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Polysaccharides-based adsorbents for removal of Congo red dyes from wastewater

Summary

Gums Arabic (GA) and Xanthan (GX) are natural polysaccharides that can be extracted by natural means for applications, such adsorption of pollutants. Structural modifications such as carboxymethylation on bio-adsorbent materials, can be performed to improve its adsorptive properties. Development of polymeric nanoparticles is an economical and favorable option for the adsorption of Congo red dye, which has high toxicity and is resistant to traditional removal processes. In this work, it was developed nanoparticles (NPs) of natural GA (NPGA) and GX (NPGX) and their carboxymethylated forms (NPCMGA and NPCMGX) aiming to evaluate the adsorption of Congo red (CR) dye. NPs are sized from 133 to 1099 nm at an average zeta potential of -13 mV, suggesting stability to absorb dyes. NPGX and NPCMGX absorbed a substantially higher amount of dye than the other NPs. The kinetic studies showed that adsorption process follow pseudo-second order model, suggesting that chemisorption control the process, and the isotherm test revealed that samples fit Langmuir model, with a homogeneous adsorption profile for the two carboxymethylated samples with a maximum adsorption capacity of 182,82 mg/g for NPCMGX and 757,58 mg/g for NPGX. These findings indicate that NPs from Xanthan Gum can be used for removal CR in contaminated water and wastewater.

Keywords: adsorption, Congo red, biopolymer

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Introduction

A few years ago, environmental issues involving industrial activities have become more frequent.[1] Textile sectors, when discarding their waste, may contain toxic dyes, such as Congo red (CR), which do not fully adhere to the fabric or do not undergo complete degradation.[2] Adsorption is one of the most efficient methods of treating material discarded by these industries, as it evaluates the ability of certain pollutants to adhere to the surface of an existing material in an aqueous medium.[3–5]

Among various types of adsorbent materials, the use of polymeric nanoparticles appears as an economical alternative with favorable environmental conditions, effective in adsorption and because they have specific functions that increase their adsorptive capacity, such as a large contact surface area and ease of diffusion.[6,7]

Natural polymers that are extracted from algae, seeds, plant exudates, tubers, cereals, animals, fungi, and bacteria such as gum arabic and xanthan. Xanthan gum is a polysaccharide produced by species of bacteria from the genus Xanthomonas and has a wide applicability in industry, being used as a thickener and stabilizer.[8]

Gum arabic is extracted from acacias, Acacia Senegal and Acacia Seyal and is commonly used in the food and pharmaceutical industries.[9] To improve the properties of polysaccharides, structural modification appears as an option in the insertion of chemical groups in different applications, such as carboxymethylation, which introduces these groups.[10] Thus, the objective is to produce nanoparticles based on gums associated with chitosan (CHT) and tripolyphosphate (TPP) to increase the adsorption potential, aiming at the applicability of water treatment contaminated with dyes.

Materials and methods

Carboxymethylation of gum Arabic and xanthan gum

For the carboximethylation of Gum Arabic (GA) and Xanthan Gum (GX), 5g of each gum was weighed, where for GA the methodology of Silva et al.[11] was followed and, for GX, the methodology of Yahoum et al.[12] Solutions of NaOH 10 M and 16M were prepared. It was added 16 mL of NaOH in the polymeric solution in portions of 2mL for every 10 minutes in constant agitation. Subsequently, 30g of Chloroacetic Acid (AC) was weighed and slowly added to the solution at 60ºC for approximately 3 hours, keeping a ratio of gum/AC of 1:6 by mass. Neutralization of the reaction medium was followed by precipitation in 96% Ethanol. Acetone was used to wash the precipitate that had been filtered into a 3 sintered plate funnel. The material was dried in an oven at 50°C for 24 hours and stored in a desiccator. Table 1 shows the reaction conditions and the substitution degree for the biopolymers.

