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Synthesis of Chitosan and Carrageenan based Hydrogels for pH Sensing, Urea Adsorption and Dye Adsorption

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Abstract: ***Naturally occurring polymers such as carrageenan and chitosan were used for the synthesis of hydrogel using glutaraldehyde as the crosslinking agent. Characterisation of chitosan and carrageenan based hydrogels for PH sensing, urea adsorption and dye adsorption were conducted. Different compositions of carrageenan-chitosan hydrogels were formulated and optimised the best compositions based on the maximum urea adsorption at hydrogel which can be employed for PH sensing, urea adsorption and dye adsorption. These hydrogels were used in several agricultural, textile industry and biomedical applications.***

Keywords: Carrageenan, Chitosan, hydrogels

1. Introduction

Hydrogels are three dimensional polymer matrices are capable of imbibing large amounts of water, and biological fluids. This property of hydrogels is that the reason behind its varied applications starting from food additives to pharmaceuticals and clinical applications [1]. Synthetic hydrogels prepared from a varied range of monomers have found many applications especially in tissue-engineering scaffolds, as carriers for implantable devices, and drug delivery devices. Out of these applications, at the forefront of this research are hydrogel based drug delivery devices [2]. Synthetic hydrogels provide a good and controlled way during which to administer protein and peptide based drugs for treatment of variety of diseases [3]. Stimuli sensitive hydrogels have enormous potential in various applications. Some environmental variables, like low and elevated temperature, are found within the body [4]. For this reason either sensitive or temperature sensitive hydrogels is used for site specific controlled drug delivery [5]. Hydrogels that are attentive to specific molecules, like glucose or antigens, will be used as biosensors in addition as drug delivery system. Environmentally sensitive hydrogels for drug delivery application also require biocompatibility [6].

Hydrogels are water swollen polymer matrices, with an inclination to imbibe water when placed in aqueous environment. This ability to swell, under biological conditions, makes it a perfect material to be used in drug delivery and immobilization of proteins, peptides, and other biological compounds. Because of their high water content, these gels resemble natural living tissue quite the other style of synthetic biomaterial [7]. Chitosan is inexpensive moreover as nontoxic and exhibits high mechanical strength, hydrophilic character, good adhesion, etc. Thus chitosan has been usually applied as an artificial additive, a supporting material for chromatography and a chelating polymer for heavy metals removal [8-11]. In bio-related applications chitosan has been used for immobilization of biomolecules on solid substrates [12] and biomedicines as a anticoagulant or a wound-healing accelerator because of its biocompatibility [13]. Chitosan is additionally employed as a coagulant in water treatment to get rid of colloidal particles, the same as other polysaccharides, thanks to a known aggregation effect of organic matters in soils [14].

Carrageenans are families of natural linear sulfated polysaccharides that are extracted from red edible seaweeds are widely utilized in the food industry, for its gelling, thickening, and stabilizing properties. Their main application is in dairy and meat products, due to their strong binding to food proteins. In recent years, carrageenans have emerged as a promising candidate in tissue engineering and regenerative medicine applications. It has been mainly used for tissue engineering, wound coverage and drug delivery [15]. Carrageenans contain 15-40% ester-sulfate content, which makes them anionic polysaccharides. It can be mainly categorized into three different classes supported their sulfate content. Kappa-carrageenan has one sulfate group per disaccharide, iota-carrageenan has two, and lambda-carrageenan has three [16]. Carrageenans are large, highly flexible molecules that form curling helical structures. This offers them the power to create a spread of various gels at temperature. It is widely utilized in the food and other industries as thickening and stabilizing agents [17].The main objective of the study is aimed to prepare chitosan and carrageenan based hydrogels for the urea absorption, pH sensing and dye absorption.

2. Experimental

Materials Used: Chitosan powder (>80% DA) and Carrageenan were purchased from Marine hydro colloids Kochi, Kerala. Acetic acid supplied by Merck life science private limited, Mumbai, Glutaraldehyde, Urea Indigo crime

dye, Hydrochloric acid were supplied by Nice chemicals (p) Ltd, Kochi.

