Facile fabrication of novel fenugreek gum/chitosan hydrogel networks through Schiff base formation: Characterization & Swelling kinetics studies

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Abstract

In the current scenario, material synthesis techniques are transitioning from traditional to safer, chemical-free routes. The current research focuses on the self-crosslinking of fenugreek gum(a medicinal seed gum) and chitosan via Schiff base production through an oxidative pathway into hybrid hydrogels. To create oxidised fenugreek gum(OFG), fenugreek gum was oxidised with sodium periodate. Periodate oxidation converts vicinal glycols in the backbone to aldehydic groups. Crosslinking occurred due to the creation of Schiff base imine connections between amino groups of chitosan and aldehyde groups of oxidised fenugreek gum without the usage of severe conditions or crosslinking and initiator systems. To confirm the structural modifications integrated as well as changes in physiochemical properties of the backbone, FTIR, powdered XRD, FESEM, EDX, and swelling experiments were performed on newly synthesized polymeric networks. To determine their suitability as drug delivery agents, swelling kinetics were examined as a function of reaction parameters and ionic strength of swelling medium.XRD data confirms an increase in crystallinity caused by oxidation, which further reflected as decline in swelling OFG. The pH responsive behaviour of OFG and OFG-*cl*-CH Schiff base matrix is validated by swelling kinetics. SEM examination validated the porous structural shape of the functionalized gel. Schiff base polymeric networks of OFG-*cl*-CH follow a pseudo-Fickian process. These newly synthesised OFG-cl-CH Schiff base could be employed as a possible drug delivery systems in the future.

Keywords: Fenugreek gum, Chitosan, oxidation, sodiumperiodate, Schiff base, Self crosslinking,

1. Introduction

Natural polysaccharides have sparked widespread attention in biological and pharmaceutical industries due to their reliable characteristics, which include renewable, low-cost, nontoxic, and abundant sources. They're biodegradable and biocompatible. Polysaccharides hold great promise as a source of future materials. Fenugreek gum is a non-starch polysaccharide that is derived from fenugreek seeds endosperm (Trigonella foenumgracecum). Fenugreek (Trigonella foenumgracecum) is a semiarid crop grown in the Mediterranean, Canada, and Northern Africa[1-3].Fenugreek gum is a heteropolysaccharide constituting of a linear chain of α-(1→4)-linked β-D –mannopyranosyl residues to which are attached with a fixed proportion of α-(1→6)-α-D-galactopyranosyl group as single unit side chain at C6.

Galactomannan, like guar gum and locust bean gum, is a polysaccharide present in fenugreek gum. In comparison to other galactomannan gums, fenugreek gum has a lower intrinsic viscosity and a higher average molecular weight Mw. The galactose to mannose ratio of fenugreek gum is 1:1, and its structure is depicted in Fig. 1[4-6].In comparison to guar gum and locust bean, fenugreek gum, which contains more galactose, has greater solubility and forms a stable colloid for a long time[7, 8].The triple-helical structure of FG, as well as its extensive intra/intermolecular hydrogen bonding networks, limit its use in drug administration[9, 10].However, because of the vast number of reactive hydroxyl groups on the backbone of fenugreek gum, chemical modification of these naturally occurring polysaccharide gums is possible [11,12].Various procedures for the modification/functionalization of fenugreek gum have been used in the literature, including amination[13],esterification[14],carbamation[15]andcarboxymethylation[16,17].

The functional characteristics of fenugreek gum were improved by these chemical changes. The reaction parameters and procedures utilised determine the modifications/functionalization. Fenugreek gum was changed to aminated fenugreek gum by reacting it with ethylene diamine (40 percent w/w of polymer) and then adding sodium borohydride (reducing agent), which has been employed as a candidate for creating bio adhesive drug delivery systems[13].

Esterification of fenugreek gum have been carried out using DDC (N, N'-Dicyclohexylcarbodiimide)/DMAP (Dimethylaminopyridine) as the activator resulting in formation of white powered FG-C_{18} nano micelles. Because of their biocompatibility, minimal toxicity, and ability to target the liver, these micelles could be used to administer poorly soluble medicines [14].Fenugreek gum has been claimed to have been changed through a carbamation process. In the carbamation process, fenugreek gum and urea were combined in different ratios in a laboratory pestle mortar and then exposed to a high temperature (165^{o}C) for an hour. Fenugreek carbamate has a variety of uses in the textile industry, including thickening agents in direct and discharge printing [15].Graft copolymerization can be used to modify natural polysaccharides with vinylic polymers while keeping their physical and chemical properties. Many pH-sensitive fenugreek gum-based hydrogel networks were created by grafting fenugreek gum–polyvinyl alcohol (PVA) with acrylamide utilising ammonium per sulphate (APS) as the redox initiator. These matrices have a wide range of uses in medication delivery [16-18] and food [19].When the right initiator system and crosslinkers are used, three-dimensional polysaccharide networks can be created. Although such crosslinkers have a wide range of applications, their toxicity poses a threat to the environment.

Different methodologies have been used in the literature to synthesise a polymeric hydrogel, including in-situ gelation, self-crosslinking, graft copolymerization, and radiation polymerization. Self-crosslinking is a relatively new approach that is now widely used due to the use of less toxic or non-toxic chemical crosslinkers, sometime accomplished without crosslinkers and become as an environmentally acceptable way for the creation of polymeric hydrogels. Plants, microbes, and animals produce biopolymers, which are natural polymeric materials. They have a number of advantages over synthetic polymers, including nontoxicity, biocompatibility, ease of availability, and hydrophilicity. Due to their uncontrolled hydrophilicity, low heat stability, and poor tensile/mechanical strength, biopolymers cannot be employed in their natural state. This provides motivation to functionalize biopolymers in light of their end–use applications.

One of the most essential and widely utilised chemical modifications for polysaccharide functionalization is oxidation. Many oxidising agents have been used by researchers to oxidise polysaccharides in the literature, including lead tetra acetate in dimethyl sulfoxide [20],

,2,6,6,6-tetramethyl-1-piperidineoxoammonium ion (TEMPO)[21],hydrogen peroxide[22,23],ozone[24], alkaline sodium hypochlorite[25,26],chlorine dioxide[27],sodium per iodate[28] and nitrogen dioxide [29].Various parameters influenced polysaccharide oxidation reactions, including pH, temperature, oxidant concentrations, and polymer backbone concentration. Most of the above-mentioned oxidising agents prefer to selectively oxidise polysaccharide gums with two or more hydroxyl groups on neighbouring carbon atoms. However, sodium per iodate oxidation is a more appealing and environmentally acceptable process than other oxidation methods since it works in an aqueous media and does not produce poisonous reagents or polluting products. The vicinal hydroxyl groups of polysaccharide are cleaved by sodium per iodate, resulting in dialdehyde polysaccharide.

This method of oxidation is commonly used to investigate polysaccharide physicochemical properties, swelling properties, structural composition, and thermal behaviour. Xanthan gum oxidises with sodium per iodate, resulting in decreased crystallinity and improved mechanical characteristics [30].The aldehyde groups in the oxidised polysaccharide gum formed a bio-based crosslinking agent after selective oxidation with sodium per iodate. Through the Schiff base reaction, these oxidised polysaccharides can form imine interlinks with complementary groups, primarily primary amino groups found in polymer such as [31], adipic acid hydrazide[32],ethanolamine (EA), hydrazine (HYD),Semicarbazide(SEMI)[33],collagen[34],urea[35] and chitosan[36-38]without the use of a catalyst or initiators. An appealing and adaptable technique is the oxidation of polysaccharides into aldehyde polysaccharides with periodate and then crosslinking the oxidised polysaccharides with multi- amino compounds to create Schiff base. Polysaccharide-amine based gels have applications in the biomedical field, tissue engineering, and environmental pollution abatement.

This technique has been used to functionalize numerous polysaccharide gums in the literature, with different amine groups incorporating synthetic and natural polymers. Chitosan is a natural amino bioactive polysaccharide made up of N-acetyl-D-glucosamine units linked together by (1, 4) glycosidic connections. Deacetylation of crustacean chitin with 40-50 percent NaOH is used to make it. It has low water solubility but is soluble in a 1 percent acetic acid solution. Chitosan is a material of first choice in the pharmaceutical and agricultural areas because of its biocompatible, biodegradable, antibacterial, non-toxic, renewable, and low production cost qualities [39, 40].

Chitosan is a good crosslinking centre because it has amino groups on its backbone. Per iodate oxidised dextran gum and chitosan were used to make macro porous scaffolds [41].Dextran was oxidised with sodium per iodate and subsequently cross-linked with thiolated chitosan to create in situ self-gelation hydrogels [42].In another study, xanthan gum was oxidised with sodium per iodate and then cross-linked with natural chitosan to create Schiff base hydrogels, which were employed as biocompatible drug carriers for controlled release of antibiotics [43].Salazar et al. have also developed polysaccharide-based self-healing hydrogels using the Schiff base reaction between oxidised Xanthan gum and chitosan at room temperature, which show significant promise in industrial and biomedical applications[44].

