RESEARCH
www.commprac.com
ISSN 1462 2815

# SWELLING STUDIES OF PHYSICAL AND CHEMICAL CHITOSAN HYDROGELS

**Gorriparthi Varalakshmi [1]*, and Anitha C. Kumar [2]**

[1] PhD Research Scholar, Department of Chemistry, Acharya Nagarjuna University,
Nagarjuna Nagar, Guntur, AP, India.
[1] Assistant Professor, Department of Chemistry, Samskruti College of Engineering and
Technology, Ghatkesar, Hyderabad, Telangana, India.
[2] Professor, School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India.
*Corresponding Author Email: vgoriparthi09@gmail.com

**DOI: 10.5281/zenodo.11407444**

### Abstract

Hydrogels have been available for more than half a century and they have many uses in various practices ranging from industrial to biological. Hydrogels are a polymeric network that can able toabsorb a large quantity of water and swells up to an equilibrium point. The water absorbing capacity of hydrogels depends on hydrophilic functional groups and space availability in the polymeric structure. Here in this work, we prepared hydrogels from an animal based natural polymer-Chitosan. Crosslinkers plays an important role in the properties of hydrogels. Chitosan hydrogels were prepared without crosslinker and by using different concentrations of glutaraldehyde, which is the most commonly used crosslinker. Chitosan hydrogels can hold a large amount of water by swelling. Swelling nature of uncrosslinked and crosslinked hydrogels were studied in aqueous medium at various temperature and in different $P^H$ mediums at different intervals of time.

**Keywords:** Chitosan, Glutaraldehyde, Swelling properties, Hydrogels.

## INTRODUCTION

Hydrogels are hydrophilic polymer materials that are cross-linked, three-dimensional and can retain, swell, and hold large volumes of water or aqueous fluids (1). The associations are comprised of homopolymers or co-polymers and are insoluble due to the presence of chemical cross-links (tie-points, junctions), or physical cross-links, such as embarrassments or crystallites (2). These gels are effective in day-to-day life and used extensively in food, husbandry manufacturing, cosmetic make up foundations, medicine, and medical discourse etc. Currently, Hydrogel get wide orbit of applications because of their lower berth price, nonpoisonous, and environment-sociable nature. Hence, these are used as biomaterials that reveal sensible purpose in several fields of biomedical or therapeutic industry (3).

Chitosan, is a linear polysaccharide collected of β-(1-4)-linked d-glucosamine and N-acetyl-d glucosamine. Chitosan is derived from Chitin, which is extracted from hard skeleton matter of shellfish, lobster, shrimp, and crabs. The structure of Chitosan is shown in figure 1. It has lots of applications in the medical, health, and pharmaceutical industry because of its biocompatible nature. Any form of chitosan (solution, dryflakes, and fine powder) can dissolve in organic acids such as acetic acid, formic acid, tartaric acid, and citric acid of $P^H$ <6. Crosslinked chitosan is frequently used to prepare microspheres of their form, they have been widely used for drug delivery such as antibiotics, anticancer agents, vaccines, etc. (4, 5). The positive amino group of chitosan is very active and readily binds with negatively charged surfaces such as mucosal membranes. The free amino group of chitosan can form crosslinked polymer networks with dicarboxylic acids to build up the material. It forms gels with several multivalent anions. The hydrogels of chitosan, like other hydrogels, contain much water. Part of this water is tightly bound to the polymer and the rest is present as free water. Chitosan and its derivatives are one of the best-opted material for medical and pharmaceutical industries, particularly in their swollen state but possess low mechanical strength, to overcome this disadvantage crosslinking is the best method most commonly used crosslinkers are aldehyde, epoxy, starch, guar-gum, epichlorohydrin, sodium tripolyphosphate etc.

