

Synthesis of biopolymer from chitosan/xanthan

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Received January 15, 2016; Accepted June 9, 2016

Abstract

It was synthesized a hydrogel based on chitosan and xanthan biopolymers, by varying the amounts of both polymers in the network. The polymer chitosan/xanthan (Q/X) ratios analyzed in this work were 75/25, 67/33 and 50/50 respectively. With the aim to improve chitosan properties in acid medium, it was performed crosslinking reactions in the hydrogels by employing glutaraldehyde (GA) as crosslinking agent and hydrochloric acid (HCl) as catalyst, by changing the concentration of each one at 0.5, 1 y 5% w/w over the total sample. Crosslinking reaction was allowed to proceed at 70° C for 3 hours at inert atmosphere. Water fraction determination results showed high values between 0.98 and 0.99, which made them high hydration materials. On the other hand hydrogels exhibit resistance to dissolve at pH 2 and 7, and the relationship of polymers 75/25 showed the lower weight lost in neutral media. Infrared spectroscopy analysis exhibit characteristic groups of both biopolymers in the network, and also appear N-H bonds or available sites that can suggest a good perform in adsorption processes. SEM analysis show homogeneous surfaces with some particles of xanthan gum without react, except to the Q/X ratio of 75/25, where it can be notice a denser surface, probable due to a good crosslinking of both polymers. It could not be possible to establish the glass transition of the xerogel, however by determining and comparing fusion heats in thermograms of materials, it was feasible to explain some possible changes in the structure hydrogel during due to crosslinking reactions.

Biopolymer, hydrogel, chitosan, xanthan, crosslinking

Citation: ANTONIO-CRUZ, Rocío, PURATA-PÉREZ, Nora Alicia, URRIETA-SALTIJERAL, Juan Manuel, GARCÍA-GAITÁN, Beatriz and SOSA-DOMÍNGUEZ, Noé. Synthesis of biopolymer from chitosan/xanthan. ECORFAN Journal-Ecuador 2016, 3-4: 40-48

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Introduction

Water pollution caused by discharges from industries of their wastewater, particularly those that contain heavy metals, is a difficult and serious problem for ecology and health, as these are considered dangerous because of its biodegradability, toxicity even at low concentrations and their ability to get accumulate in the body. The growing concern for environmental care, and compliance with strict legislation on the discharge of these products that contain heavy metals, has produced the need of the development of new technologies for the removal of these contaminants. Currently, there are various treatments for its removal, such as chemical precipitation, ion exchange, separation by membrane electrolysis, among others (*Baroni et al., 2008*), however they present the drawback of being expensive or ineffective in removing trace metal ion in dilute solutions. Adsorption is recognized to be an effective, efficient and economical method for achieving this end, whereby the search and development of new adsorbent materials has been necessary, based on natural polymers such as polysaccharides and their derivatives.

Hydrogels are cross-linked structures in a network having good physicochemical characteristics, such as its ability to absorb large amounts of water, and its responsiveness to stimuli, which has made have applications in several areas, including the removal of metals, particularly those based on chitosan.

Chitosan is one of the most used materials, because presents good physicochemical properties such as high reactivity and excellent selectivity to aromatic compounds and metals, due to the presence of hydroxyl and amino groups in the polymer chains.

It has been found that hydrogels based on chitosan, improve the ion adsorption capacity, however one of the major limitations of poor resistance to it acidic conditions, and mechanical strength (Bailey et al., 1999). It has been discovered that through the crosslinking reaction, and on the other hand, by combining or mixture of polymers, these properties are improved, making it possible to obtain materials with desired properties. In this research synthesis based on chitosan and xanthan gum, chemically cross-linked by using glutaraldehyde as crosslinking agent, studying the effect of three relationships hydrogel polymers developed, and three concentrations of crosslinking agent and catalyst (HCl) in the material, for further characterization, by determining the water fraction, solubility tests in various media, swelling tests, and analysis by Fourier Transform Infrared Spectroscopy (FTIR).