Although there are numerous publications in the literature describing various strategies for modifying fenugreek gum. There have been no previous research on the oxidation of fenugreek gum with sodium periodate as an oxidising agent to produce oxidised fenugreek gum to our knowledge. In this study, we used the Schiff base reaction to make oxidised fenugreek gum-chitosan based self-crosslinked hydrogels at room temperature (40^{o}C). FTIR, XRD, FESEM, EDX, and swelling tests were used to characterise chemical functionalities in hydrogel networks. Swelling experiments have been conducted as a function of reaction parameters (oxidising system, backbone quantity) and pH. Different swelling properties of hydrophilic systems, such as the diffusion exponent, gel characteristic constant, and diffusion coefficients, have been analysed using swelling kinetics. This new polymeric network has the potential to be used in drug delivery.

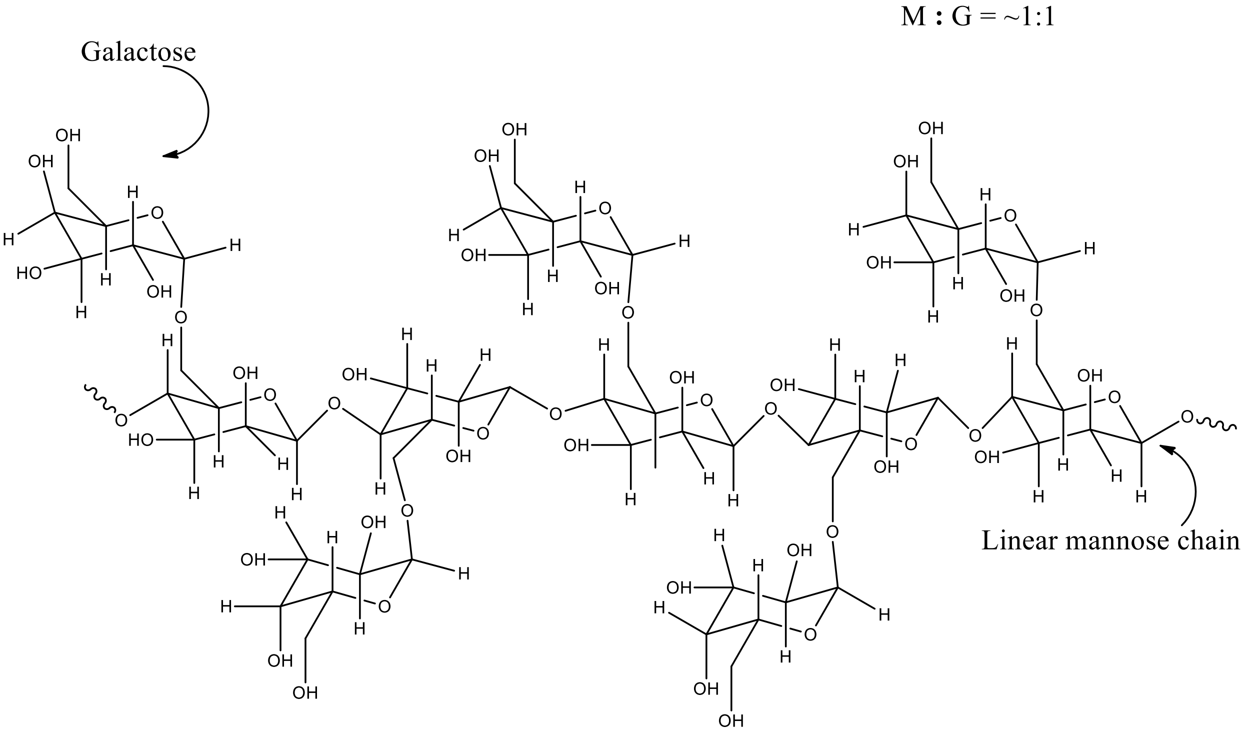

Fig.1.1:Chemical structure of fenugreek gum[4]

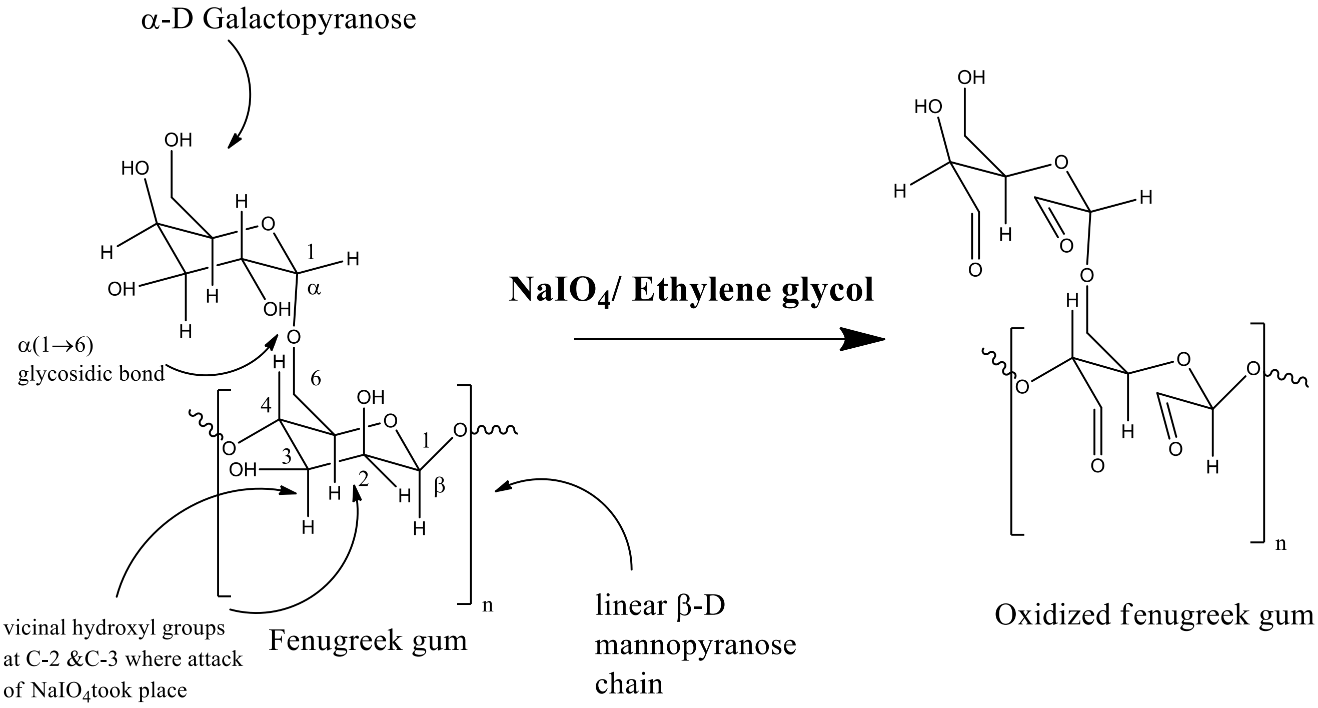

Fig.1.2: Proposed mechanism of oxidation of fenugreek gum

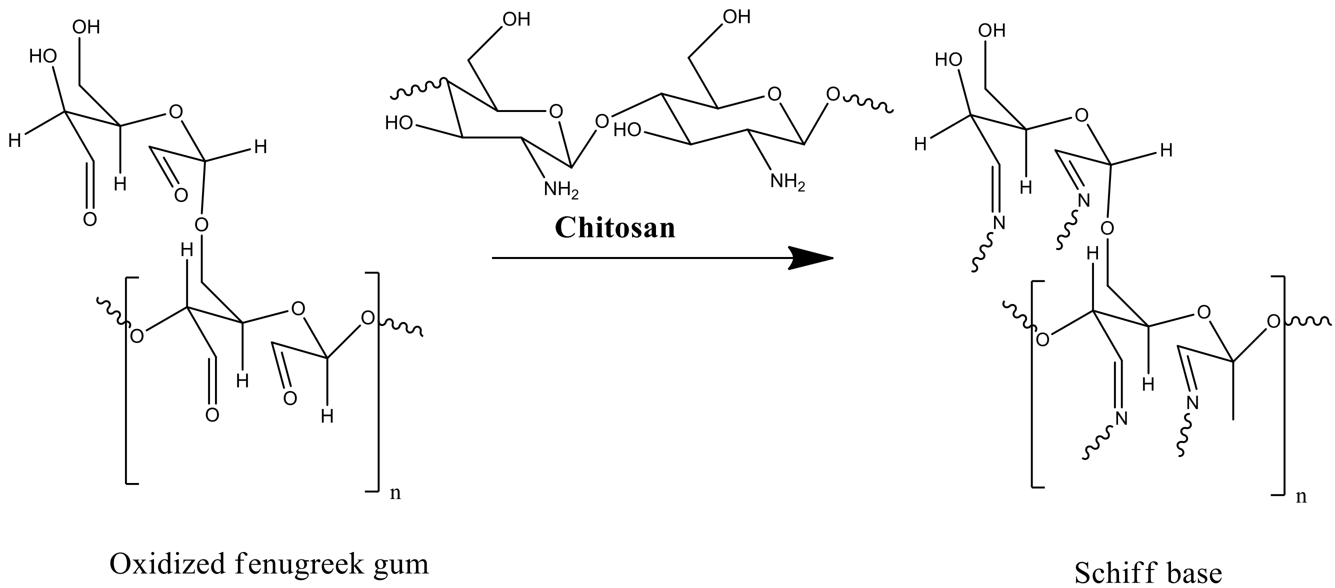

Fig.1.3:Proposed mechanism of Schiff base formation between oxidized fenugreek gum and chitosan