Hydrogel Preparation: The carrageenan was taken as base component and chitosan solution was mixed with it with the help of magnetic stirrer. Chitosan was also prepared by adding carrageenan in various proportions to it. Crosslinking agent glutaraldehyde was added to the mixed solutions. The resulting solution of different composition are transferred to petri dishes and dried under 80^0C in air oven. Resultant films are collected.

Measurement of Urea: 1% urea solution was prepared and exposed to the hydrogel films and the amount of urea adsorbed was measured at equal intervals of time (24 hr, 48hr, 72hr) for continuous 7 days. The sample solution are taken out from the container and placed in to weighted petri dish and also weighted and dried at 70^0C at oven and weighed.

Measurement of Dye Adsorption: Dye adsorbed was conducted by UV spectrometer. Dye selected was indigo crime (289nm). 1% of indigo crime solution was prepared by adding 0.01g of indigo dye in 100ml water then made in contact with the hydrogel and measured the UV spectroscopy reading for continuous 7 days.

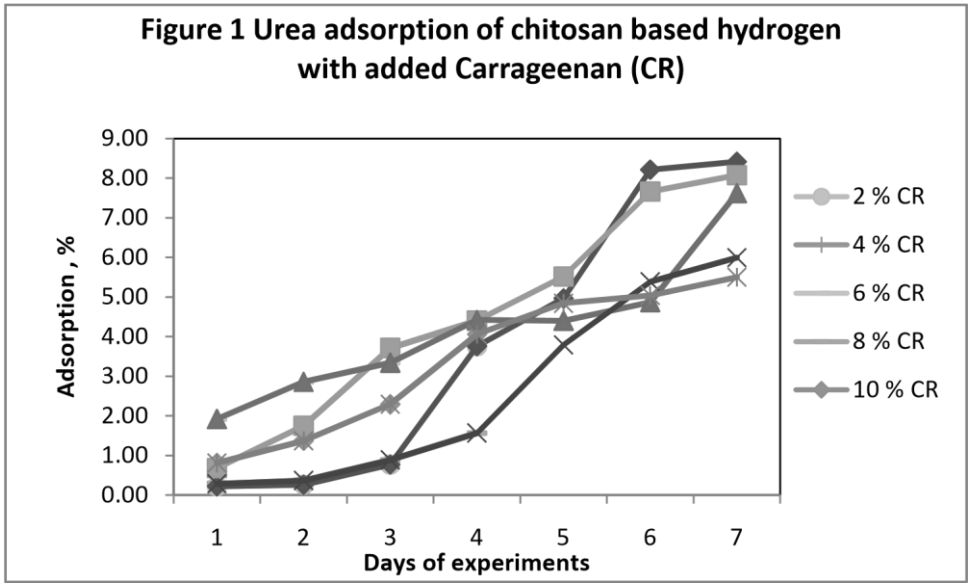
The pH Sensing: Acidic solution was prepared by 1ml of HCL in 100ml water. The acidic solution is added to the samples containing beaker. At equal intervals of time at continuous 7 days determined the p H of the each solution using pH meter.

FTIR Analysis: FTIR offer quantitative and qualitative analysis for organic and inorganic samples. Fourier transform infrared spectroscopy identifies chemical bonds in a molecule by producing an infrared adsorption spectrum. The spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to screen and scan samples for many different components. FTIR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information. The measurements were carried out on chitosan/carrageenan and carrageenan/chitosan film and compare with spectrum.

DSC: Differential scanning calorimetry (DSC) was used to measure the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. The measurements were carried out on chitosan/carrageenan and carrageenan/chitosan film and compare with graphs.

3. Results and Discussion

Figure 1 shows the Urea adsorption results of Chitosan based hydrogen when modified with Carrageenan in various percentages. Figure 2 shows the same experiments results with Carrageenan based hydrogel with varying quantity of Chitosan. In both the cases the adsorption increases as days proceeded. It shows that the hydrogels are successful in urea adsorption process and can be used in urea adsorption in fertilizers.