Methodology

Hydrogels were obtained based on the proposed method by Li and Bai, in 2005, adapted for the synthesis of the biopolymer chitosan-xanthan. For the crosslinking reaction it was necessary to prepare a solution of glutaraldehyde [$2.5 \cdot 10^{-3}$ M], and a solution of hydrochloric acid [$1 \cdot 10^{-2}$ M], according to the method described by Park et al. (2000). 1500 mg total sample was used to prepare biopolymers Q/X. For the synthesis of hydrogels, solutions of each polymer with a final concentration of 0.65% by weight, and solvent for the chitosan powder was a solution of acetic acid [0.4 M] were used, while for xanthan, water was used deionised . It was stirred at 200 rpm, at a temperature of 35 ° C for 2 h until completely dissolved.

The solution was injected xanthan dropwise in chitosan, with the help of an insulin syringe (in order to keep the size of the formed sphere constant) all with slow stirring for 2 h. Both polymers were allowed to interact, for 2 h after complete addition of the xanthan to chitosan solution, to complete formation of the physical hydrogel. To make the crosslinking reaction, the temperature was raised to 70 ° C and stable once rose, glutaraldehyde solutions (GA) and catalyst HCl (0.5, 1.0 and 5% by weight) were added, and allowed to react for a period 3 h, while maintaining an inert atmosphere and constant stirring. After this time, we proceeded to filtering hydrogels and washed with deionized water until a neutral pH. The spheres were placed in a petri plastic box, which took a stove at 40 ° C for 48 h, for drying. A hydrogel spheres obtained, were performed to determine the water content, known as water fraction (by weight). Once obtained films of chitosan-xanthan biopolymer, tests were performed at pH solubility, acidic, basic and neutral, to study their physical endurance, in different media. Furthermore, tests prior to testing solubility, swelling in deionized water were made. Properties were also evaluated, and characteristics of the materials obtained using the technique Fourier transform infrared spectroscopy (FTIR).

Results

Synthesis of hydrogels

The synthesis was performed using hydrogels proposed by Li and Bai in 2005, with some modifications to the addition of xanthan gum method.

The ratio of chitosan-Xanthan polymers, taken as a starting point for the development of materials, was to 67/33, selected as reference previous work done by Martinez in 2007, varying this relationship with the addition of more and lower content of chitosan in 75 and 50%, considering a maximum content of xanthan gum 50%, since at higher concentrations not the complete dissolution thereof was achieved because forming very viscous solutions, hindering adding to the solution as drops chitosan.

After the crosslinking reaction, spheres of smaller size were obtained, approximately 1 mm in diameter, which after performing corresponding washing with deionized water to remove residual acetic acid, increased its size considerably to about 3 mm diameter, due to the expansion of the chains within the formed network, allowing the entry of water, swelling. The hydrogel showed uniform appearance and was soft to the touch; physical appearance can be seen in Figure 1 (a), which shows the hydrogel with 50/50 ratio and a concentration of 5% GA.

Once in xerogel form, after drying for 48 h at 40 ° C, the surface showed a nonuniform formed, thin and somewhat brittle, rough appearance due to air bubbles formed during drying. Its physical appearance is presented in Figure 1 (b). The appearance and characteristics presented were the same for other synthetic materials, regardless of the ratio Q / X used. Only for relations with higher content of xanthan gum was obtained.