Table 1 Reactions conditions and substitution degree of CMGA and CMGX

Sample	NaOH	Ratio acid: Gum	Substitution degree
CMGA	10M	6:01	0.9
CMGX	16M	6:01	0.34

Synthesis of nanoparticles

To produce nanoparticles (NPs) by polyelectrolytic complexation of gum with chitosan, the methodology of Sipauba[13] was followed. Using a solution of CHT at 0.5% and a solution of Tripolyphosphate (TPP) at a concentration of 30 mmols. Solutions at a concentration of 0.3% m/v of gum arabic (CMGA) and carboxymethylated xanthan gum (CMGX) and of gum arabic (GA) and commercial xanthan gum (GX) were used each. Then, 50 ml of the (QUI) solution in 100 ml of TPP was added by dripping to this CHI/TPP mixture, the solutions of CMGA, CMGX, GA and GX were added separately, producing samples of NPCMGA, NPCMGX, NPGA and NPGX. The NPs were centrifuged and lyophilized.

Characterization

Infrared measurements were performed on a Fourier transform infrared (FTIR) spectrophotometer (Nicolet is5, Thermo Scientific) in a spectral range from 4000 to 400 cm^{-1}. The characterizations of the nanoemulsions in relation to Particle Size, Polydispersity Index and Zeta Potential were performed in the Zetasizer/Nano Series Z590 equipment from Malvern. The sample was diluted in a proportion of 1:100 and remained under continuous agitation for 24 hours.

Adsorption kinetics

For the adsorption test, a calibration curve (Eq.1) of Congo Red Dye was constructed using a UV-VIS spectrophotometer model IL-593-BI at a wavelength of 484 nm. For adsorption kinetics, 100 mg of NPCMGA, NPCMGX, NPGA AND NPGX were used for a 100 ppm Congo Red Dye solution in phosphate buffer pH 7.01 at intervals of 1, 5, 10, 20, 30, 40, 50, 60, 70 and 80 minutes removing aliquots and diluting 5x.[14] Kinetic models were analyzed from Eq. 2 pseudo-first order and Eq.3 pseudo-second order.

$$Y = 0{,}0213x + 0{,}0029 \; R^2 = 0{,}9998 \quad (1)$$

$$ln\left(qe - qt\right) = lnqe - kt \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Adsorption isotherm

To carry out the adsorption isotherm, the same NP/Congo Red system was used in dye concentrations of 30, 50, 100, 150, 200, 250, 300 and 500 ppm in phosphate buffer solution with pH 7.01 in constant stirring for 80min determined by kinetics.[15] After the specified period, all samples were analyzed in the spectrophotometer. The values obtained were evaluated according to the Langmuir (Eq.4) and Freundlich (Eq.5) isotherms.

$$\frac{c_e}{q_e} = \frac{c_e}{q_{máx}} + \frac{1}{q_{máx}\, k_l} \quad (4)$$

$$logq_e = logk_f + \frac{1}{n} logC_e \quad (5)$$

Results and discussions

Infrared spectra

Figure 1 shows the infrared spectra of guns and its derivatives. Carboxymethylated gum arabic (1a) has a low peak in the 3427 cm^{-1} it is an increase in the 2972 cm^{-1} band which indicates an increase in functional group asymmetry of the hydroxyl (-OH), a carbonyl (C=O) band broadening with bonds weak ones indicated by the band represented by 1750 cm^{-1} beyond the present fold of the 1423 cm^{-1} band indicating the presence of C-O-H also indicating the presence methyl group is effective in inserting the gum, confirmed by the band 1249 cm^{-1} that the stretching vibration occurs in a primary structure of alcohols. Increase of the 771 cm^{-1} band due to the insertion of monochloroacetic acid (PAVIA,2010).

For carboxymethylated xanthan gum there is an increase in the 3435 cm^{-1} and 2939 cm^{-1} bands, indicated increase of asymmetry in hydroxyl group (O – H) and broadening with weak bindings in the 1752 cm^{-1} band (C=O). A decrease in the absorption band at 1605 cm^{-1}, indicates that the number of double bonds between carbons were undone for interaction with other ligands shown by band increase 1065 cm^{-1} with C-O bonds favoring the insertion of the group methyl in the gum in the 1419 cm^{-1} band in addition to the 673 cm^{-1} band stretch due to the introduction of monochloroacetic acid.[16]

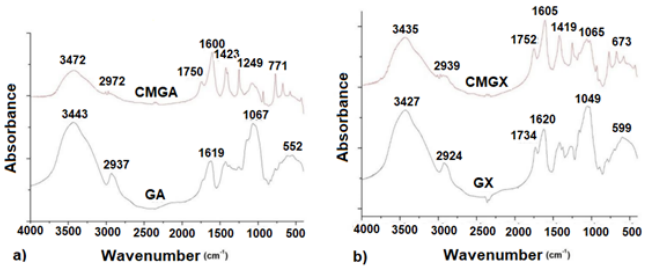

Figure 1 Infrared spectra of GA and CMGA (a) and GX and CMGX (b).