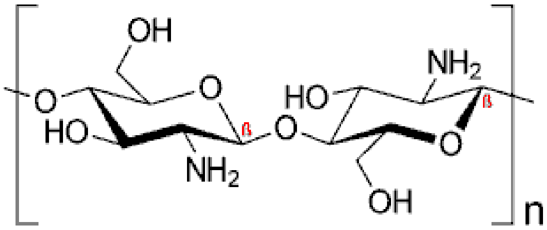


**Figure 1: Structure of Chitosan**

In the present study we have chosen glutaraldehyde as the crosslinker. We were prepared chemically crosslinked chitosan hydrogels with glutaraldehyde, which is an extreme crosslinker. The aldehyde group of glutaraldehyde interacts with the amino group of chitosan, thus forming Schiff's bases. The potentiality of hydrogel membrane depends on many factors. This paper also reports the variation of swelling ratio dependents on temperature, $P^{H,}$ and concentration of the crosslinking agent.

## MATERIALS AND METHODS

### Materials:

Chitosan (Ch), Glutaraldehyde (GA) & Acetic acid (Ac) are all chemicals purchased from Avra Synthesis Private Ltd, Hyderabad, Telangana, India. All obtained chemicals were used withoutany further purification. Buffer solutions of $P^{H}$=4, 7&9.2 purchased from Quality traders, Gorantla, Guntur.

Millipore water is used from the Merk Millipore system

### Methods:

**Hydrogel Preparation:** Chitosan hydrogels were prepared with varying concentrations of glutaraldehyde from 0% to 0.125%. Initially chitosan allows for dissolution in a dilute acetic acid medium with stirring for 8-10 hours, after completion of dissolution chitosan is added with glutaraldehyde of various concentrations and continued stirring for 30-60 min.

**Swelling experiments:** For the swelling studies we prepared the dry films from the gels. The swelling property of dry film of hydrogels with and without cross-linker were examined by dropping 0.15gm of dry film in deionized water at room temperature at particular intervals of time until reached constant (stable weight) weight, simultaneously measuring the film weight in swollen state at each interval, In the same way, dry sample of known mass (wd) allow to float in a buffer solution of $P^{H}$=4,7 & 9.2. After a particular period (t) dry film remove from the buffer and their swollen sample weight (Wt) was noticed after whipping with filter paper to remove excess water, the water-retaining capacity of the film known Experimentally, the percentage swelling ratio of a polymeric hydrogel can be defined by mass difference process and is characterized by the following equation.

$$\text{Percent of Inflammation} = [(Wt-Wd)/Wd] \times 100$$

Where, Wt= mass of inflamed gel and

Wd = mass of dehydrated gel (dry gel).

**FTIR Studies:** Cary 630FTIR with diamond ATR, Agilent Technologies Ltd., was used to study the hydrogel samples within the wavelength range of 4000-600cm$^{-1}$. Each spectrum was measured on an average of 64 scans at aspectral resolution of 4cm$^{-1}$.

## RESULTS AND DISCUSSION

Polymeric gels are inter-linked either physical and chemical interconnecting or thus the cross-linking implicit as a molecule at any rate of its size. The minor modifications are takes place in a polymeric gel by varying upon ecological factors such as temperature, pH, electric charge, and enzyme or ionic species, which lead to different physical texture of the gel. The inflammation property of hydrogels is due to degree of ionization of the cross-linking of monomers with the functional groups present in a polymer chain (6). Chitosan-based hydrogels are of two types (a) physically crosslinked gel and (b) chemically crosslinked gels. The first one is obtained by the weak wander Waals interaction and the second one is obtained via covalent crosslinking agents or ionic crosslinking agents. Figure 2 shows the schematic representation of the crosslinked hydrogel formation.