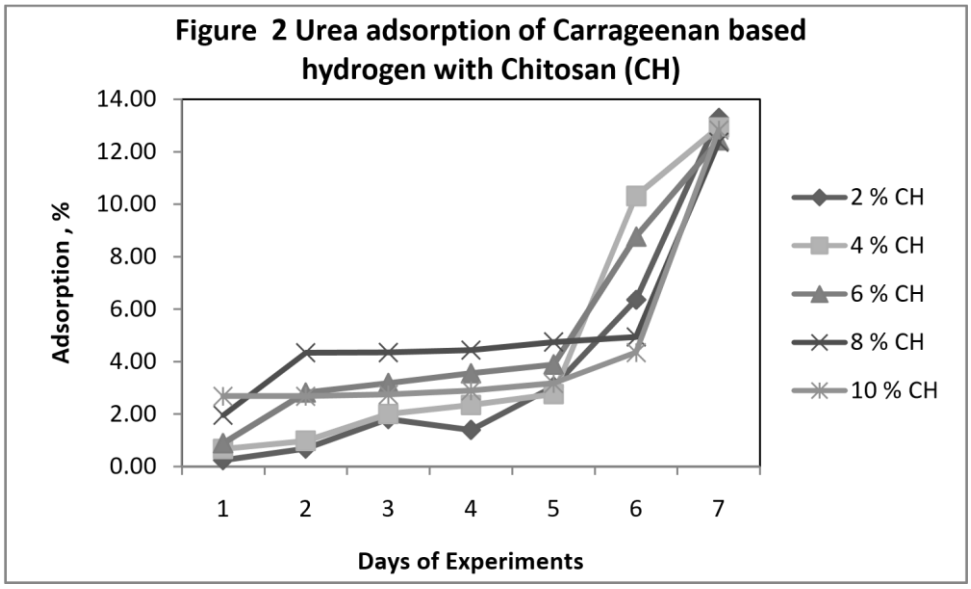


Figure 3 shows the dye Adsorption characteristics of Chitosan / Carrageenan blend (contains 6 % carrageenan) and Carrageenan / Chitosan (contains 6 % Chitosan) based hydrogels. It shows the UV absorbance values of the solutions in contact with the hydrogels. The absorbance is getting reduced as the hydrogels are absorbing the dyes as time proceeded. The time increases, the presence of dye in the solution is getting reduced due to the adsorption of dyes with the hydrogel present in it. Within 7 days it is found the presence of dye negligible.

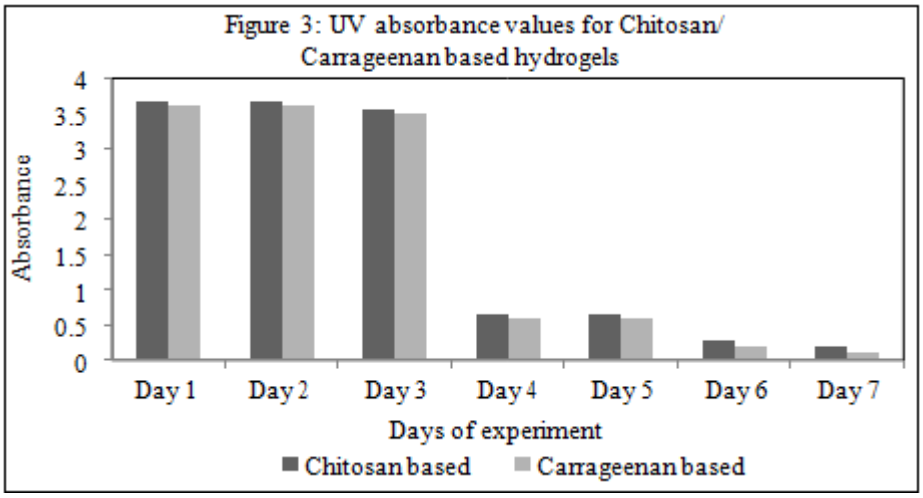
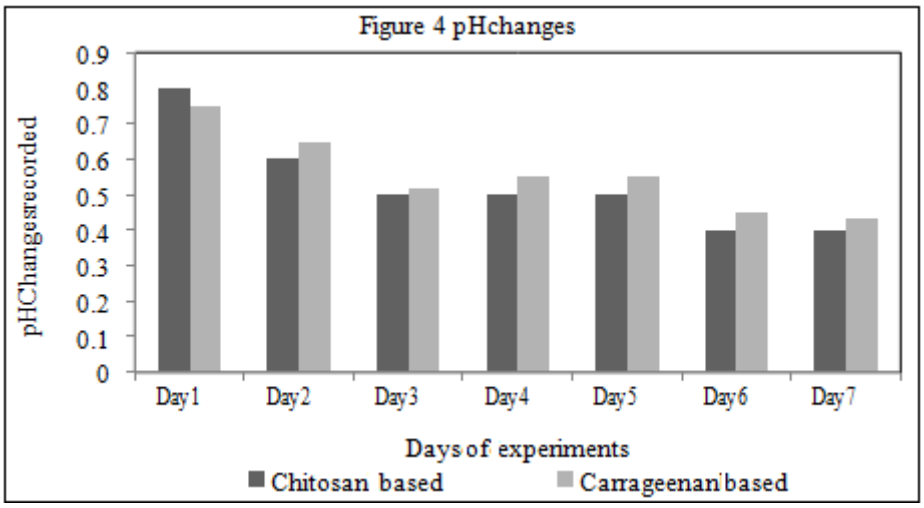