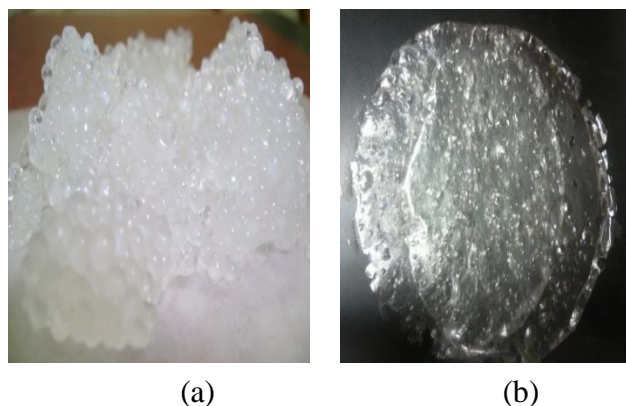
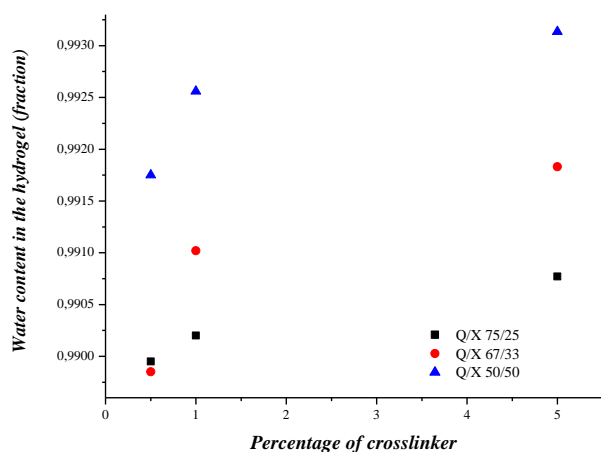


Figure 1 Biopolymer Q/X, 50/50 and 5% crosslinker (a) hydrogel and (b) xerogel

Determining the percent water (by weight)

The water content in the gel is one of its main features, providing versatility, to a wide number of applications, being the holding capacity, a function of the structure of the materials that compose it, being higher for materials with lot of hydrophilic groups. The graphic 1 show the values of the fraction of water in hydrogels obtained for each of the relations Q/X used in the synthesis as well as the effect of crosslinking agent concentration on these values.



Graphic 1 Effect of percent crosslinking agent on the values of the water fraction by weight of Q/X hydrogels, the three relationships polymers studied: 75/25, 67/33 and 50/50

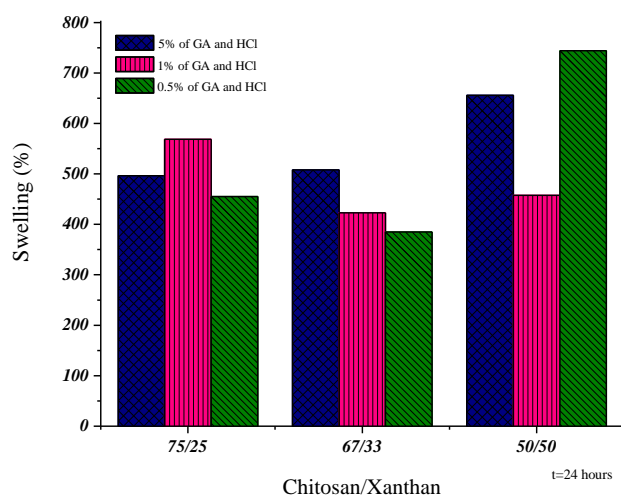
It can be seen that the ratio of polymers showed the highest values in water content was corresponding to 50/50 followed by 67/33 and 75/25 of. For each ratio Q/X is observed that larger fractions are obtained the highest concentration of crosslinking agent, means, those with 5% GA. This may contradict those reported in the literature for crosslinked materials in which at higher concentrations of crosslinking agent, the absorption capacity of water decreases due to the increase in the density of nodes in the network, hindering liquid inlet.

However, this phenomenon can be explained considering the helical structure of xanthan, assuming that during the crosslinking reaction and the effect of high temperature, this structure is destroyed and therefore a part of the hydroxyl groups which stabilize this helical structure by hydrogen bonding take part in the reaction and another part was available to interact with the water during the swelling process. Thus a network that the initial, less compact is created with spaces in the larger network, which allow increased water absorption. The values of the determinations of water fractions are high and range between 98 and 99% in water content, having some significant changes, these percentages between the studied relations of both polymers in the network.

Swelling tests

In the swelling of the hydrogel is carried out the diffusion of water into the polymer matrix, this process involves the migration of water with preexisting spaces formed between the polymer chains. The swelling of the hydrogel involves a large movement of the segments of the polymer as it is the result of increased spacing between the chains of the hydrogel (Crini, 2005).