2. EXPERIMENTAL

2.1.Materials and methods

Fenugreeek gum (FG) was purchased from Chemtotal Labs Pvt. Ltd., Rajasthan India. Ethylene glycol was obtained from CDH Pvt. Ltd., New Delhi, India. Sodium periodate was obtained from Nice Chemicals Pvt.Ltd.,Kochi ,India. Ethanol was obtained from Changshu Hongsheng Fine Chemical Co. Ltd. Chitosan (CH) (Deacetylated >95%) was obtained from Benzochem industries Pvt. Ltd. Maharashtra. Sodium chloride, Sodium hydroxide (NaOH), Potassium chloride, methyl orange and hydroxylamine hydrochloride were purchased from Merk chemicals. Double distilled water was used in the preparation of all solutions. Potassium dihydrogen orthophosphate (KH_2PO_4), and Hydrochloric acid (HCl) were purchased from Ranchem Pvt. Ltd., New Delhi; India. Buffer solutions of pH (2.2, 6.8 and 7.4) and 0.9% NaCl solutions were prepared as reported in the Pharmacopoeia of India[45].All chemicals were used of analytical grade without further purification.

2.2. Preparation of oxidised fenugreek gum (OFG)

Fenugreek gum was oxidised using sodium periodate by according to the procedure as reported in literature with little modification [46,47].Two different composition 2% and 4% concentration (w/v) of fenugreek gum dispersion were obtained by adding 2g and 4g fenugreek gum separately in 100 cm^3 double-distilled water in continuously stirring conditions for two hours at room temperature. 25 cm^3 of 0.05M and 0.075M sodium periodate solution was added in each (2% & 4%) fenugreek gum dispersion solution. Reaction system is covered with silver foils and vigorously stirred on a magnetic stirrer for 24 hours at room temperature under dark conditions. Oxidation reaction was ceased by adding 5cm^3 ethylene glycol and stirred the reaction mixture for another 1 hour. Oxidized product, referred to as oxidized fenugreek gum (OFG) was precipitated by pouring the reaction mixture into excess of ethanol (approximately 500 ml). The oxidised product was filtered, washed with ethanol and then with double distilled water until all iodic compounds were removed. Finally the oxidized product was air dried at room temperature and preserved in vacuum desiccator for further use. Ethanol used in the process was recovered by simple distillation and reused.

2.2.1. Determination of aldehyde content in oxidized fenugreek gum (OFG)

Extent of oxidation on fenugreek gum has been evaluated titrimetrically. Aldehyde content in oxidized fenugreek gum was determined via titration method as reported in literature [48].0.1g of oxidized fenugreek gum was dispersed in 25 ml of 0.25M hydroxylamine hydrochloride solution. Reaction mixture was covered with watch glass and stirred for 4 hours. Aldehyde groups present on oxidized fenugreek gum matrix were reacted with hydroxylamine hydrochloride and formed their corresponding oxime with the libration of HCl as shown in equation below. Released HCl was then titrated with 0.1M sodium hydroxide solution, using methyl orange as an indicator. Light pink colour changed to pale yellow at the end point. The numbers of moles of aldehyde present in oxidized fenugreek gum are equivalent to the number of the moles of NaOH consumed during the titration.

$$\underset{\text{OFG}}{FG\text{-}(CHO)_n} + \underset{\text{Hydroxylamine hydrochloride}}{H_2N\text{-}OH.HCl} \longrightarrow \underset{\text{Oxime}}{FG\text{-}(CH{=}N\text{-}OH)_n} + H_2O + HCl$$

2.3. Preparation of fenugreek gum /chitosan hydrogel networks through Schiff base formation

Fenugreek gum /chitosan hydrogel networks through Schiff base formation between oxidized fenugreek gum and chitosan was prepared by using the method described in literature with minor modifications [38,49]. 2% (w/v) concentration solution of oxidised fenugreek gum (0.5g) was dispersed in 25cm^3 of double distilled water and continuously stirred on magnetic stirrer at 40^{o}C for two hours. 4% (w/v) concentration solution of chitosan was obtained by dissolving 1g of chitosan in 25cm^3 (2% acetic acid) solutions through continuously stirring on magnetic stirrer for 2 hours at 40^{o}C to obtain a clear dispersion of the same. Afterwards, equal volume of the two solutions (2% OFG and 4% chitosan) were mixed with simultaneous stirring at ambient temperature i.e. 40^{o}C for 5 hours. Afterward, resulting mixture was transferred into a clean petri dish. Petri dish was kept in refrigerator to accomplish the gelation process to obtain the cross linked hydrogel. Gelation time was recorded continuously. The textures of the hydrogel were not very smooth due to the inherent coarseness of chitosan. Newly synthesized polymeric matrix was designated as oxidized fenugreek-*cl*-chitosan (OFG-*cl*-CH). Polymeric matrix was washed with distilled water to remove any unreacted components, dried under ambient temperature and stored in a desiccator for further use.

2.4. Characterization

Native fenugreek gum (FG), oxidized fenugreek gum (OFG) , chitosan(CH) and cross-linked oxidized fenugreek gum-chitosan Schiff base (OFG-*cl*-CH) network were characterized by FTIR(Perkin Elmer spectrum RX-IFTIR spectrophotometer using KBr pellets), powered X-ray diffraction method (Panalytical's X'pert pro X-ray diffractometer), Field emission scanning electron microscopy (FESEM) and EDX(Su8010FESEM,Hitachi).

2.5 Swelling behaviour and Kinetics

The swelling behaviour of FG, OFG, chitosan and oxidized fenugreek-cl-chitosan (OFG-cl-CH) have been carried out in distilled water, buffer solution of different pH(2.2,6.8 and 7.4) and 0.9% of NaCl solution by gravimetric method according to reported procedure[50].To achieve equilibrium swelling, a known weight of dried polymers were placed in tea bags and dipped in an excess amount of the above specified swelling media at a given temperature (37^{o}C). After every 30 minutes, samples were removed from the various swelling mediums, excess surface solvent was carefully cleaned away with basic tissue paper, and water uptake was monitored on an electronic scale. All of the experiments were done in triplicate.The swelling ratio (SR) and the degree of swelling or percentage swelling (P_S) of swollen polymeric samples were evaluated by the following formula:

$$\text{Swelling ratio, SR (water uptake per g of gel)} = \frac{W_t - W_o}{W_o} \quad \text{g/L} \qquad (1)$$

Where W_O and W_t represent initial dry weight and swollen weight of the hydrogels at fixed interval of time expressed in gram respectively.

The percentage swelling (P_S) of the polymeric networks was calculated as:

$$P_s = \left(\frac{W_t - W_o}{W_o}\right) \times 100 \qquad (2)$$

Polymer swelling behaviour was investigated as a function of amount of backbone, oxidant concentration at various pH levels, and swelling media containing 0.9 percent NaCl. The power law expression proposed by Ritger and Peppas[51] was used to assess swelling kinetics.

$$\frac{W_t}{W_\infty} = Kt^n \qquad (3)$$

Where W_t and W_∞ are the swollen weight of the hydrogels at fixed interval of time and equilibrium swelling expressed in gram respectively. 't' is the time expressed in minutes , 'n' is the diffusion exponent and K is the diffusion constant .

By taking the natural log of equation (3) we get:

$$\mathrm{Ln}\ \frac{W_t}{W_\infty} = \mathrm{Ln}\ (K) + n\ \mathrm{Ln}\ (t) \qquad (4)$$

The initial diffusion coefficient (D_i), the average diffusion coefficient (D_A) and late diffusion coefficient (D_L) has been evaluated by using the following equations.

$$\frac{W_t}{W_\infty} = 4\left(\frac{D_i t}{\pi l^2}\right)^{0.5} \qquad (5)$$

$$D_A = \frac{0.049 l^2}{t^{\frac{1}{2}}} \qquad (6)$$

$$\frac{W_t}{W_\infty} = 1 - \left(\frac{8}{\pi^2}\right)\exp\left[\frac{\left(-\pi^2 t D_L\right)}{l^2}\right] \qquad (7)$$

3. Result and discussion

3.1. Synthesis of fenugreek gum/chitosan hybrid hydrogel networks through Schiff base formation

Fenugreek gum belongs to the galactomannan family of polysaccharides, which are neutral polysaccharides with no charged groups such as uronic acid residues. It's made from endosperm seeds and has a sugar composition similar to guar gum, locust bean gum, tara gum, and cassia gums. Fenugreek gum consists of a (1→4)-linked β-D mannopyranose backbone with α-D –galactosyl sugar attached on the C-6 of about 50% of the mannose residues (Figure 1.1). During the oxidation of FG with sodium periodate, the carbon–carbon link between vicinal hydroxyl groups in the polysaccharide chain is selectively oxidised. The hydrolysis of glycosidic bonds resulted in the breakdown of fenugreek gum. This approach introduces a huge number of aldehyde groups into polysaccharide strands.Polymer chains were broken into smaller segments by oxidation, resulting in a drop in polymer molecular weight (Figure 1.2). Schiff base reaction caused an in-situ condensation reaction between the aldehyde groups of OFG and the amino groups of CH (Figure 1.3).