NPS characterization

The size and the zeta potential of the particles produced play a crucial role in the adsorption capacity of NPs. Agglomerated nanoparticles formed by flocculation present reduced potential as bioadsorbent, because of their increase in size and consequently lower contact surface with the adsorbate. Another factor that describes the influence of particle size is the polydispersity index, which can vary from 0 to 1, and when values are close to 1.0 indicates that particles have varied sizes, thus it is observed that all nanoparticles presented some degree of variation in size. (RAVAL et al., 2019).[6] Table 2 presents the particle size, polydispersity, and zeta potential for the nanoparticles produced.

Table 2 Nanoparticles code, zeta potential, particle size and Polidispersity index

Sample	Zeta potential (mV)	Particle size (nm)	PDI
NPGA	-17.5±4.0	133.9±41.0	0.499
NPGX	-11.5±5.0 (90%)	1116.0±208 (85%)	0.68
	-31.7±3.0 (10%)	342.6±41.0 (15%)	
NPCMGA	-13.7±7.5	444.7±42.4	0.558
NPCMGX	-7.97±3.0	665.0±48.6	0.576

Results showed that the NPGA and NPCMGA have PDI values around 0.5, therefore showed a similar agglomeration pattern. However, NPGA presented lower particle size than NPCMGA, with values of 133.9 and 444.7 nm, respectively. NPGA also presented a zeta potential with higher value in modulus, indicating possibly a higher stability of the particles and a lower tendency to agglomerate, corroborating with the lower particle size values.

On the other hand, NPGX and NPCMGX presented higher PDI values (0.680 and 0.576). NPGX presented a bimodal distribution, with a majority fraction with higher size, above 1000 nm, and a minority fraction with nanosized dimensions, around 340 nm, and this heterogeneity resulted in the increase of the PDI values. This heterogeneity also appeared in the zeta size values, with a minority fraction with high potential values in modulus. NPCMGX presented higher particle size, but with average values of nano-sized dimensions.

Usually, NPs with a size range of 200nm would enhance adsorption because of the higher surface: volume ratio. However, sometimes, intra-, and interionic interactions between the particles

would lead to aggregation that would cause the formation of larger particles (ABREU et al., 2018), what seems to be the case of NPs produced with xanthan gum. NPGX and NPCMGX presented higher size, suggesting that the branched structure of the xanthan gum may have favored the formation of higher and aggregated particles.

Effect of contact time

Figure 2 shows the percentage of adsorption of CR in function of time for the nanoparticles of gums and its derivatives. It is possible to observe in Figure 2a that the equilibrium time of NPGA is 40 min with 82.72% removal of CR obtaining a greater variation between the studied time intervals reaching with 70 min 94.23% of adsorption and the NPCMGA assumes equilibrium from 5 min of 70.63% and in 80min a percentage removal of 97.51%.

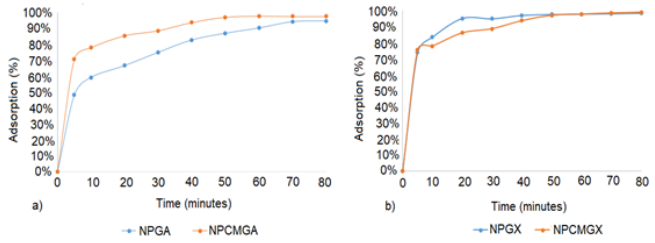

Figure 2 Counting time in the NPGA and NPCMGA (a) and NPGX and NPCMGX (b) with Congo red solution.

In Figure 2b, the equilibrium time of NPGX is 20 min of contact with the sample with a percentage of 95.28%, reaching with 80 min the adsorption percentage of 98.22%, obtaining little variation until the stipulated time and the NPCMGX assumes equilibrium from 5 min with 75.68% obtaining a variation between the studied time intervals reaching with 80 min to 99.15% of adsorption.

