

Study of Spirulin Algae Adsorption in Hydrogels of Chitosan



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Abstract

In the research, hydrogels of chitosan with glutaraldehyde were synthesized as a cross-linking agent to carry out the adsorption of Spirulina algae and to establish bases for the development of a controlled release system via transdermal for patients with low levels of iron. The determination of functional groups and the adsorption was carried out by IR spectroscopy where decreases of these groups in the fingerprint zone were verified and the results were verified through XRD through the formation of two crystalline zones.

Keywords: Spirulina algae; Chitosan; Hydrogels; FTIR; DRX

Introduction

Hydrogels are materials with three-dimensional structure that can increase their volume due to the thermodynamics of hydrophilic groups with polar groups of water or biological fluids [1,2]. Hydrogels are normally synthesized from natural materials such as gelatin, marine algae and animal collagen, which are called polysaccharides and are constituted by ortho-glycosidic repeating units, although they are also obtained from acrylate polymers. The excellent biocompatibility, biodegradation, smooth consistency as well as porosity of the structure allows the hydrogels to be used in medical applications such as tissue engineering, controlled release systems, biosensors and hemostasis sales [2-4]. A characteristic of hydrogels is the bioavailability where from the adsorption of enormous amounts of drugs the side effects are reduced by improving the release at the specific site [5].

Currently, hydrogels are synthesized by biodegradable and biocompatible natural polymers. Chitosan represents the most important natural polymer in the synthesis of hydrogels, which is obtained from the alkaline deacetylation of chitin and is the most widely used polysaccharide in medical areas attributed to the amino groups and the cationic charge of their structure. The adsorption of drugs for the development of controlled release systems both oral and subcutaneous in treatments

against cancer and diabetes [6]. In addition, biocompatibility with biological systems allows to be used as scaffold for cell and tissue growth [5].

At present, natural polymer based nanostructures are being used with the aim of obtaining a controlled release system in iron adsorption because the low concentration of iron in the bloodstream represents one of the main nutritional problems to Worldwide, attributed to it is responsible for oxygenation, hormone synthesis, cell cycle control, as well as enzymatic reactions in the human body and a low iron diet, infections, intestinal diseases among others are factors that represent a low level of iron in the blood system and over time anemia occurs [7]. The Spirulina algae is composed of

- The central region containing the nucleic acid,
- The peripheral region, is constituted by cytoplasmic structures and is responsible for the process of photosynthesis and
- The cell wall formed by peptidoglycan [8].

Spirulina represents a source of natural iron source and can be found in green foods, meat and cereals [9]. In 2002, it was determined that it can be used in treatments against anemia,

cancer, hepatotoxicity, cardiovascular problems, high cholesterol and triglycerides, hypoglycemia, chronic fatigue and ulcers [10]. This was attributed to the fact that Spirulina has 60% protein in addition to amino acids, vitamins (A, B1, B2, B3, B6, B9, C, D, E), minerals (calcium, copper, chromium, phosphorus, iron, magnesium, manganese, potassium, selenium, sodium, iodine and zinc) as well as 15–20% carbohydrates [11,12].

On the other hand, although there is no universal methodology, there are several techniques of physicochemical analysis for the study of adsorption of drugs like DSC, DTA and DTG, however, the main techniques of spectroscopic analysis (FTIR, XRD and NMR) allow an analysis Qualitative and quantitative in the development of release systems [13]. FTIR and RAMAN techniques have become increasingly important in pharmaceutical and biopharmaceutical applications from physicochemical characterization to kinetic analysis in drug adsorption and release to determine drug performance. FTIR allows the study of adsorption and release of semi-solid formulations, pellets, transdermal systems, as well as in vivo studies [14]. Thus, the objective of the investigation was to analyze the adsorption of Spirulina algae in hydrogels of chitosan using FTIR spectroscopy and DRX to establish the bases for a transdermal release system.

Methodology

Materials

Chitosan from shrimp shells degree of deacetylated $\geq 75\%$, Aldrich), Acetic acid (PM 60.05gr/gmol, J.T. Baker), Glutaraldehyde 25% (J.T. Baker), Methanol (anhydrous 99.8%, Aldrich).

