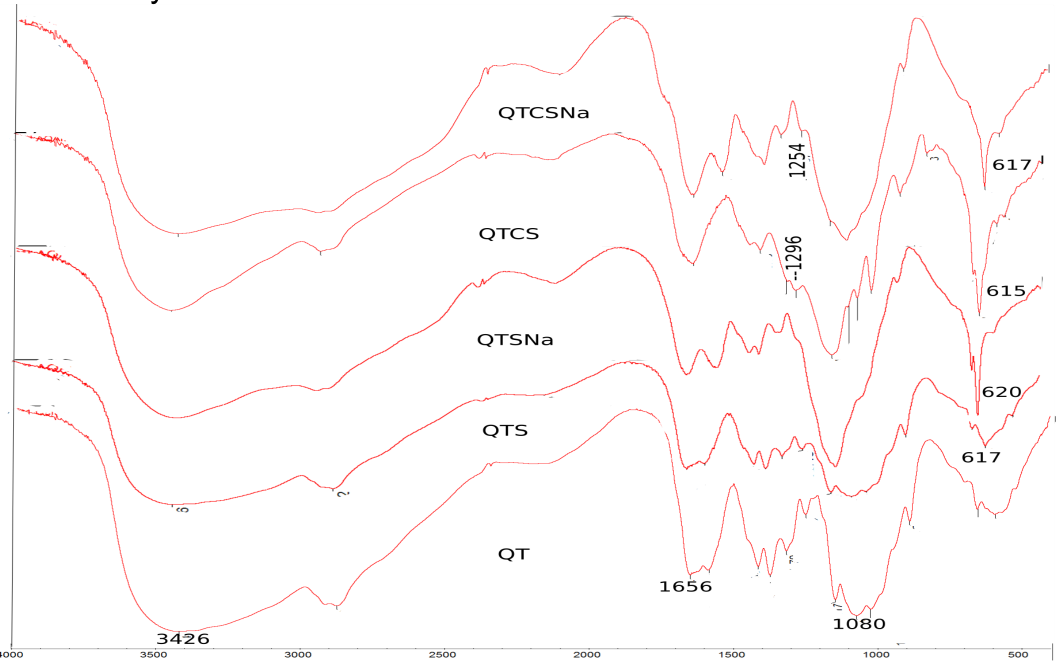

Figure 1: FTIR spectrum of chitosan (QT), sulphating agent sulphated chitosan (QTS), sodium sulphate sulphated chitosan (QTSNa), sulphating agent sulphated carboxymethyl chitosan (QTCS) and sodium sulphate sulphated carboxymethyl chitosan (QTCSNa) .
Source: Prepared by the author.

3.2 Elementary Analysis

Elemental analysis was performed only of pure chitosan (QT) and sulphated chitosan with surfactant agent (QTS) since it obtained a high reaction yield and was also one of the ones that had a higher percentage of adsorption. Thus, it is possible to observe in table 1, that there was an insertion of sulfate groups through the percentage of sulfur present in the structure of the same, which was 7.79%. By calculating the degree of substitution, it was possible to observe that the sulfated chitosan with sulfating agent has a degree of substitution of 1.96%, which in comparison with other

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works has a much higher substitution result. Moura Neto and collaborators (2011) made the sulfation of cashew tree gum, it was observed that it obtained a substitution of at most 0.88%. In comparison with the modification of chitosan by sulfation made by Moraes (2016), QTS also obtained a superior result, since in the work done by Moraes the degree of substitution was at most 1.37%. Thus, it was possible to observe that the method used to modify chitosan using the sulfating agent was successful, having a high degree of substitution.

Table 1: Elementary analysis of QT and QTS.

Sample	%Ç	%H	%N	%S	Degree of replacement (%)
QT	39.58	6.63	9.47	2.37	0.37
QTS	24.83	4.19	6.69	7.79	1.96

Source: Prepared by the author.

3.3 Adsorption study

The insertion of sulfate groups in the chemical structure of QT causes the material surface to have a high density of negative charge, thus favoring the adsorption of metals since they have a positive charge (MORAES, 2016). In this study, all analyzed samples obtained a removal percentage greater than 90%, as can be seen in table 2. Sulfated chitosan obtained a superior result than pure chitosan due to its insolubility at all pHs and it remained at 24 h without lose their proper properties, they become a more promising material for removing metals from industrial effluents.

In table 2 it is also possible to observe the adsorptive capacity of the materials where all obtained a similar capacity and above 60 mg/g in relation to copper, thus showing a high efficiency against this material. Among the 5 analyzed samples, it was possible to observe that the pure chitosan had an adsorptive capacity similar to the modified ones, however, due to its solubility in acid pH, it cannot be used in industrial effluents, which often have a certain acidity. The sulfated chitosans had a high adsorptive capacity and

In addition, they only have one type of modification, different from sulfation against carboxymethyl chitosan . In an article by Futalan *et al.* (2011), where chitosan immobilized with bentonite was used, obtained a capacity of 26 mg/g of copper much lower than the sulfated chitosan . Thus, there are two more promising products, QTS and QTCS, because the QTS is made with only one reaction, it becomes a lower cost product, in addition to a methodology having a high degree of substitution compared to methodologies already carried out in other countries. articles, so it can be considered the most viable product for this purpose, although the others also obtained positive results in relation to the adsorption of metals.

Table 2: Yield and adsorption study

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Sample	Performance (%)	Adsorptive capacity (mg/g)	adsorption percentage (%)
(QT)	-----	64.98 ± 0.009403	97.83 ±0.0014
(QTS)	91.4	64.08 ± 0.2079	98.17 ±0.3185
(QTSNa)	89	64.42 ± 0.02339	97.47 ±0.0352
(QTCS)	68.4	64.15 ± 0.05068	98.53 ±0.0778
(QTCSNa)	57.4	63.76 ± 0.067344	97.16 ±0.1026

Caption: Pure Chitosan (QT); Sulfated chitosan with sulfating agent (QTS); Chitosan sulfated with sodium sulfate (QTSNa); Sulfated carboxymethyl chitosan with sulfating agent (QTCS); Carboxymethyl chitosan sulfated with sodium sulfate (QTSNa).
Source: Prepared by the author.

4. CONCLUSIONS

We sought to modify the structure of chitosan through two sulfation methods in order to expand some of its properties. Thus synthesizing 4 different materials, QTS, QTCS, QTSNa and QTCSNa . Where all of them obtained a similar copper adsorption potential, greater than 90% and with an adsorptive capacity greater than 60 mg/g of copper, the QTS obtained a high degree of substitution and stood out in terms of yield and adsorption percentage , being the product with a high potential for adsorption of metals. Thus, it is possible to use the modification by sulfation for large-scale use in a potential use in the decontamination of industrial effluents contaminated with copper and new tests can be carried out in relation to the adsorption capacity of this material against other heavy metals.

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