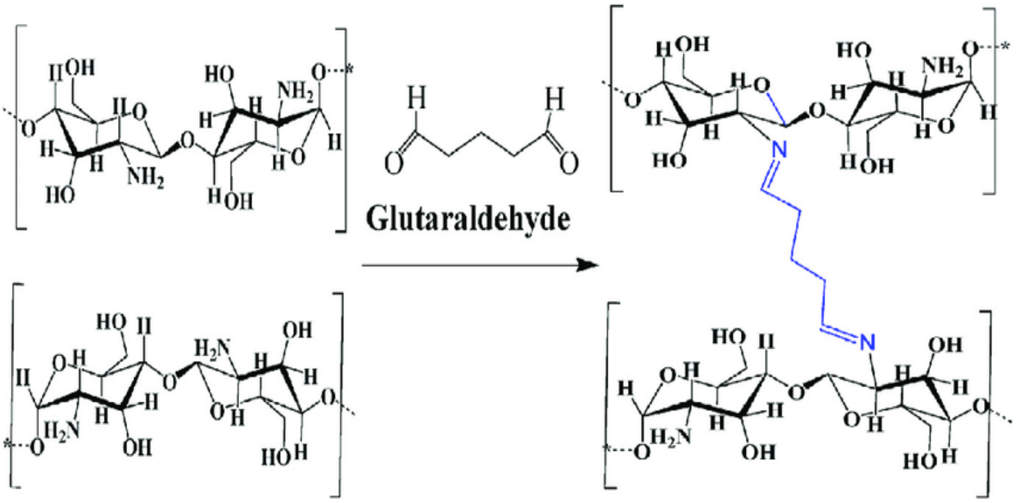


**Figure 2: Schematic representation of the crosslinked hydrogel (cross linker – glutaraldehyde)**

**Preparation of chitosan hydrogel without crosslinker(Physical Hydrogel)**: Prepared 0.5, 1, 1.5, 2, 2.5, 3 and 3.5 percentages of chitosan in 10ml of 2% aqueous acetic acid at room temperature with continuous stirring for complete dissolution (8-10 hrs) and results a clear and viscous fluid. Transfer it to a sample bottle, gel nature was observed with concentrations (%) of 2.5, 3 & 3.5. These gels were a stable minimum of 2 days at room temperature, no gel was observed with remaining concentrations even after 7-10days. In this case, gels formed due to self-crosslinking of chitosan polymer, but at low concentrations, it fails. Decaying of gels nature was observed while keeping samples at room temperature with time and mentioned in table 1.

**Table 1: The chitosan gel preparation at various concentrations of chitosan**

| s.no | %chitosan(ch) | volume of ch(ml) | Status of Gel formation | Gel formation time(hrs) | Gel decay time (days) |
|---|---|---|---|---|---|
| 1 | 0.5 | 10 | No gel | ----------- | ---------- |
| 2 | 1 | 10 | No gel | ----------- | ----------- |
| 3 | 1.5 | 10 | No gel | ----------- | ----------- |
| 4 | 2 | 10 | No gel | ----------- | ----------- |
| 5 | 2.5 | 10 | Gel | 6-8 | 1 |
| 6 | 3 | 10 | Gel | 6-8 | 2 |
| 7 | 3.5 | 10 | Gel | 6-8 | 2 |

**Preparation of chitosan hydrogel with varying concentrations of glutaraldehyde crosslinker:** Since we got comparatively stable hydrogels with 3% of chitosan, it was selected for crosslinking. Solutions were prepared in the similar method and we prepared five different hydrogel samples by kept constant concentration of chitosan and varied the glutaraldehyde concentration from 0% to 0.125%. The details are given in the table 2.

**Table 2: The chitosan gel preparation at various concentrations of glutaraldehyde crosslinker (Gha)**

| s.no | %ch | Vol. of ch (ml) | %Gha | Vol. of Gha(ml) | Status of Gel formation | Gel formation time(mins) | Gel(5ml) decay time (days) |
|---|---|---|---|---|---|---|---|
| 1 | 3 | 10 | 0.025 | 0.33 | No gel | 30 | ------ |
| 2 | 3 | 10 | 0.05 | 0.33 | No gel | 30 | 1 |
| 3 | 3 | 10 | 0.075 | 0.33 | Gel | 30 | 2 |
| 4 | 3 | 10 | 0.1 | 0.33 | Gel | 30 | 3 |
| 5 | 3 | 10 | 0.125 | 0.33 | Gel | 30 | 4 |

As have seen in table 2, glutaraldehyde 0.125 % gels were stable up to 4 days. The photographs of the same gel on day 3 and day 5 are shown in figure 3.