Figure 4 shows pH changes for the Chitosan/ Carrageenan blend (contains 6 % carrageenan) and Carrageenan/ Chitosan (contains 6 % Chitosan) based hydrogels. The values of pH is decreasing as the contact time increases, it indicates the adsorption characteristics of hydrogels. The change in pH is marginal which may be due to the neutralisation process of hydrogels by acidic and basic groups.



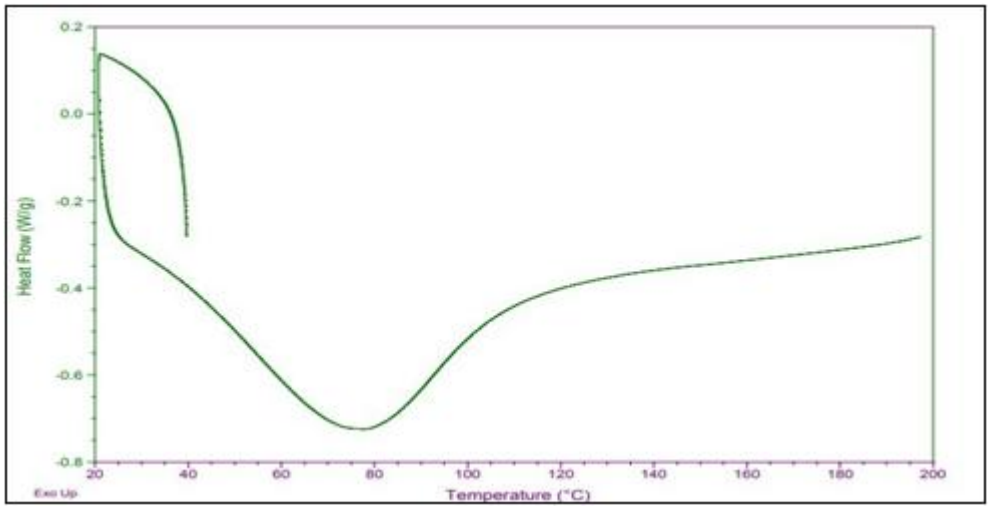


Figure 5: DSC spectrum of Chitosan / Carrageenan hydrogel

Figure 5 is the DSC graphs of Chitosan/ Carrageenan blend hydrogels. DSC gives the thermal analysis technique in which the heat flow in to or out of a sample is monitored as a function of temperature or time while the sample is exposed to a controlled temperature program. Here carrageenan blended with chitosan the standard melting point range of carrageenan 50-70^{0}C. The standard temperature range of chitosan is 101-200^{0}C. Based on the DSC curve the melting temperature range between 70-85 ^{0}C, so that the melting point slightly increased because of the presence of chitosan.