The residual aldehyde contents in oxidized fenugreek gum (2% and 4% fenugreek gum oxidizing using 0.05M and 0.075M $NaIO_4$) were estimated by titrimetric method and are found to be 5×10^{-3}mol/g, 8×10^{-3}mol/g, 5.2×10^{-3}mol/g and 6.5×10^{-3}mol/g respectively .The maximum aldehyde content 8×10^{-3}mol/g was observed when 2% fenugreek gum has been oxidizing using 0.075M $NaIO_4$ and the minimum aldehyde content 5×10^{-3}mol/g was observed when 2% fenugreek gum has been oxidizing 0.05 M $NaIO_4$.

3.2 . Characterization

FG, OFG, CH and Schiff base (OFG-*cl*-CH) network were characterized by FTIR, XRD, FESEM and EDX studies.

3.2.1 FTIR Analysis:

FTIR is a very useful and less expensive tool to determine the molecular structure of polymer. FTIR spectra of FG, OFG, CH and OFG-*cl*-CH polymeric network were recorded in the range of 4000-500 cm^{-1} in order to confirm the chemical composition, different functionalities and crosslinking of oxidized fenugreek gum with chitosan (Fig.2).In the FTIR spectrum of native fenugreek gum, the broad and strong absorption band around 3650-3200 cm^{-1} was due to O-H stretching vibrations. The peak at 2929 cm^{-1} corresponds to C-H stretching,-CH_3 stretching and the asymmetric stretching was due to CH_2 group [52]. A peak at 1640 cm^{-1} was due to the scissoring vibration of two OH bonds of adsorbed water for native gum and the peak at 1420 cm^{-1} was due to the C-H bending vibration. The peak at 1019 cm^{-1} represents -C-O stretching mode of primary alcohol(-C-O-H) [13].In the range of 700-1000cm^{-1},weak absorption band at 817cm^{-1} are due to the CH oscillation of β-mannopyranose residue .The absence of absorption band approximately at 1560cm^{-1} was due to amide II indicate the FG is free from protein contaminants [12].The broad and strong peak in the 3400-3200 region was also present in the spectrum of oxidized fenugreek gum indicating that hydroxyl group at 4-C and 6-C of α-D-galactopyranose remain unchanged during the process of oxidation. The intensity of (-OH) broad band slightly decreased and narrowed at 3418 cm^{-1}due to oxidation of hydroxyl groups to aldehyde groups. A characteristic band at 1650 cm^{-1} increased remarkably in the spectra of OFG as compared with that of FG ,which is attributed to the stretching vibration due to C=O. This indicated that CHO groups have been successfully introduced into the structure of FG by selective oxidation with sodium periodate[55]. In OFG, a strong peak around 1046 cm^{-1} has been observed due to C-O stretching vibrations. The peak at 885cm^{-1} was due to the hemiacetal structure between the aldehyde and neighbouring –OH groups. In FTIR spectra of chitosan, stretching vibrational band appear at 3390cm^{-1}which corresponds to O-H and N-H stretching vibrations. Another noticeable peak at 2884cm^{-1} is due to C-H stretching. An intense band at 1646cm^{-1} is due to the C=O stretching mode of N-acetylgucosamine and NH_2 bending vibration modes [38]. In the spectra of OFG-*cl*-CH polymeric network, a strong peak appeared at about 1611cm^{-1}which confirmed the –C=N vibrations characteristic of imines and this indicated coupling reaction between –CHO groups and –NH_2. Apart from other peaks, there was noticeable decline in peak intensity of -OH and N-H stretching band since maximum OH groups have been consumed in oxidation and further in Schiff base formation.

3.2.2 XRD analysis:

The powdered XRD is a good technique to characterise the crystal structure of a material. The powdered XRD spectra of FG, OFG, CH and OFG-*cl*-CH have been shown in figure 3.The presence of broad peak in the powdered XRD of fenugreek gum and Chitosan are due to their crystalline nature and for Schiff base is to due their amorphous nature. The sharp and broad peak in the 2θ region equal to 20.1894 ^{0} ,which is attributed to crystalline nature of fenugreek gum as the hydroxyl groups may exhibit intermolecular H- bonding . The effect of oxidation of FG on the crystallinity of OFG was characterized by powdered XRD .The oxidation of fenugreek gum with sodium periodate increase the degradation of OFG ,which is attributed to the decrease of crystallinity and structure change. The powdered XRD of OFG was different from that of fenugreek gum. As intensities for modified gum (OFG) are higher than native fenugreek gum. Two sharp peaks were present at 2θ = 20.9828^{0} and 2θ = 26.7610^{0} indicated the crystalline nature of oxidized fenugreek gum. The degree of crystallinity of oxidized fenugreek gum was maximum due to a well packed structure and it was disrupted during Schiff base formation. The X-ray diffraction analysis of fenugreek gum with weak peaks conforming the amorphous nature of the gum while the XRD of oxidized fenugreek gum shows more regular pattern with sharp peaks conforming the level of crystallinity of the oxidized fenugreek gum (Fig. 3).Chitosan consisted of two peak at 2θ = 22.3994^{0} and 2θ = 29.5564^{0} respectively. The two peaks at 2θ = 22.7054^{0} and 2θ =26.5564^{0}, which is mainly due to the formation of imine groups and cleavage of hydrogen bonds of Chitosan.

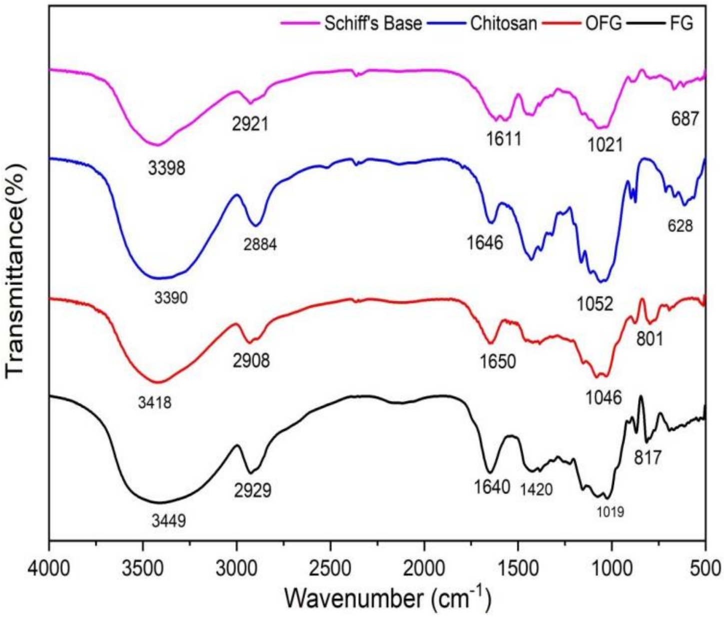

Fig.2: FTIR of fenugreek gum (FG), oxidized fenugreek gum (OFG), chitosan (CH) and Schiff base (OFG-*cl*-CH)crosslinked network.

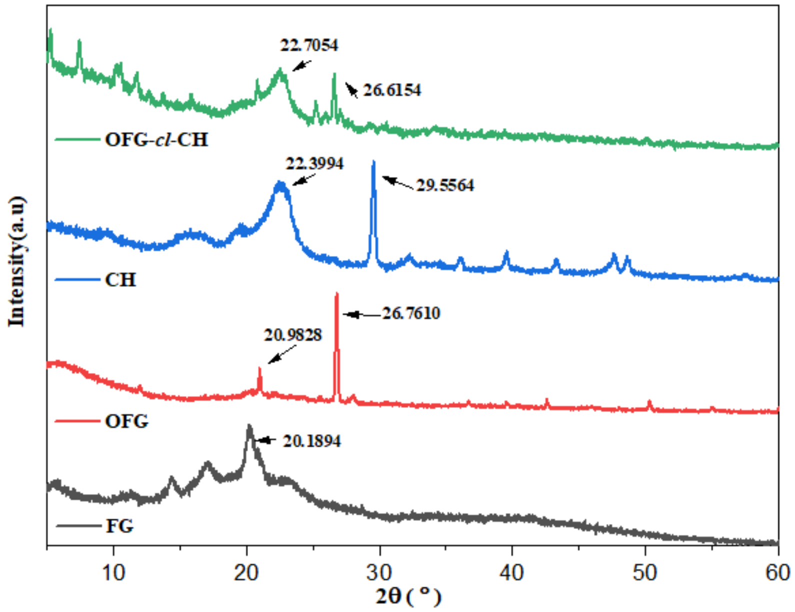

Fig.3: XRD of fenugreek gum (FG), oxidized fenugreek gum (OFG), chitosan (CH) and crosslinked network of Schiff base (OFG-*cl*-CH).