**Figure 3: Hydrogel on day 3 followed by day 5(3% chitosan with 0.125%gluteraldehyde)**

**Swelling studies:** These studies help to know the gel's stability in a water medium. Dry films were prepared from the same gel combination solutions. To study the swelling nature, a piece of film is weighed and dropped in deionized water (PH-7). The weight of the swollen film is measured in a regular interval. The swelling nature of chitosan physical gel at different temperature were studied and the results are shown in figure 4. The swelling ratio increases from with increase in temperature. It might be due to the temperature help to break the internal bonds ie; hydrogen bonds in hydrogel and freely allow the water and attained an equilibrium point in approximately 100 mins.

The crosslinked gel with crosslinker 0.125% is also analyzed the same way at varying temperatures in deionized water (PH-7) for 100minutes in an interval of 10mins. The results are shown in the same figure4. In this case equilibrium was attained so early at 50 to70min and noted maximum swelling ratio (%S) is 250 at $46^0$c which is low compared to physical gels. In the case of physical gel, the value is 965. This low value in crosslinked hydrogel might be due to strong covalent bonds in the internal structure, it does not allow the hydrogels to swell by restricting the free movement of the chain and water absorption capacity.

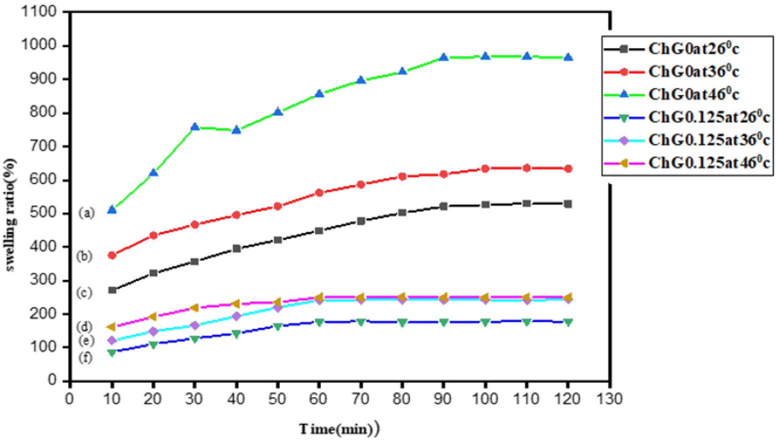


**Figure 4: Swelling studies of noncrosslinked chitosan and crosslinked chitosan in water ($P^H$=7) at various temperatures.**

Hydrogels are normally formed by the crosslinking of linear polymers, depending on the type of crosslinker, hydrogel membranes are of two types Covalent and ionic, glutaraldehyde is one of the best covalent cross-linker which leads to the formation of covalent linkages between the polymeric chain. Crosslinked hydrogels vary in properties compared to noncrosslinked, particularly in their molecular structure, ionizing capacity, hydrophilicity, and degree of crosslinking. Owing to a change in crystallinity, swelling behavior differs from crosslinked to noncrosslinked.

The swelling behavior of covalent/ionic hydrogel membranes depends on external factors including the nature of the crosslinker, degree of crosslinking, the effect of time, temperature, theproportion of the crosslinker, the volume of the cross-linker, and the $P^H$ of medium. During the swelling amino group of chitosan polymer undergoes protonation, which describes the rate of swelling. Interactions of polymer to crosslinker and degree of swelling are determined by many factors, $P^H$ of the swelling medium is one among them.

The swelling behavior of the hydrogels in different $P^H$ were also studied. Figure 5 shows the swelling behavior of noncrosslinked hydrogel in buffer solutions of $P^H$=4, 7and 9.2 at room temperature. It was shown high values at $P^H$=4 and low values at $P^H$=7and 9.2, which indicates the swelling properties of hydrogel films elevated at low values and not significant with increasing values of $P^H$. Figure 6 shows the behavior of crosslinked hydrogels with crosslinker 0.125% at various $P^H$ values (4,7&9.2). The results shows that the swelling ratio is predominately high at lower $P^H$=4 and gradually decreases with increasing $P^H$ (7&9.2). Noncrosslinked Gels swollen more in acidic media ($P^H$=4) and shows a high swelling ratio than crosslinked gels. Usually, we are expecting a high swelling ratio with increasing densities of crosslinker 0.125>0.1>0, but practically it has proven the reverse order. The swelling ratio %S is dependence on $P^H$ in the case of crosslinked membranes and they are high at $P^H$=4, but low at $P^H$ (7&9.2). The change in $P^H$ causes for protonation of an amino group of chitosan and various concentrations of crosslinker were responsible for obtaining different values of the swelling ratio. The swelling behavior of crosslinked gels at various $P^H$ are shown in figure 6.