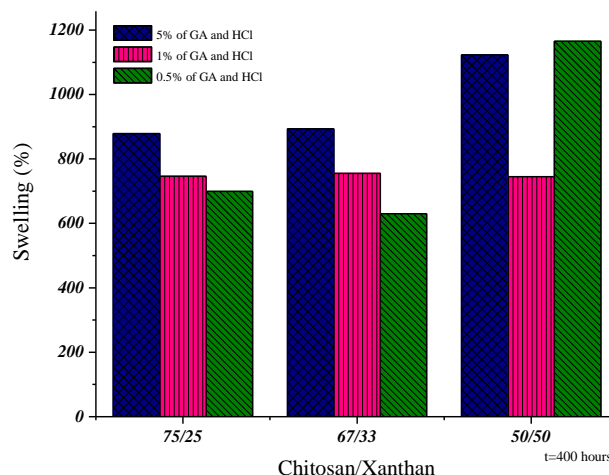
Graphic 2 shows the percentages of swelling obtained after 24 h of starting the dive, materials in deionized water. Inside it there are the three relationships chitosan/xanthan studied, each of the concentrations of glutaraldehyde added to the materials. For the ratio of Q / X of 67/33, A trend is visible towards a higher percentage of swelling for the hydrogel with a concentration of 5% GA, reaching a percent swelling of 508%, followed by 1 and 0.5%.



Graphic 2 Percentage of swelling at 24 h of hydrogels three relationships biopolymer Chitodan/Xanthan and three concentrations of glutaraldehyde employed

In the case of hydrogel 75/25 with 1% crosslinking agent, showed the highest value of water absorption with 496%, and finally the 50/50 ratio, was the one that threw the highest percentages water content, for hydrogels with 5 and 0.5% GA, with 655 and 744% respectively. In the graphic 3 the percentages of swelling of hydrogels are observed in a time of 400 h for each ratio Q/X, at concentrations of GA studied. For the 67/33 ratio remains the trend observed in the previous graph, the largest percentage of swelling hydrogel for 5% to 893% of fluid retention, followed by crosslinked materials with 1 and 0.5%.

In the case of hydrogel to the ratio 75/25, a new trend is observed in a similar ratio 67/33, the material with 5% GA which the highest percentage of swelling, having increased 382 presents % compared to the previous value at 24 h. Similarly this trend is followed by the hydrogels with 1 and 0.5% crosslinking agent. The highest percentages of swelling values of all materials Q / X were for the relationship with higher content of xanthan gum, 5 and 0.5% respectively, there being a significant difference between these values.



Graphic 3 Percentage of swelling to 400 h of hydrogels three relationships biopolymer Chitosan/Xanthan and three concentrations of glutaraldehyde employed

This behavior, somewhat variable, presented in hydrogels, may be that in the course of time, there is a rearrangement of the chains into the hydrogel, allowing greater water retention. That is, it is possible that the large number of ionizable groups present in xanthan, suffer repulsions, for example between COO-groups, increasing the spaces in the hydrogel network, leading to increased swelling.

A behavior very similar to that observed in this research project was found, by Rubio in 2009, which made the synthesis of materials based on natural sources, including xanthan gum, karaya gum and hydroxyethylcellulose.

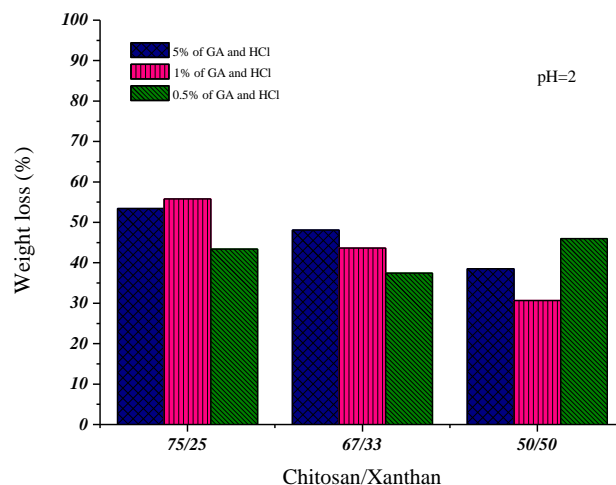
He used equally GA, as crosslinking agent, finding that in general, materials with the highest concentration of it, throwing the highest values in the percent swell, reaching a peak of 10211%, attributing the author this behavior to nature own materials (in this case xanthan gum) and the large number of loads present in the system.