Methods

Chitosan crosslinking: The crosslinking of the chitosan was first carried out by preparing a 1 and 3%w/v solution of chitosan in 2%v/v acetic acid, then agitation was carried out for 5mins. For a subsequent rest of 24hrs. In petri dishes [15,16]. Cross-linking was carried out for 24h and various concentrations of glutaraldehyde were used from 3-10%, then methanol was added to remove unreacted reactive groups, then washed with distilled water and finally placed in an oven at 25°C for 24h [15]. The degree of swelling (SR) was calculated by measuring the weights before (W_0) and after (W_s) of the addition of water using the equation (1): $SR = [(W_s - W_0) / W_0] * 100$ [17].

Adsorption of Spirulina algae: The dried gels were placed in a solution of water and Spirulina algae in different proportions for 24h under constant agitation and the percentages of swelling were subsequently determined.

FTIR: FTIR were recorded using a NICOLET iS10 spectrometer. The freeze-dried hydrogels were ground into powders, blended with dry spectroscopic grade KBr powders, and pressed into small disks for FTIR measurements. Samples

were scanned a resolution of 2cm^{-1} in the scan range of $400\text{--}4000\text{cm}^{-1}$.

DRX: X-ray diffraction patterns of the composite films were measured using an X-ray diffractometer (model D8 Advance; Bruker, Germany) with Ni-filtered Cu radiation generated at 30 kV and 30mA as the X-ray source. The diffraction patterns were determined over a range of diffraction angles $2\theta = 5^\circ$ to 70° and a step of 0.060° (2θ).

Results

Spirulina algae

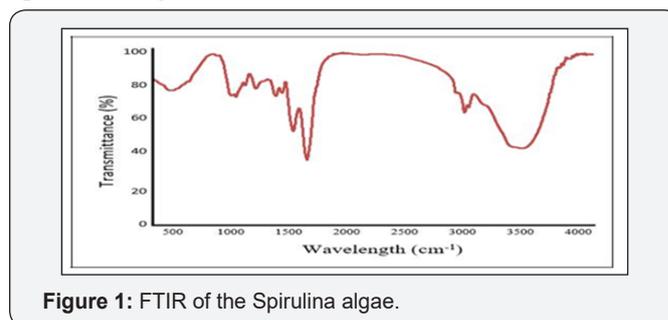


Figure 1: FTIR of the Spirulina algae.

Figure 1 show the FTIR of pure Spirulina algae where the vibrations at $3560\text{--}3500\text{cm}^{-1}$ were attributed to the OH stretching of carbohydrates and amino acids [18] in addition to the presence of alcohols and phenols [19]. In the range of $3500\text{--}3300\text{cm}^{-1}$ the presence of the NH stretching vibration of the secondary amines corresponding to the protein and lipids was observed while from 3000 to 2850cm^{-1} the aliphatic CH stretching vibration of the alkenes. The frequency ranges $3300\text{--}2500\text{cm}^{-1}$ represent the presence of the aliphatic OH stretching vibration of the carboxylic acids. With respect to the signals of $2260\text{--}2100\text{cm}^{-1}$ was assigned to the triple bond C-C of the alkynes [20]. The vibration of the carbonyl group (C=O) was located between $1750\text{--}1735\text{cm}^{-1}$. From $1680\text{--}1640\text{cm}^{-1}$ corresponded to the stretching vibration of the C=C bond whereas the NH flexion of the ketone appeared between $1650\text{--}1580\text{cm}^{-1}$ and the flexion of the CH₂ group was observed between $1435\text{--}1405\text{cm}^{-1}$, respectively [18]. The range of 1550 to 1475cm^{-1} was observed asymmetric stretching N-O corresponding to the nitrogenous compounds of the alga [19]. The frequencies attributed to the C-O stretching vibrations and the O-H flexions were appreciated between $1350\text{--}1260\text{cm}^{-1}$.

The presence of the C-O and O-H asymmetric stretching of the COC group and the symmetrical stretching between $1120\text{--}1030\text{cm}^{-1}$ of the esters, carboxylic acids, ethers and alcohols [18], the C-N bond characteristic of the aliphatic amines was located between $1250\text{--}1020\text{cm}^{-1}$; while the antioxidant enzymes present in the alga were located from 1050 to 1010cm^{-1} attributed to symmetrical stretching of SO₃ as well as ionic sulfonates. From 700 to 620cm^{-1} the SO vibration of the sulfonic compounds was appreciated and the N-H vibrations of the primary and secondary amines were found between

910–665 cm^{-1} . Finally, the C–Br bond due to the presence of the alkyl halide compounds were determined in the area between 690–515 cm^{-1} [19,20].