3.2.3 FESEM and EDX analysis:

FESEM was used to study the surface morphology and three dimensional structure of FG, OFG and OFG-*cl*-CH and have been presented in figure 4 (a-f). Homogeneous nature of fenugreek gum shows their uniform dispersion in water. The oxidized fenugreek gum has been found to be fibrillar [26] and smooth structure with small pore size as compared to native fenugreek gum. The rough and uneven structure of OFG-*cl*-CH Schiff base showed the crosslinking between oxidized fenugreek gums with chitosan. The EDX of the OFG showed that the OFG contained various elements such as C, O and N and elemental composition were 43.43%wt. C, 54.3838 %wt. O and 2.19% wt. N and in OFG-*cl*-CH contained 48.50% wt. C and 51.50 %wt. O .The decrease in the oxygen content in EDX of OFG-*cl*-CH as compared to oxidized fenugreek gum also confirmed the formation of Schiff base between carbonyl group of OFG and NH_2 groups of chitosan and represented in fig.5 (a) and 5(b) respectively.

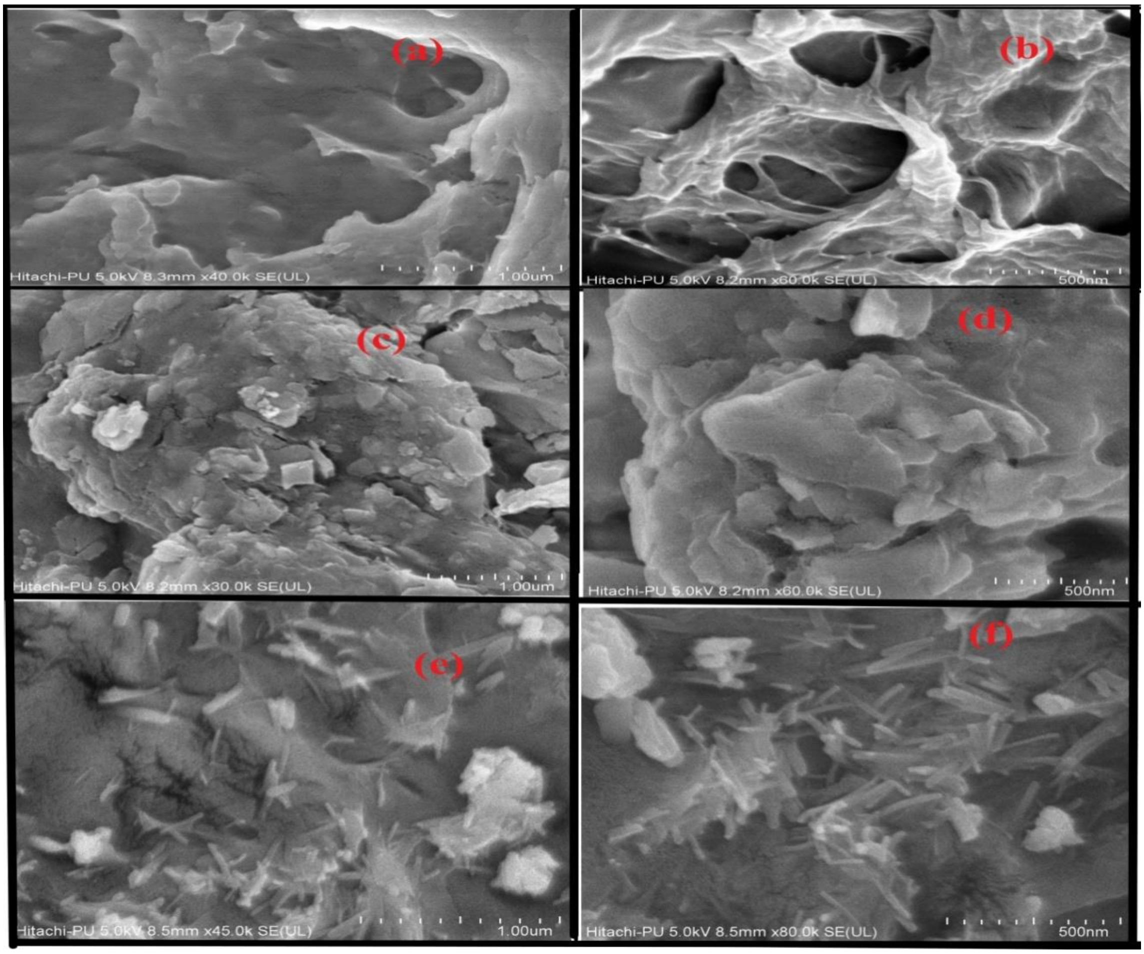

Fig.4: FESEM of fenugreek gum (a, b) oxidized fenugreek gum(c, d) andOFG-*cl*-CH Schiff base (e,f).

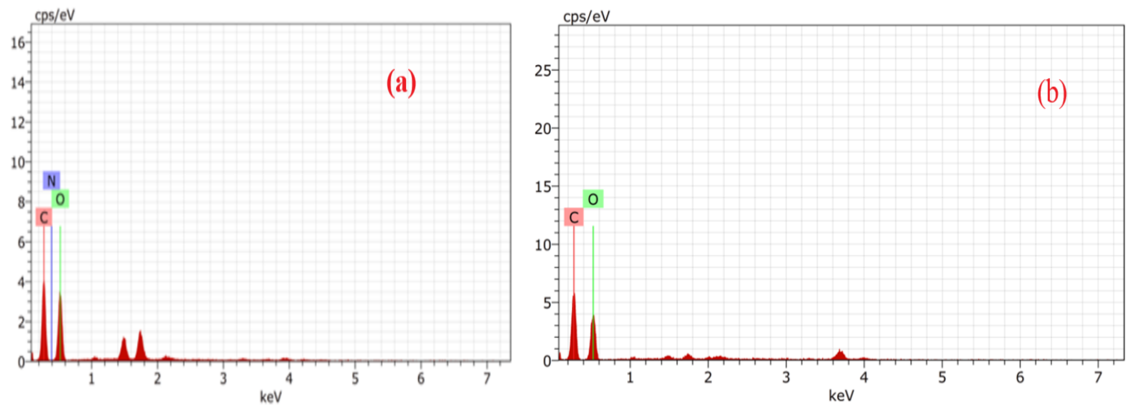

Fig.5: EDX of oxidized fenugreek gum (OFG) (a) and OFG-*cl*-CH Schiff base (b)

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3.3.Swelling behaviour of oxidized fenugreek gum(OFG) and oxidized fenugreek gum crosslinked chitosan(OFG-*cl*-CH) Schiff base hydrogel

Swelling is a critical characteristic that influences the surface properties and application of a hydrogel network. The ability of the polysaccharide hydrogel to be loaded with pharmaceuticals and on the other hand, the transport of these drugs via the polymeric network is determined by swelling behaviour. The ability of a polymeric hydrogel network to swell in diverse media is crucial for determining its biocompatibility.

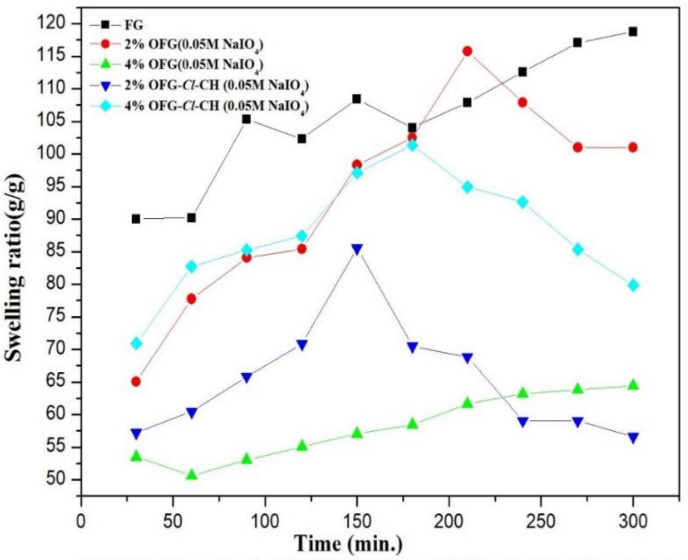

Fig.6.1:Swelling rario of oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of backbone.