Solubility tests

A xerogels obtained was subjected to tests solubility in different media: basic and neutral acid, to evaluate their behavior and physical endurance in different pH ranges. To do this, it was necessary first films swell to its maximum capacity of water retention, to further suspend the material in buffer solutions of pH 2, 7 and 10, with constant agitation of 120 rpm for a period of 24 hours. The results obtained during tests solubility subsequent swelling of hydrogels are presented.

Graphic 4 shows the percentage weight loss hydrogels, after 24 h of being in contact with the solution of pH = 2, showing that high values of weight loss in the material is obtained, having higher values of chitosan content higher, reaching up to 55% loss ratio 75/25.

However there was no gels solubility in such media, since it reached to record each of the weights without the total loss of the materials. The loss of material is greater in the hydrogels in contact with this medium, and the ionic strength there is increased, leading to an interaction of the counterions of the medium, therefore the hydrogel loses ionizable groups to form ionic bonds with polyvalent ions of the medium (Katime, 2003).

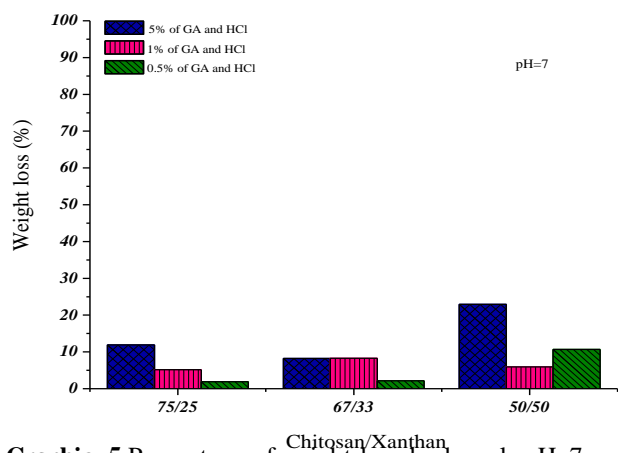


Graphic 4 Percentage of weight loss hydrogels pH=2

Graphic 5 presents the percentages of weight loss in the hydrogels after 24 h of being in contact with the solution of pH = 7. It can be seen as the percentages are much lower compared to thrown to pH = 2. The hydrogel which present the highest value was the highest content of Xanthan i.e. 50/50, with 22% loss of material.

Hydrogels had the lowest values were those with ratios of 75/25 and 67/33, with the lowest percentage of crosslinking agent, with values of 1.88 and 2.13% respectively. This behavior is due to low ionic strength exists in the middle, and the ionized functional groups attached to the chain hydrogel attraction or repulsion suffers with said medium.

A basic pH was not possible to record the weights for the material after 24 hours in contact with the solution pH 10, as they lost their properties and resistance, mostly solubilized. This can be attributed to that between, basic those corresponding to xanthan, carboxylic groups pass carboxylate groups, and because of repulsion between them and the environment, the hydrogel network relaxes completely, allowing more liquid inlet until solubilized completely.



Graphic 5 Percentage of weight loss hydrogels pH=7

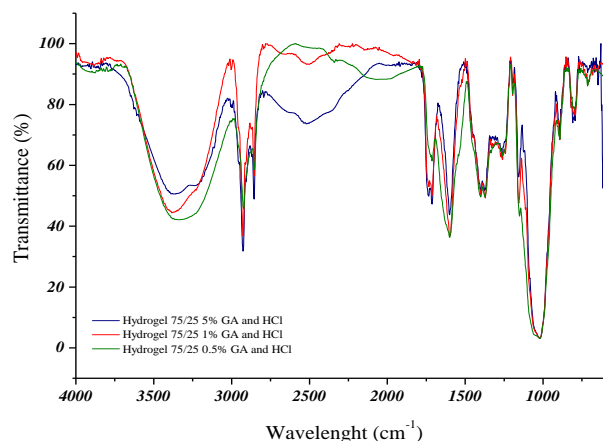
Infrared Spectroscopy Fourier Transform (FTIR).