Adsorption of spirulina algae in chitosan hydrogels

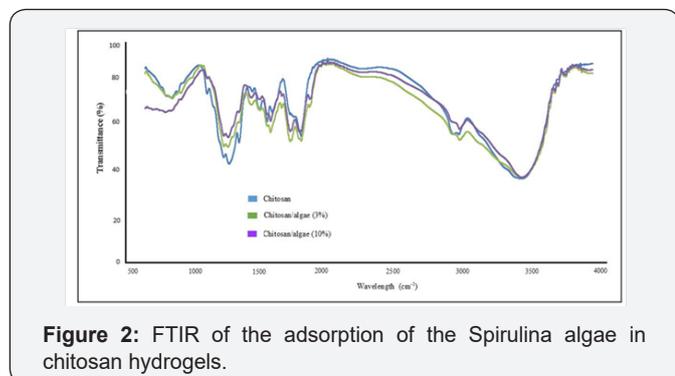


Figure 2: FTIR of the adsorption of the Spirulina algae in chitosan hydrogels.

The percentages of swelling using the equation 1 were 25 and 26% respectively. Figure 2 shows that in the range of 4000–3400 cm^{-1} there is a wide overlap of the OH stretching vibrations of the water present in the hydrogel, as well as the NH stretching of the primary amines. Stretching bands at 1800–1770 cm^{-1} (asymmetrical and symmetrical) corresponded to carbonyl groups (C=O) of primary amides. The bands at 1550–1600 cm^{-1} were attributed to the stretching vibrations of secondary amides (NH). Between 1330 and 1250 cm^{-1} was assigned to free CO bond, meantime the stretching vibrations at 1100 cm^{-1} represented to C–O relation of polysaccharides ethers. The range of 1200–1100 cm^{-1} were observed the hydroxyl bands [21]. Stretching of the secondary amine appeared between 3250–3000 cm^{-1} .

The area between 2900–2800 cm^{-1} shows a decrease in the CH (symmetrical and asymmetric) stretches of the hydrogels that are replaced by the amino acids of the Spirulina algae during adsorption at different concentrations. Halogenated compounds were located at 1400 cm^{-1} was assigned to the C–F and 1000–750 cm^{-1} stretching corresponding to the C–Br and C–I stretches. The fingerprint region of chitosan decreases with respect to the algae increase. This is attributed to the hydrogen bonds and van der Waals interactions of the hydroxyl and carboxylic groups of algae and the amino groups of chitosan.

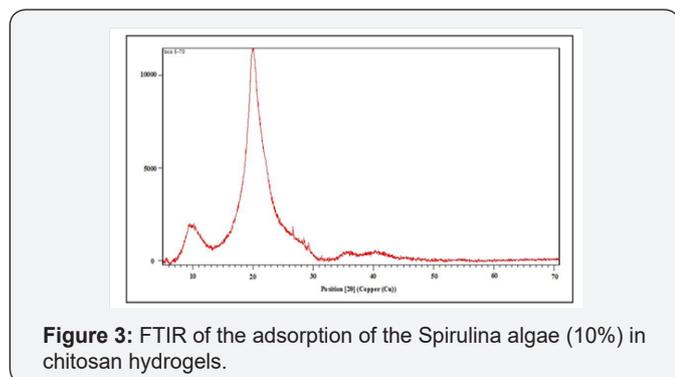


Figure 3: FTIR of the adsorption of the Spirulina algae (10%) in chitosan hydrogels.

Figure 3 shows two peaks at 9–11° and 20° on the 2 θ scale which indicate that the adsorption of the algae is carried out on the surface of the chitosan because if there were a low compatibility the crystalline peaks of each material, in addition, we observed the formation of the amorphous phase indicating that there is a consistency with the FTIR of Figure 2 [22].

Conclusion

Chitosan-based hydrogels can absorb different drugs to develop controlled release systems via transdermal. Greater swelling was observed in hydrogels with 3% chitosan and 10% glutaraldehyde due to an increase in the cross-linking that allows greater water adsorption. A percentage of swelling was obtained between 25–26%. FTIR spectroscopy allowed the observation that the adsorption of amine groups from the Spirulina algae in the fingerprint zone is also verified by the formation of an amorphous phase.