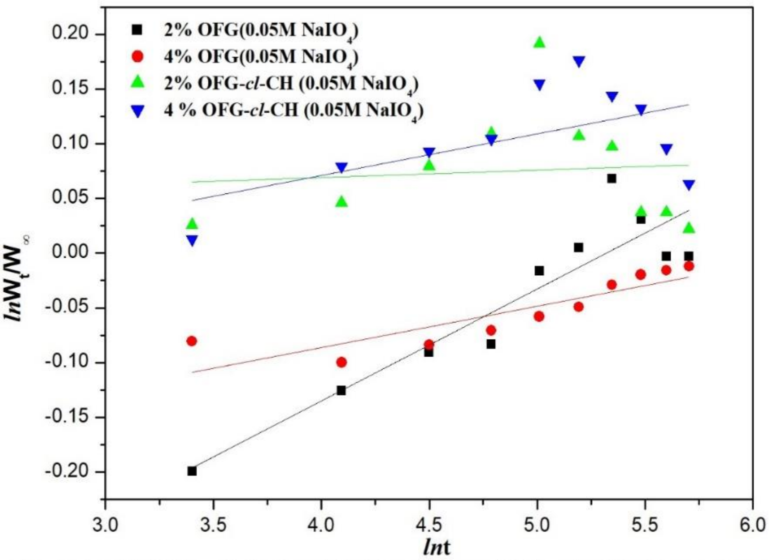

Fig.6.2: Plot of ***ln***W_t/W_∞ with ***lnt*** for oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of amount of backbone.

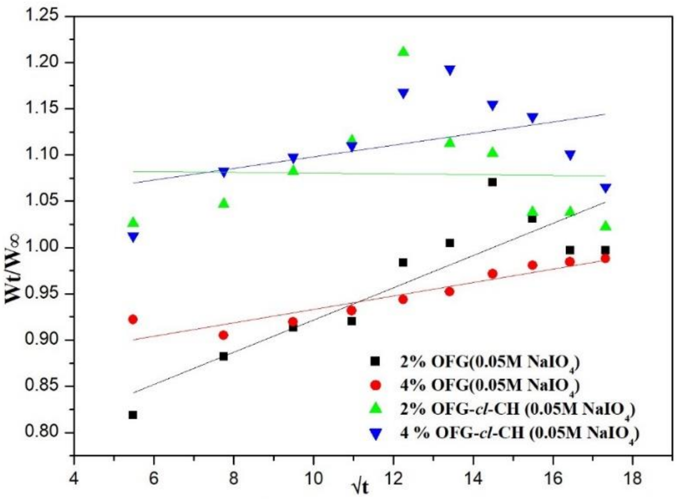

Fig. 6.3:Plot of **Wt/W∞** with **√t** for oxidized fenugreek gum and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of amount of backbone.

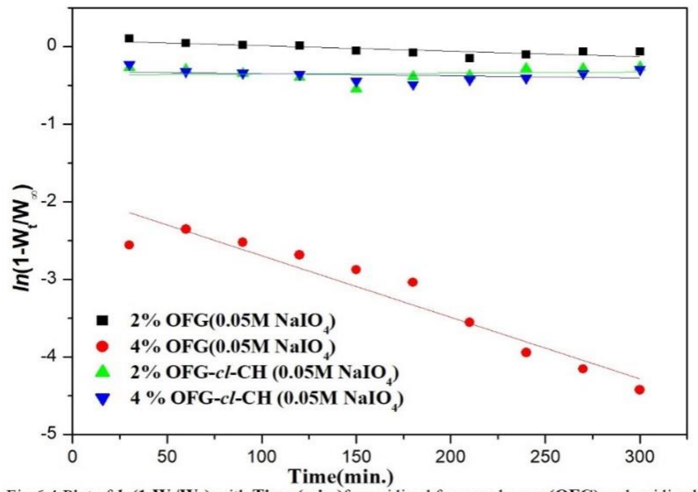

Fig.6.4:Plot of ***ln***$(1-W_t/W_\infty)$ with **Time (min.)**for oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of amount of backbone.

3.3.1Swelling of OFG and OFG-*cl*-CH Schiff base hydrogels as a function of amount of backbone (fenugreek gum):

In present study, swelling behaviour of oxidized fenugreek gum and OFG-*cl*-CH were evaluated at pH 7 as a function of amount of backbone. OFG and OFG-*cl*-CH Schiff base hydrogels synthesized using different oxidizing conditions (0.05M and 0.075M $NaIO_4$) and varied amount of backbone (FG) i.e.2% and 4% fenugreek gum have been used for swelling (Figure 6.1 and Figure 7.1). In OFG and OFG-*cl*-CH synthesized at variable amount of backbone with 0.05M $NaIO_4$, when oxidised fenugreek gum was compared to native fenugreek gum, the swelling ratio was found to be lower. This is due to the progressive breakdown of larger galactomannan chains and the conversion of hydroxyl groups to aldehyde that occurs during oxidation. As a result, the matrix's crystallinity rises, increasing OFG solubility. Crosslinking OFG with chitosan through Schiff base reaction further lowered swelling behaviour in the OFG-*cl*-CH hydrogel matrix due to increased degree of crosslinking and usage of polar water absorption sites in imine link formation(Figure 6.1).Maximum swelling obtained for FG, OFG and OFG-*cl*-CH Schiff base polymeric gel synthesized using 2% FG was 132.48%, 102.50% and 85.54% respectively. Whereas polymeric matrix synthesized using 4% FG &0.05M sodium periodate, 66.40%swelling was observed. The amount of swelling of OFG decreased with increase in the amount of parent fenugreek gum (2% and 4%) which is due to increase in the extent of oxidation. Similar observations have been reported by Yu, Huiqun and co-workers for Konjac Glucomannan oxidized with sodium periodate[38]. In another set of matrix swelling of OFG and OFG-*cl*-CH matrix synthesized using 0.075M $NaIO_4$have been studied as a function of amount of backbone. Maximum swelling (176.09 %) was achieved in matrix with composition 2% FG and 0.075 $NaIO_4$ (Figure 7.1) whereas other compositions show decrease in swelling as compared to native FG. For OFG synthesised using 4% FG& 0.075M sodium periodate, 119.24% swelling was obtained. Similarly swelling decreased with the increase in amount of backbone because with the increase in the extent of oxidation the degree of crosslinking also gets increased and the swelling get decreased.

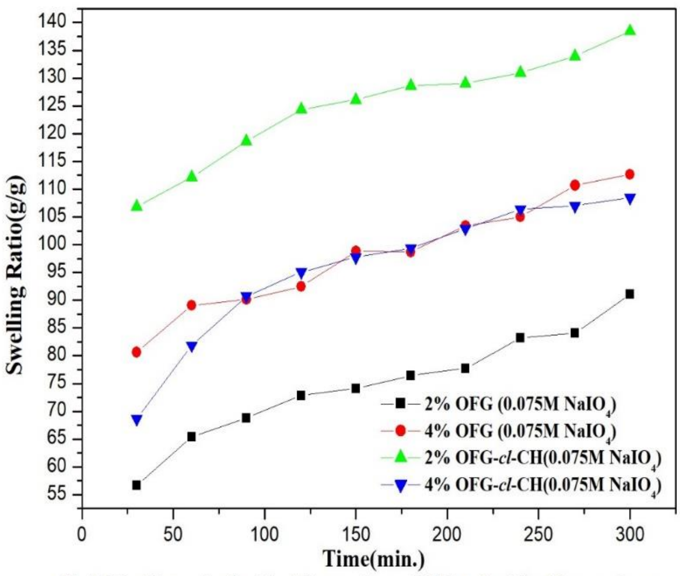

Fig.7.1:Swelling ratio of oxidized fenugreek gum(**OFG**) and oxidized fenugreek gum crosslinked chitosan(**OFG-*cl*-CH**) hydrogel as a function of amount of backbone.

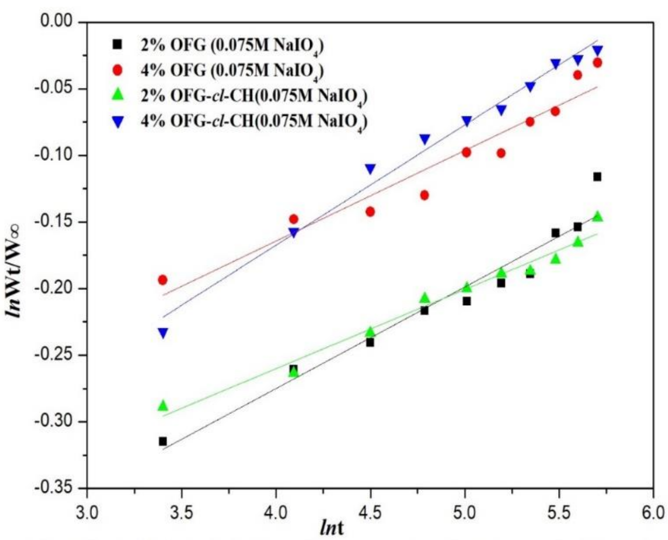

Fig.7.2:Plot of lnW_t/W_∞ with ***lnt*** for oxidized fenugreek gum (**OFG**) and oxidized fenugreek gum crosslinked chitosan (**OFG-*cl*-CH**) hydrogel as a function of amount of backbone.