After the synthesis of chitosan-xanthan biopolymer, and having the same shaped xerogel, we proceeded to carry out the characterization by FTIR hydrogel Q/X, in order to identify key functional groups present in each ratio Q/X.

In this work the FTIR spectrum for the hydrogel Q/X ratio 75/25 at three different concentrations of HCl and studied crosslinking agent (0.5, 1 and 5%) is presented. In the three spectra (see graphic 6) a broad band between 3600 and 300 cm^{-1} , corresponding to stretching vibration characteristics of the O-H and N-H groups present in both polysaccharides are presented.

There is evidence of bands characteristic related to free aldehyde group around 1740 cm^{-1} , which may be due to not react with the amino groups of chitosan, as Baroni mentioned in 2008, in this type of crosslinks, the molecules of bifunctional glutaraldehyde not necessarily have both aldehyde groups bound or linked to the chitosan molecule and therefore functions the same group may remain unreacted, remaining available in the matrix crosslinked end.

The peaks present at 2918 and 2855 cm^{-1} are due to vibrations of symmetric and asymmetric stretching of C-H bonds, while the signals present at 2500 cm^{-1} , may correspond to stretching vibrations of bonds N-H. The peaks located at 1370 cm^{-1} and 1259 cm^{-1} , attributable to deformation vibrations of the OH groups and the peak at 1406 cm^{-1} located deformation vibration of C-H bonds. The weaker signals present at 793 cm^{-1} and 713 cm^{-1} , due to vibrations shake N-H bonds and C-H respectively.



Graphic 6 FTIR spectra of the hydrogel 75/25 to different concentrations of crosslinking agent and catalyst: 5%, 1% and 0.5%

The signal located at 1630 cm^{-1} may be attributed to stretching vibration of C=N, corresponding to the formation of the imino groups during the crosslinking reaction. Baroni in 2008 reports this signal around 1655 cm^{-1} in its work on chitosan membranes crosslinked with glutaraldehyde, used for adsorption of chromium ions. The signal located between 1100 cm^{-1} and 1000 cm^{-1} corresponds to vibrations of symmetrical and asymmetrical stretching of the bonds C-O-C.

Conclusions

Biopolymer synthesis chitosan-xanthan was performed, in which thin, flexible, transparent films were obtained, regardless of the ratio of Q/X used. Determining the water content in the material, as a fraction of water, high values between 0.98 and 0.99 was obtained, which classifies it as a hydrogel high hydration, wherein the maximum value more content ratio of xanthan (50/50) and the highest percentage of glutaraldehyde (5%).

Swelling tests showed the highest percentages for the 50/50 ratio with 5% and 0.5% glutaraldehyde, reaching values of 1123 and 1165% respectively, which may favor when used on adsorption of metal ions facilitating the diffusion process in the hydrogel.

The solubility tests performed show that all materials have good properties, when their physical resistance to pH 2 and the neutral, since no solubilized, not so for the pH 10, as loss of material was. A suitable range for the use of materials in serious adsorption tests 4 to 8, still more favorably pH 7, using the relative 75/25 hydrogel with 5% crosslinker because it presented the least loss of material, 1 during testing in a neutral context, with a value of 1.88%.

By characterization by FTIR, the major groups present on both polymers were determined in the network, such as absorptions present of OH, C=O, NH, N=H, CH₂ and CO groups in which a greater intensity in the corresponding peaks in the region of the carbonyl group and CH bonds, as the concentration of crosslinking agent is increased, which can be attributed to the aldehyde group and the signal around 1630 cm⁻¹, may correspond to a imino bond, reaction product of chitosan with glutaraldehyde.

Spectra is equally materials containing functional groups still present N atoms, which means sites still available to take place a good adsorption process with metal ions.

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