References

- Chirani N, Yahia L, Gritsch L, Motta FL, Chirani S, et al. (2015) History and Applications of Hydrogels. *Journal of Biomedical Sciences* 4(13): 1-23.
- Shetye SP, Godbole A, Bhilegaokar S, Gajare P (2015) Hydrogels: Introduction, Preparation, Characterization and Applications. *Human Journals* 1(1): 47-71.
- Ahmed EM (2015) Hydrogel: Preparation, characterization, and applications: A review. *Journal of Advanced Research* 6: 105-121.
- Chai Q, Jiao Y, Yu X (2017) Hydrogels for Biomedical Applications: Their Characteristics and the Mechanisms behind Them. *Gels* 3(1): 6.
- Nilsen-Nygaard J, Strand SP, Vårum KM, Draget KI, Nordgård CT (2015) Chitosan: Gels and Interfacial Properties. *Polymers* 7(3): 552-579.
- Bhattarai N, Gunn J, Zhang M (2010) Chitosan-based hydrogels for controlled, localized drug delivery. *Advanced Drug Delivery Reviews* 62(1): 83-99.
- Shukla A, Dasgupta N, Ranjan S, Singh S, Chidambaram R (2017) Nanotechnology towards prevention of anaemia and osteoporosis: from concept to market. *Biotechnology & Biotechnological Equipment* 31(5): 10.1080/13102818.2017.1335615.
- Margulis L, Sagan D (2002) *Acquiring genomes. A theory of the origins of species.* Perseus Books Group, New York City, USA.
- Qaseem A, Humphrey LL, Fitterman N, Starkey M, Shekelle P (2013) Treatment of anemia in patients with heart disease: a clinical practice guideline from the American College of Physicians. *Annals of Internal Medicine* 159(11): 770-779.
- Adams M (2009) Spirulina helps treat anemia. *Natural News*.
- Lin YC, Tayag CM, Huang CL, Tsui WC, Chen JC (2010) White shrimp *Litopenaeus vannamei* that had received the hot-water extract of *Spirulina platensis* showed earlier recovery in immunity and up-regulation of gene expressions after pH stress. *Fish Shellfish Immunol* 29(6): 1092-1098.
- Cox L (2014) Spirulina: Nutrition Facts & Health Benefits. *Live Science*.
- Mohamed AI, Elsayed AM, Motagaly A, Ahmed OA, Amin S et al. (2017) Investigation of Drug-Polymer Compatibility Using Chemometric-Assisted UV-Spectrophotometry. *Pharmaceutics* 9(1): E7.
- Wartewig S, Neubert RH (2005) Pharmaceutical applications of Mid-IR and Raman spectroscopy. *Adv Drug Deliv Rev* 57(8): 1144-1170.

15. Sánchez A, Sibaja M, Vega-Baudrit J, Madrigal S (2007) Síntesis y caracterización de hidrogeles de quitosano obtenido a partir del camarón langostino (*Pleuoncodes planipes*) con potenciales aplicaciones biomédicas. *Revista iberoamericana de Polímeros* 8(4): 241-267.
16. Romero-Peñaloza EL (2011) Obtención de hidrogeles de quitosano a partir del micelio de *aspergillus níger* y su estudio en la liberación controlada de cefalexina. Tesis de Licenciatura. Universidad del Valle. Colombia.
17. Domènech B, Romero V, Vázquez MI, Avila M, Benavente J et al. (2016) Chemical and electrochemical characterization of Nafion containing silver nanoparticles in a stripe-like distribution. *RSC Advanced* 6(12):9923-9931.
18. Venkatesan S, Pugazhendy K, Sangeetha D, Vasantharaja C, Prabakaran S et al. (2012) Fourier Transform Infraed (FT-IR) Spectroscopic analysis of spirulina. *International journal of Pharmaceutical & Biological Archives* 3(4): 969-972.
19. Theivandran G, Ibrahim SM, Murugan M (2015) Fourier Transform Infrared (Ft-IR) Spectroscopic analysis of spirulina *Fusiformis*. *Journal of Medicinal Plants studies* 3(4): 30-32.
20. Borgen K (2012) Evaluation of phphysicochemical properties of modified algae protein adhesives. Tesis de Maestria. Kansas State University. USA.
21. Dmytryk A, Saeid A, Chojnacka K (2014) Biosorption of Microelements by Spirulina: Towards Technology of Mineral Feed Supplements. *The Scientific World Journal* 2014: 356328.
22. Wang G, Wang X, Huang L (2017) Feasibility of chitosan-alginate (Chi-Alg) hydrogel used as scaffold for neural tissue engineering: a pilot study in vitro. *Journal Biotechnology & Biotechnological Equipment* 31:766-773.



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