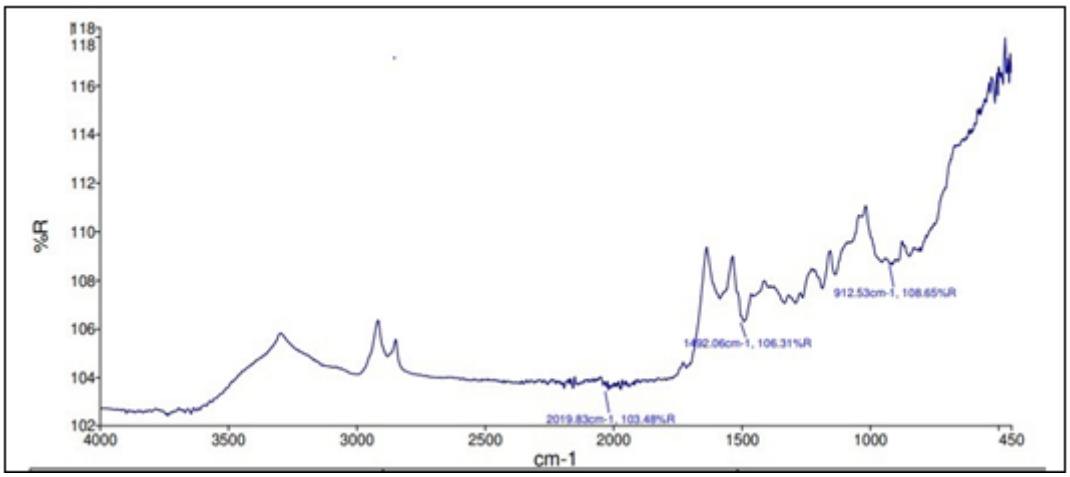


Figure 6: FTIR spectrum of chitosan /carrageenan hydrogel

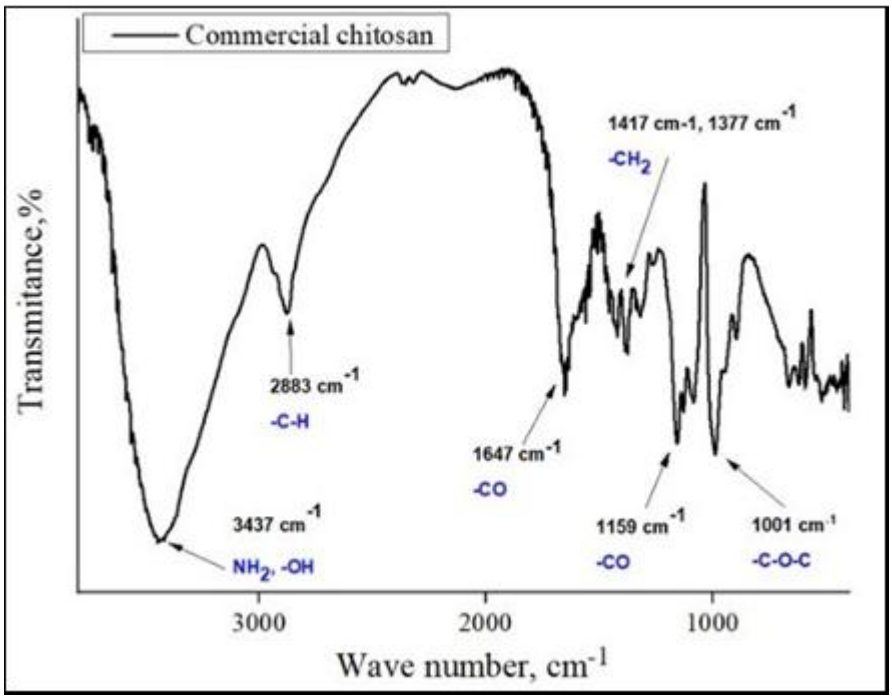


Figure 7: FTIR of Chitosan [18]