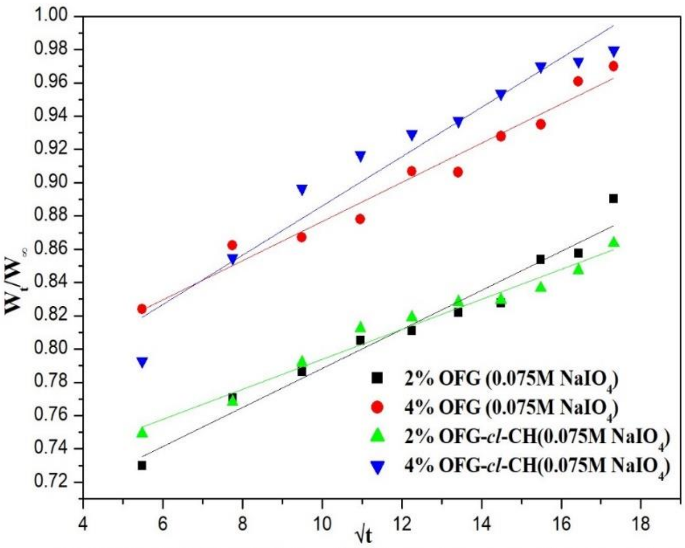

Fig.7.3:Plot of **Wt/W∞** with **√t** for oxidized fenugreek gum and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of amount of backbone.

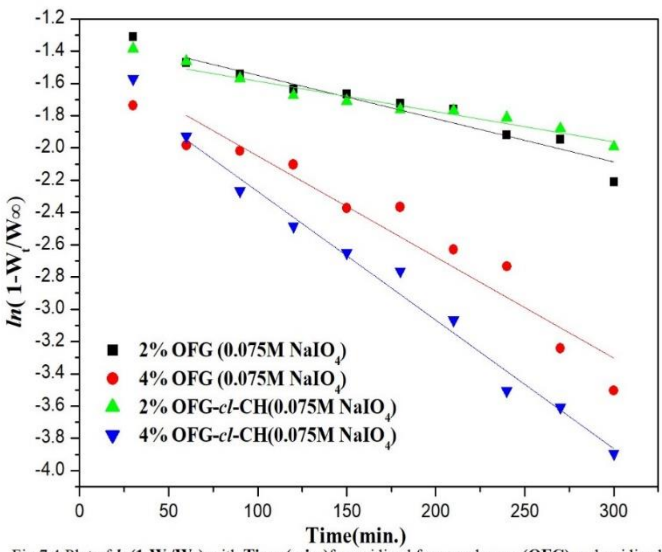

Fig.7.4:Plot of ***ln*(1-W_t/W_∞)** with **Time (min.)**for oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of amount of backbone.

3.3.2 Swelling of OFG and OFG-*cl*-CH Schiff base hydrogel as a function of concentration of the oxidizing agent (sodium periodate):

Swelling behaviour of OFG and OFG-*cl*-CH Schiff base hydrogel have been evaluated at pH 7 as a function of concentration of oxidant(0.05M and 0.075M sodium periodate)and results are shown in figure 8.1 and figure 9.1 respectively. OFG and OFG-*cl*-CH Schiff base polymeric matrix have been prepared with 2% and 4% fenugreek gum with variable concentration of oxidant. It is observed from the figure that oxidation of fenugreek gum drastically alter the swelling behaviour of parent fenugreek gum. Swelling behaviour of OFG is less as compared to native fenugreek gum. Swelling decreased with increase in the concentration of oxidant (0.05M and 0.075M) and this can be explained on the basis of extent of oxidation. Maximum swelling ratio was observed for 2% fenugreek gum oxidized with (0.05M $NaIO_4$) was 102.5% and for the same amount of backbone oxidized with (0.075M $NaIO_4$) was 90.05% respectively. This is due to the fact that with rise in concentration of oxidant there is extensive oxidation of vicinal hydroxyl groups which is also reflected as rise in crystallinity which is correlated to rise in solubility. In case of OFG-*cl*-CH polymeric matrix prepared with 2% FG, there is drastic increase in swelling with increase in concentration of oxidant. This is due to the fact that with the increase in the extent of oxidation the degree of crosslinking also gets increased and more hydrophilic sites are available on polymeric network responsible for rise in swelling (Figure 8.1). In case of OFG and OFG-*cl*-CH Schiff base prepared with 4% FG, similar results have been obtained (Figure 9.1).Maximum swelling ratio was observed for 2% fenugreek gum oxidized with (0.05M $NaIO_4$) was 115.74 % and same amount of backbone oxidized with(0.075M $NaIO_4$) was 91.09% % respectively .Whereas swelling ratio for OFG-*cl*-CH Schiff base prepared with 2% FG oxidized with 0.05M sodium periodate and for 4% FG oxidised with 0.075 M were 85.55% and 108.46 % were observed respectively.

Swelling kinetics of the OFG and OFG-*cl*-CH) Schiff base polymeric matrix has been evaluated according to Ritger and Peppas equations. Diffusion constant (n) and gel characteristics constant (K) of OFG and OFG-*cl*-CH) Schiff base matrix as a function of backbone fenugreek gum (2% and 4%) and as a function of oxidizing agent $NaIO_4$ (0.05M and 0.075M) at pH 7 have been evaluated using equation (4).The value of diffusion constant (n) and gel characteristics constant (K) of OFG and OFG-*cl*-CH were calculated from the slope and intercept of the plot of *ln* W_t/W_∞ vs. *ln*t at pH 7 as function of backbone (2% and 4%) FG (Figure 6.2) and oxidant (0.05M$NaIO_4$ and 0.075M$NaIO_4$) (figure 7.2)and there results have been shown in table 1.Normal Fickian diffusion is characterized by n=0.5 and case II diffusion by n=1.A value of n between 0.5 and 1 is usually called non Fickian or anomalous diffusion [53].When the value of n is less than 0.5($n<0.5$) then it is termed as pseudo-Fickian. In present case, value of diffusion exponent was less than 0.5 for OFG, OFG-*cl*-CH Schiff base matrix as a function of backbone as well as concentration of oxidant. This shows apseudo-Fickian diffusion and its curves resemble with Fickian curves but with slower approach to equilibrium[54].Values of gel characteristic constant was found little higher for OFG-*cl*-CH Schiff base matrix as compared to OFG (Table1). Initial diffusion coefficient (D_i) and average diffusion coefficient (D_A) for OFG and OFG-*cl*-CH Schiff base polymeric matrix have been calculated by equations (5) and (6) and observed by plot of $\sqrt{t}$ vs W_t/W_∞ for matrix as a function of backbone and oxidant as shown in figure 6.3 and figure7.3 respectively and value of D_i and D_A have been shown in table2. In case of OFG, D_i is higher than D_A where as in OFG-*cl*-CH Schiff base polymer gel, D_A is higher than D_i which shows a gradual penetration of solvent front into the three dimensional gel networks as swelling progress (Table2). In case of OFG, D_i value more than the D_L, when backbone (2%FG)of the polysaccharide was small .But when backbone of the polysaccharide gum increased the D_i have less value than the D_L at concentration of 0.05M $NaIO_4$.Except 4% fenugreek gum oxidized with 0.05M sodium periodate ,D_A have reported less value than D_i. The value of late diffusion coefficient(D_L) for each variation (backbone and concentration of oxidant) have been evaluated by plotting the graph *ln* (1-W_t/W_∞) vs. time (t) as shown in figure 6.4 and figure 7.4 and results have been shown in Table 3 respectively. D_i for OFG was recorded as higher as compared to OFG-*cl*-CH Schiff base polymer gel.

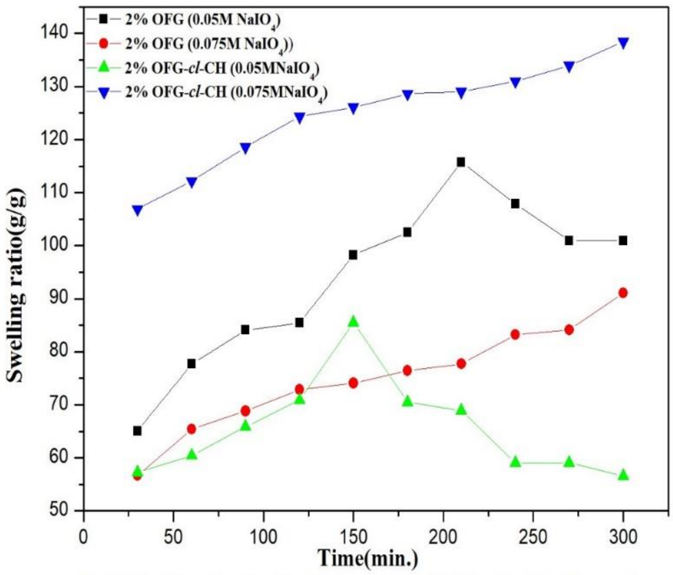

Fig.8.1:Swelling ratio of oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of amount of oxidant.