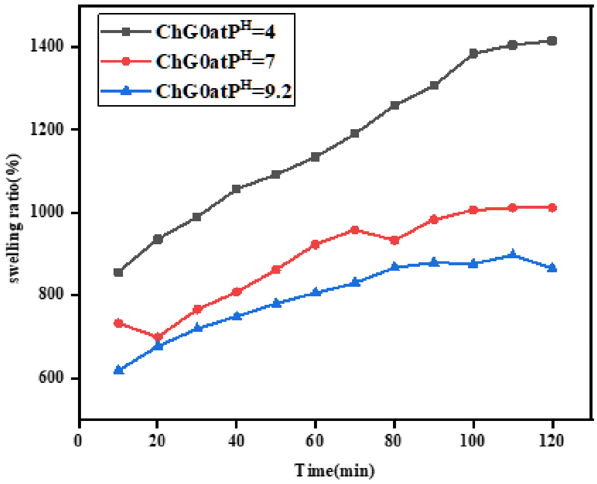
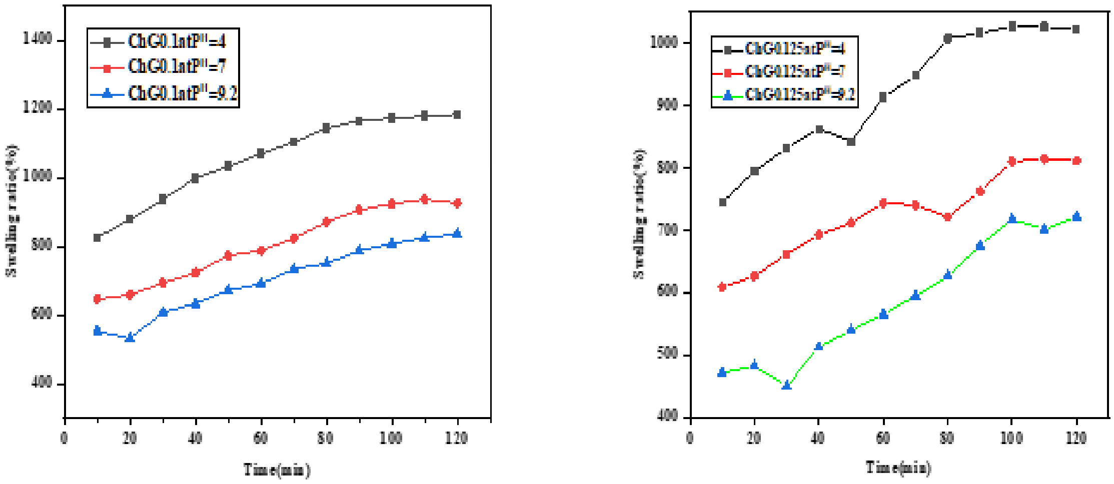