Adsorption kinetics

The studies were carried out analyzing the counting time of the nanoparticles with the fixed concentration of adsorbate to determine a linear regression and if the kinetic model of pseudo-first order or pseudo-second order fits better to the obtained results as described in Table 3.

Table 3 Determination coefficient (R^2) values obtained from kinetic tests

Sample	Pseudo-first order	Pseudo-second order
NPGA	0.98285	0.99381
NPGX	0.86318	0.99826
NPCMGA	0.93906	0.99943
NPCMGX	0.95227	0.99802

Observing the values of the determination coefficient (R^2) the Nps fit into the pseudo-second order model that contains adsorption rates as a function of ionic exchanges by coordination or complexation that are chemosorptive characteristics as a limiting and controlled step with R^2 values to closer to 1, as also demonstrated in other studies (SIPAUBA, 2018). This effect is due to the presence of different functional groups like, hydroxyl and carboxymetheyk that contribuite to thhis mechanism adsorption.[17]

Other studies with carboxymehtyl derivatives for Congo Red adsorption obtained similar results regarding carboxymethylation being used to improve the performance of nanoparticles in dye adsorption.[14]

Adsorption isotherm

Isotherm studies help to understand the ability of nanoparticles to adhere to Congo Red dye ions that are in an aqueous medium until equilibrium is established and the dye concentration in the medium is constant. To evaluate this process, there was a variation in dye concentration with a contact time of 80min. Table 4 shows the results of the parameters obtained from Langmuir and Freudlich Isotherms.

Table 4 NPS adsorption parameters obtained from Langmuir and Freudlich isotherms

Isotherm	Constant	NPGA	NPGX	NPCMGA	NPCMGX
Langmuir	Qmax	140.65	757.58	102.35	182.82
	R^2	0.9775	0.7285	0.8871	0.8479
Freudlich	R^2	0.7666	0.9085	0.6956	0.7128

We were able to observe that the NPs that presented linear correlation values, close to 1, thus adapting more to the Langmuir isotherm, are the NPGA, NPCMGA and NPCMGX, which indicates that there are defined sites that have equivalent energies, where the adsorption occurs confirming homogeneous adsorption, in a monolayer and the molecules do not interact with each other. The amount of adsorbed dye can be represented by Qmax, which indicates the concentration of adsorbed dye on the surface of the nanoparticles, with all active sites filled in with complete coverage.[5]

The NPCMGX was the only one that presented the linear correlation value adapting to the Freundlich isotherm, reinforcing the heterogeneous and multilayer adsorption, indicating that the sites may present non-uniform energies and low value of adsorptive capacity of this isotherm.[15]

Table 5 shows results of Qmáx of CR Dye from different materials for comparison the capacity of adsorption. The NPGA and NPCMGA showed comparable values of Qmáx with those in the literature. NPGX and NPCMGX showed significant higher value of Qmax, highlighting the high potential to NPs from Xanthan Gum in the removal of Dyes in contaminated water and wastewater.[18–21]

Table 5 Comparison of Qmáx with other materials for adsorption of Congo red dye

Adsorbent	Qmáx(mg/g)	Reference
Magnetic Fe_3O_4/chitosan nanocomposites	47	KADAM et al., 2020
Water treatment sludge biochar	116,4	He et al., 2022
Magnetic aerogel based on hemicellulose and chitosan	137,8	Guan et al., 2020
Chitosan modified nanocoposite	104,6	AHMAD, R.; ANSARI, K., 2020
NPGA	140,65	This work
NPCMGA	102,35	This work
NPGX	757,58	This work
NPCMGX	182,82	This work

Final considerations

The results obtained from the study show that the production of NPs with the commercial gums and carboxymethylated derivatives were satisfactory, with good stability due to zeta potential and low particle size, where GX was more efficient than GA. NPCMGX and NPGX showed the best adsorption capacity, above 98% after 80 min. The kinetic of process is better described by pseudo-second order

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model and the equilibrium is fitted by Langmuir model of isotherm for NPGX, that present monolayer adsorption, and NPCMGX that present multilayer adsorption, both being efficient in the congo red dye adsorption. Therefore, those NPs have the potential for the removal of dyes from contaminated water and wastewater.

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Conflicts of interest

Author declare that there is no conflict of interest for the publication of this scientific article.

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