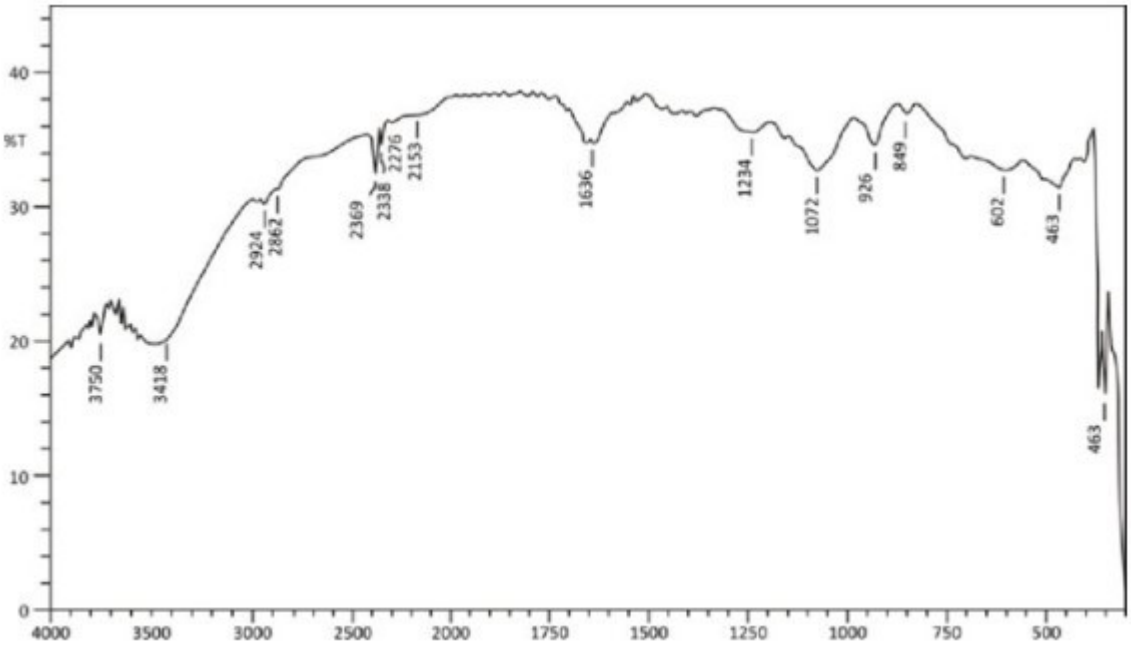


Figure 8: FTIR of Carrageeenan [19]

Figure 6, Figure 7 and Figure 8 represents the FTIR spectrum of the Chitosan / Carrageenan blend, Commercial Chitosan and Carrageenan respectively. The peaks reveal the presence of Chitosan and carrageenan peaks in the blend hydrogels. The peak at 1450 cm^{-1} is indicating the presence of CH_3 group. The peak at 2019 cm^{-1} is indicating of O-H group. Chitosan FTIR peak at 912 cm^{-1}out of plane bending N-H_3 out of plane bending C-O, 3437 peak for NH_2, 2883 for C-H, 1647 for C-O.

4. Conclusion

Chitosan and carrageen an blend based hydrogels were cross linked and super adsorbing hydrogels were prepared and used for pH sensing, urea adsorption and dye adsorption. Various composition of hydrogel was prepared by varying the composition of chitosan and carrageenan. The most adsorbed hydrogel was studied by urea adsorption analysis. For urea adsorption most highly adsorbed composition was with 6 % Carrageenan. It can be visually identify the colour reduction. At increasing the time increasing the adsorption was observed. The hydrogels were characterization by FTIR and DSC. Based on the DSC curve the temperature of melting observed range between 70-85 ^{0} C, the melting point slightly increased because of the presence of chitosan. Hydrogels can give good adsorption of urea adsorption and dye adsorption which is highly economical and environmental-friendly. The adsorption of urea indicated that the carrageenan based chitosan hydrogel composition had promising application in agriculture. The dye adsorption

property wildly use in textiles industry etc. These hydrogels can be used in several agricultural, textile industry and biomedical applications.

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