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Chemistry

AGAR / CHITOSAN BLENDS FOR THE PREPARATION OF NOVEL HYDROGELS FOR PH SENSING, UREA ADSORPTION AND DYE ADSORPTION

Sravan Krishna P	Department Of Chemistry MPMMM SN Trusts College, Shoranur, Kerala, India.
Neetha John*	CIPET: IPT -Kochi, HIL Colony, Edayar Road, Udyogamandal. P.O. Eloor, Kochi, Kerala, India- 683501. *Corresponding Author
S. Anbudayanidhi	CIPET: IPT -Kochi, HIL Colony, Edayar Road, Udyogamandal. P.O. Eloor, Kochi, Kerala, India- 683501.
K. A. Rajesh	CIPET: IPT -Kochi, HIL Colony, Edayar Road, Udyogamandal. P.O. Eloor, Kochi, Kerala, India- 683501.

ABSTRACT Hydrogel posses a degree of flexibility very similar to natural tissues, due to their significant water content. Thus they find potential biomedical applications owing to their excellent bio-compatibility, bio degradability and non toxicity. The main highlight of the work is that it is taking naturally occurring polymers such as agar and Chitosan for the synthesis of hydrogel. Different compositions of Chitosan/Agar hydrogels were formulated and optimised with respect to pH sensing, Urea absorption and dye adsorption. Chitosan/Agar hydrogels are found to be suitable and a potential candidate for several agricultural and bio medical applications.

KEYWORDS : Agar, Chitosan, Hydrogels, Biosensors etc.

INTRODUCTION:

Hydrogels are cross-linked networks of the same or different types of polymers with high capacity for water absorption [1, 2]. Hydrogel forming polymers have hydrophilic functional groups in their polymeric structure [3]. The hydrophilic groups enable the hydrogel to absorb water and watery fluids that results in hydrogel expansion and occupation of larger volume, the process which is known as swelling. During swelling, the cross-linked structure of hydrogels prevents the dissolution and destruction of the hydrogel cross-links [4, 5].Cross-linking density, the quantum of cross-linked chains, governs the hydrogel swelling ratio and is inversely proportional to water volume. In addition, presence of hydrophilic or hydrophobic functional groups on the polymer chain determines the swelling rate [6, 7]. Hydrogels have ability to swell in water or water based solutions. Because of high quantity of water absorption, these structures can be analogous to mortal body apkins.

To get chemical crosslinking, a low molecular weight crosslinking agent and a polymer must be added to the reaction mixture. The hydrophilic linear polymer chains dissolve in water in the absence of crosslinking points due to the polymer chain and water thermodynamic compatibility. In the presence of crosslinking points, solubility is counterbalanced by the retractive force of the elasticity of the network's crosslinking points [8, 9]. Hydrogels are classified based on their physical properties, swelling nature, method of preparation, origin, ionic charges, sources, rate of biodegradation, and observed nature of cross linking. It has recently been used to overcome the disadvantages of using only physical or chemical hydrogels with a high liquid uptake capacity over a wide pH range and a higher sensitivity to pH changes when compared to chemical hydrogels. Environmental conditions similar as pH, temperature, certain chemicals [10-12], light, pressure and electrical field [3] are influential on hydrogel lump.

In the current work it is proposed to develop novel hydrogel based on Agar/ Chitosan crosslinked with gluteraldehyde in various proportions and studied the Dye, Urea adsorption and effect on pH.

Experimental:

Materials Used:

Chitosan powder (>80% DA) and Agar 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 Agar was taken as base component and Chitosan solution was mixed with it with the help of magnetic stirrer. Chitosan was also prepared by adding Agar in various proportions to it. Crosslinking agent Glutaraldehyde was added to the mixed solutions. The resulting solution of different composition are transferred to petridishes and dried under 80^{0}C in air oven. Agar and Chitosan blends were prepared with Chitosan was considered as the base. Chitosan solution was made by dissolving in 1% acetic acid solution. Magnetic stirrer was primarily employed in mixing acetic acid and Chitosan. Agar solution was made by mixing agar in minimum amount of water. Two solutions were thoroughly mixed using a magnetic stirrer. Glutaraldehyde which acts as the crosslinking agent was added drop continuously until it reaches complete homogenization. The resulting solutions of different composition were transferred into sterile Petri dishes and dried less than 80 ^{0}C in air oven. Same method was followed with Agar as the base material.