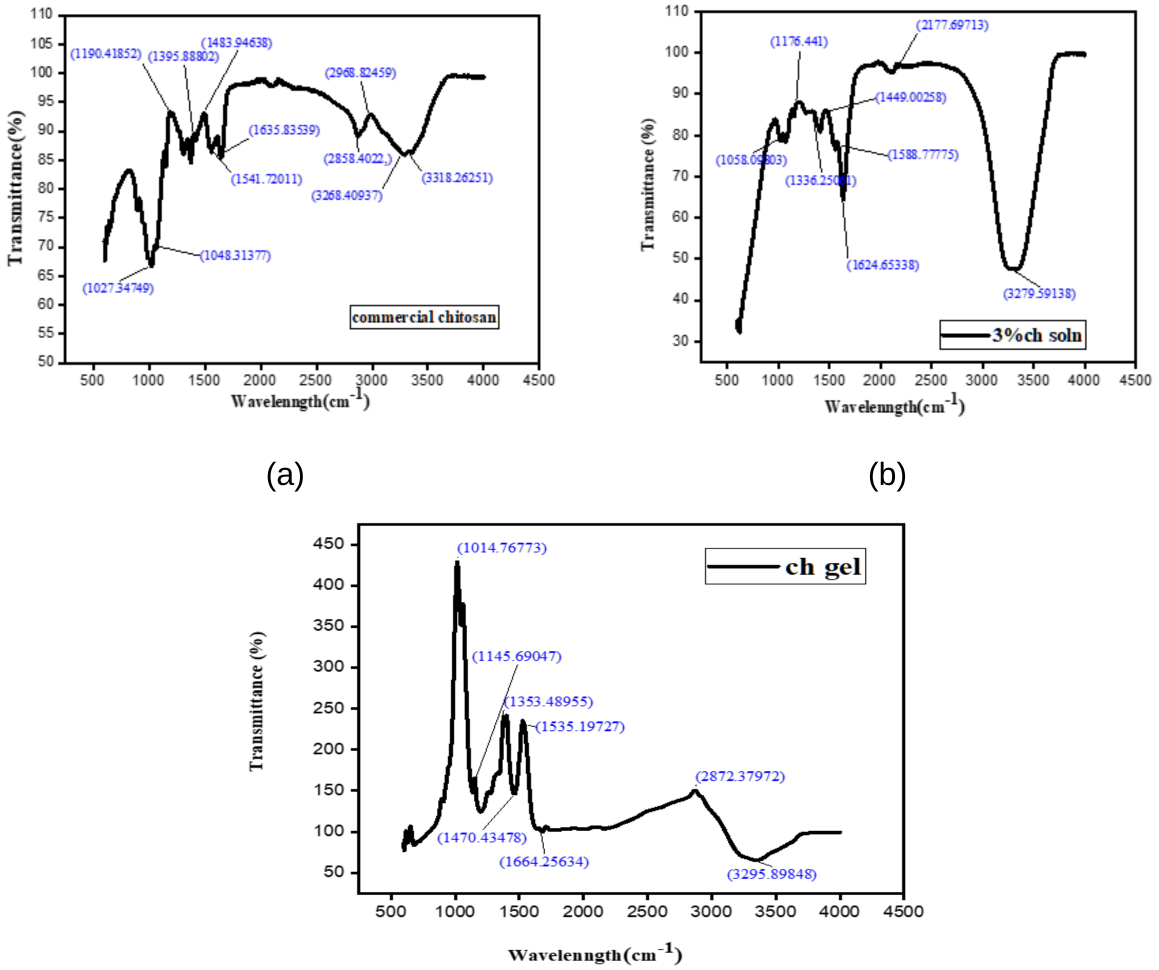
**Figure 5: Swelling behavior of uncrosslinked hydrogel at various $P^H$ =4, 7&9.2**



(a) (b)

**Figure 6: Swelling behavior of crosslinked hydrogels at various $P^H$ (a) 0.1% and (b) 0.125%.**

**FTIR Studies:** Commercial chitosan, 3%chitosan solution in acetic acid, which is noncrosslinked and crosslinked chitosan with glutaraldehyde (0.125%Gha) were analyzed and the results are shown in figure 7a,b and c.



(a) (b)

(C)

**Figure 7: FTIR Spectrum of commercial chitosan (a), 3%chitosan solution in acetic acid(noncrosslinked) (b) and crosslinked chitosan with glutaraldehyde (c).**