Urea Adsorption: Small pieces of samples of each composition were pre weighed and are kept in bottles. 1% urea solution was added to them separately; add samples of each composition into the Petri dishes and then once again weight was taken. Petri dishes were kept in oven to dry. This method was followed for all compositions for 7 consecutive days.

Dye Adsorption: Dye employed in this process was indigo crime (289nm), dye solution was made and sample was introduced into it and tested for 7 consecutive days. UV Spectroscopy was employed to check colour adsorption for 7 days.

Sensing of pH: 1% HCl solution is used in this process, selected sample were immersed in acid solution and using pH meter reading was taken for 7 consecutive days. DSC and FTIR were also taken for the hydrogel samples.

RESULTS AND DISCUSSION:

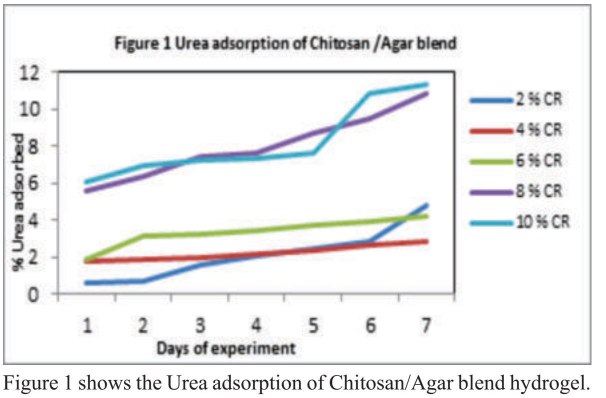

Figure 1 shows the Urea adsorption of Chitosan/Agar blend hydrogel. The results are clearly giving evidence that as the time increases adsorption increases due to the hydrophilic nature of the hydrogels. As the amount of Agar increases the effect is more pronounced, agar is supporting the Chitosan and enhancing the adsorption characteristics.

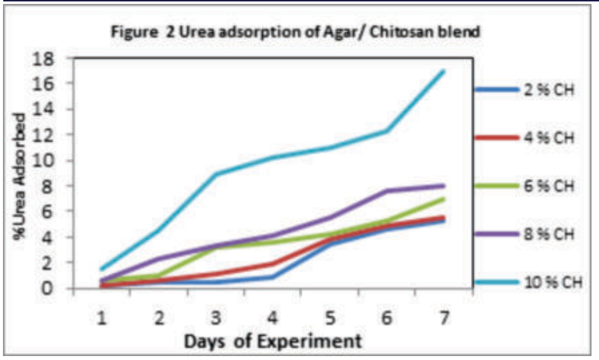

Figure 2 shows an exactly similar behavior for Agar based hydrogels. The Urea adsorption increases as the amount of Chitosan increases in the blends. Therefore both Chitosan based and Agar based formulations are working in similar manner as shown in the figures. Among the two proportions Agar based hydrogels are showing higher values compared to Chitosan based hydrogels.

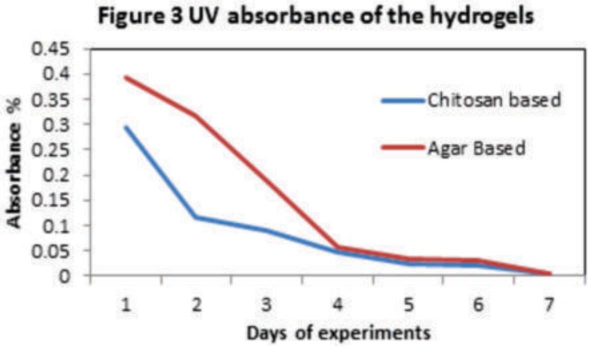

Figure 3 shows the UV absorbance values of hydrogels based on Chitosan and Agar with the days of experiments. It is showing the absorbance values decreases as day's increases. The Colour of the dye got reduced. Both the types of hydrogels show similar results.