With commercial chitosan, N-H and O-H stretching vibration bands were observed at corresponding wavelengths were found at 3268 cm$^{-1}$, 3318 cm$^{-1}$respectively, same stretching vibrations were found at 3279 cm$^{-1}$, 3295 cm$^{-1}$ for solution and gel. 2968 cm$^{-1}$, 2858 cm$^{-1}$ can be attributed to C-H stretching vibrations of symmetric and asymmetric forms and the same (C-H) stretching vibration of the corresponding wavelength reported as 2177 cm$^{-1}$ for solution and 2873cm$^{-1}$ for gels.1635 cm$^{-1}$ intensity band observed due to $C{=}O$ stretching of amide I which is slightly varied as 1624 cm$^{-1}$ in solution and 1664 cm$^{-1}$ in gel. The characteristics peak of N-H bending usually appears in the range of 1650-1550 cm$^{-1}$(7), which is recorded at 1540 cm$^{-1}$ with commercial chitosan after protonation with acetic acid peak shifted to1588 cm$^{-1}$&1535cm$^{-1}$. This can be attributed to the modification of chitosan structure with glutaraldehyde by crosslinking.1483 cm$^{-1}$, 1449 cm$^{-1}$, 1470 cm$^{-1}$&1395 cm$^{-1}$, 1336 cm$^{-1}$, 1353 cm$^{-1}$ from the figures indicates C-H bending vibrations of alkyl and methyl groups consecutively. The peak range of 1300-1000 cm$^{-1}$ characteristic of Ethers(C-O-) observed as 1190 cm$^{-1}$ (Fig.7a),1176 cm$^{-1}$ (Fig.7b) & 1145 cm$^{-1}$ (Fig.7c). Usually wavelength range of 1690- 1640 cm $^{-1}$ significance of imine bond ($C{=}N$), the sharp peak of 1664 cm$^{-1}$ noticed in thecase of gel which confirms Schiff's base structure (8).

## CONCLUSION

Chitosan hydrogels were prepared without crosslinker and with varying concentrations of crosslinker. These gels were examined for swelling behavior at various temperatures, in water, and at different ranges of buffer solution. Crosslinked hydrogels reported a high swelling ratio concerning the above conditions because crosslinked hydrogels are internally linked with each other, acidic medium ($P^H$=4) more favor to swelling behavior which is comparatively less in the case of ($P^H$=7) & ($P^H$=9.2). Swelling behavior of noncrosslinked hydrogels varies considerably with varying temperatures, but it is negligible in the case of the crosslinked hydrogel.

FTIR analysis attributed to confirm the formation of the amide linkage, in the crosslinked hydrogels.

### References

1) Klouda L, Mikos AG, Thermo responsive hydrogels in biomedical applications. *Eur J Pharm Biopharm* 68:34–45, 2008

2) P.K. Prashant, B.R. Vivek, N.D. Deepashree, P.P. Pranav. “Hydrogels as a drug delivery system and applications: a review”, *International Journal of Pharmacy and Pharmaceutical Sciences*, vol. 4, pp. 1-7, 2012.

3) L. Takashi, T. Hatsumi, M. Makoto, I. Takashi, G. Takehiko, S. Shuji. “Synthesis of porouspoly (N-isopropylacrylamide) gel beads by sedimentation polymerization and their morphology”, *Journal of Applied Polymer Science*, vol. 104, pp. 842, 2007.

4) Sheng Lin-Gibson, Howard J. Walls, Scott B. Kennedy, and Eric R. Welsh. Chitosan Hydrogels: Crosslink Kinetics and Gel Properties. *Journal of Polymeric Materials: Science &Engineering.* 2003, Vol.88, PP 199-200.

5) Sushmit S. Rithe, Pravin G. Kadam, and Shashank T. Mhaske. preparation and analysis ofnovel hydrogels prepared from the blend of guar gum and chitosan: cross-linked with glutaraldehyde. *Journal of Advances in Materials Science and Engineering*. December 2014, Vol.1, No.2.

6) Zhang Y, Zhu W, Ding J. Preparation of thermosensitive microgels via suspension polymerization using different temperature protocols. *J. Biomed. Mater. Res. Part A.*2005;75A:342–349

7) C.Yuen, S. Ku, P. Choi, C. Kan, S. Tsang .Determining Functional Groups of Commercially Available Ink-Jet Printing Reactive Dyes Using Infrared Spectroscopy. *Research Journal of Textile and Apparel*.2005, Vol.9, No.2, PP 26–38. Doi: 10.1108/rjta-09-02-2005-b004.

8) Ragaa EL-sheikh, Moustafa M. S. Abo-ELfadl, Mohamed E. A. Ali, Khalid Khader, Impactof sludge produced from drinking water plants on groundwater and its treatment by a natural polymer. *Journal of American Science*. 2017, Vol.13, No.2.