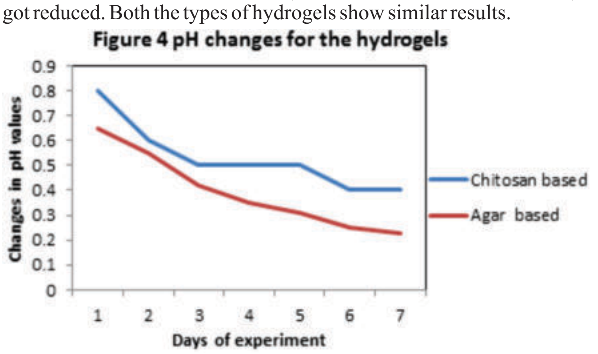

Figure 4 shows the pH changes when the hydrogels which are in contact with the solutions. It shows the hydrogels are sensitive to the presence of Hydrogen atoms.

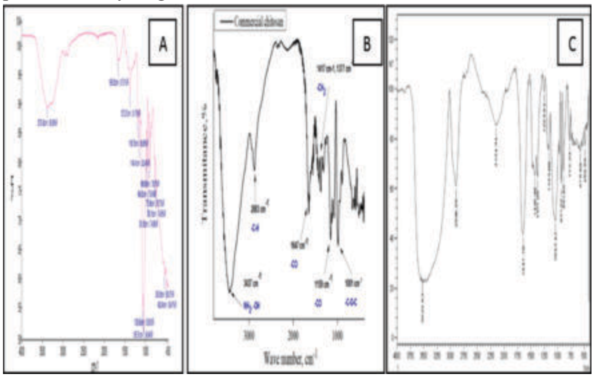

Figure 5 A) FTIR spectrum of Agar / Chitosan blend, B) FTIR of Commercial Chitosan [13] C) FTIR of AGAR pure form [14]

FTIR spectra of agar based Chitosan hydrogel film shows absorption bands attributed to N-H stretching at 3375.42cm^{-1}.Which is the backbone of Chitosan chain. The peak corresponding to CH_3 group is found at 1373.37cm^{-1}. The peak corresponding to the stretch O-H is found to be at 3375.42cm^{-1}.The peaks revealed at 1180.78 cm^{-1}, 1149.41cm^{-1}, 1067.61 cm^{-1}, represents C-O-C stretching.

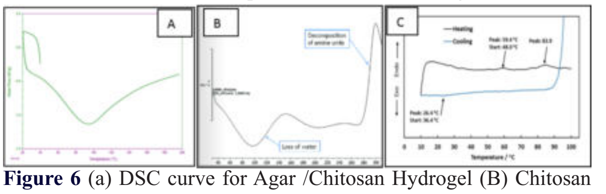

Figure 6 (a) DSC curve for Agar /Chitosan Hydrogel (B) Chitosan Pure [15] (C) DSC curve of Agar [16]

DSC result of the Agar based Chitosan hydrogel film is shown in the Figure 6. From the figure it is evident that the melting point of the synthesized film ranges from 85^{0}C -95^{0}C which corresponds to the melting point of Agar that is 85^{0}C -95^{0}C itself. This can be finalized that the thermal properties of the Agar based Chitosan film does not have a significant change while comparing with the properties of the pure agar. It is evident from the graph that the thermal resistance of Agar got improved by blending with Chitosan.

CONCLUSIONS:

From this study about synthesizing Agar and Chitosan based hydrogels, it has been concluded that the Agar based Chitosan hydrogel composition is found to be the best and most suitable combination for Urea adsorption. And in further study this composition of Agar and Chitosan was further subjected for dye adsorption and pH sensing. It was evident that the subjected composition was found suitable for dye adsorption and for pH sensing as well. By analyzing the characterization techniques, from FTIR all the peaks of the functional groups were identified from the FTIR spectrum and from the DSC curve, it shows there aren't any significant changes in the thermal properties while comparing with the pure Agar and the synthesized film has a thermal stability up to 85^{0}C. Agar based Chitosan hydrogel is a potential candidate for several agricultural and bio medical applications Especially for Controlled desorption of urea for agricultural purposes, Removal of dye effluents in the textile and other dye related industries and as a medium for sensing pH.

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