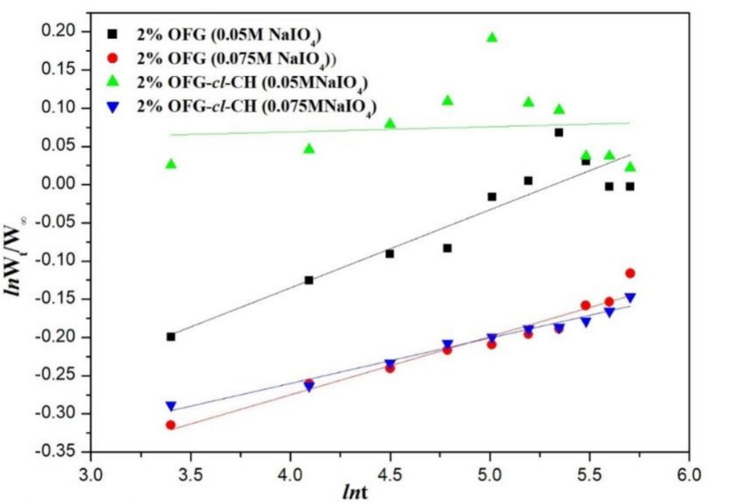

Fig.8.2:Plot of ***ln*** W_t/W_∞ with ***ln* t** for oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of amount of oxidant.

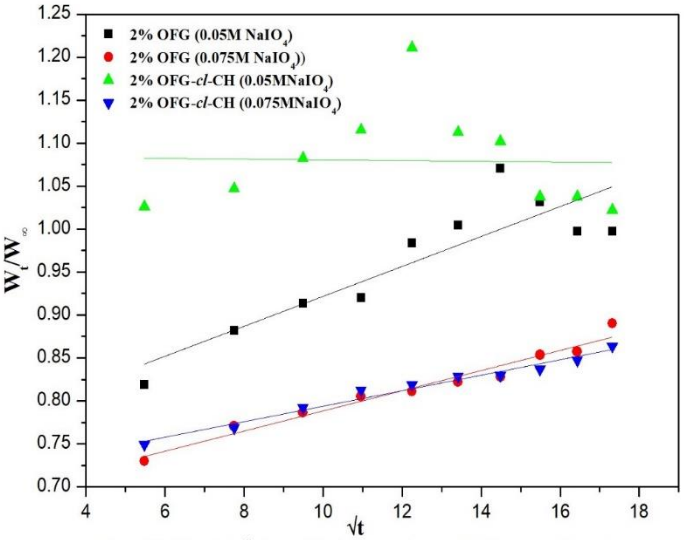

Fig.8.3: Plot of W_t/W_∞ with √t for oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked **(OFG-*cl*-CH)** hydrogel as a function of oxidant .

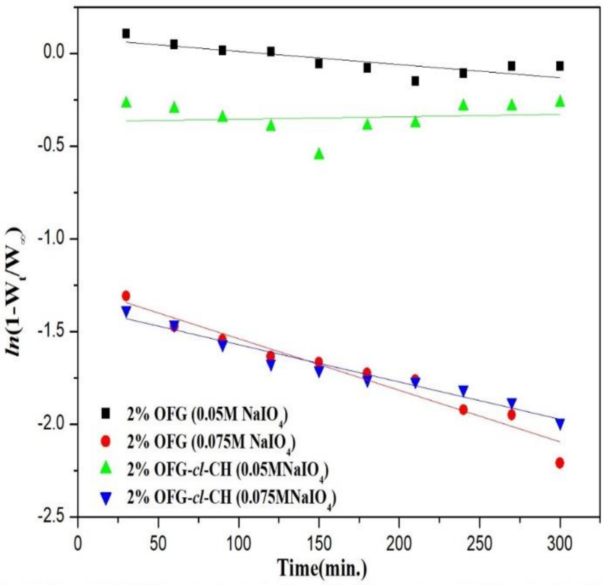

Fig.8.4: Plot of ***ln***$(1-W_t/W_\infty)$ with **Time(min.)** for oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of amount of oxidant.

This might be due to the fact that there was higher diffusion in initial phase in crosslinked networks and equilibrium has been achieved earlier. On the basis of swelling profile and structural consistency of polymeric matrix, final optimum conditions for synthesis of OFG-*cl*-CH polymeric matrix using2% fenugreek gum and 0.05M $NaIO_4$ oxidizing agent have been utilized for further study.

3.3.3 Swelling of OFG and OFG-*cl*-CH Schiff base hydrogel as a function of pH and 0.9% NaCl solution of swelling medium:

Swelling profile of optimized gel matrix has been evaluated on the basis of pH of swelling medium. The swelling profile of fenugreek gum, chitosan, OFG and OFG-*cl*-CH have been evaluated in buffer solution of different pH (2.2, 6.8, 7. and 7.4) and the results are as shown in Fig.10.1 and 10.2, Figure 11.1 and figure 12.1 respectively. The equilibrium swellings by polymeric matrix were carried out after 24 hours at different pH. The parent galactomannan fenugreek gum showed maximum swelling about 132.49% in distilled water (Figure 10.1). Water uptake by native chitosan was increases with rise in pH (Figure 10.2). Since $CONH_2$groups present have not ionised at lower pH, keeping the hydrogel network folded, whereas at pH 7.4, they are partially ionised, and the charged groups repel each other, increasing the swelling ratio [50]. Similarly, oxidation of native gum changes the swelling behaviour. Swelling percentage of OFG increases with increase in pH. In basic medium, acidic groups present on OFG get deprotonated to O^- and COO^-, which increased the electrostatic repulsion between negatively charged groups and hence swelling percentage increased. Since, swelling ability of a polymeric hydrogel is due to their porous nature. In a pH 7.4 environment, OFG polymeric matrix (2% FG oxidised with 0.05M sodium per iodate ($NaIO_4$) swells to a maximum of 176.55%, while OFG oxidised with 0.075M ($NaIO_4$) swells to a minimum of 59.90%. This was attributed to the former having less crystallinity than the latter due to various degrees of oxidation caused by differing oxidising agent concentrations. Contrary to OFG, swelling of OFG-*cl*-CH matrix shows highest swelling in acidic pH (Figure 12.1).

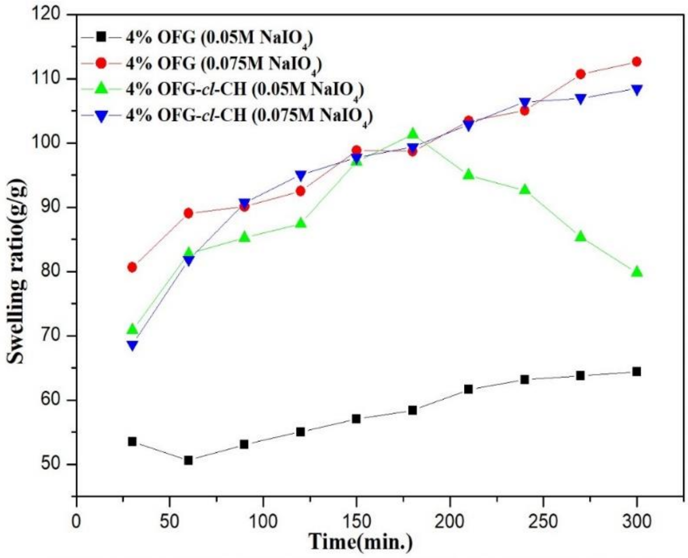

Fig.9.1:Swelling ratio of oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of amount of oxidant.

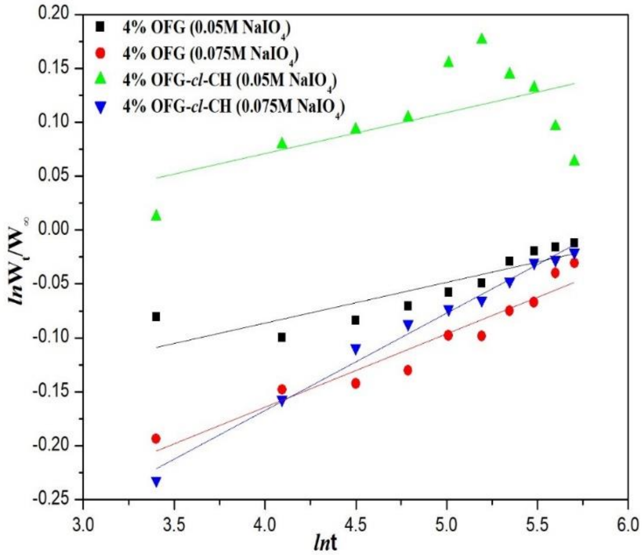

Fig.9.2: Plot of lnW_t/W_∞ with ***ln* t** for oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of amount of oxidant.

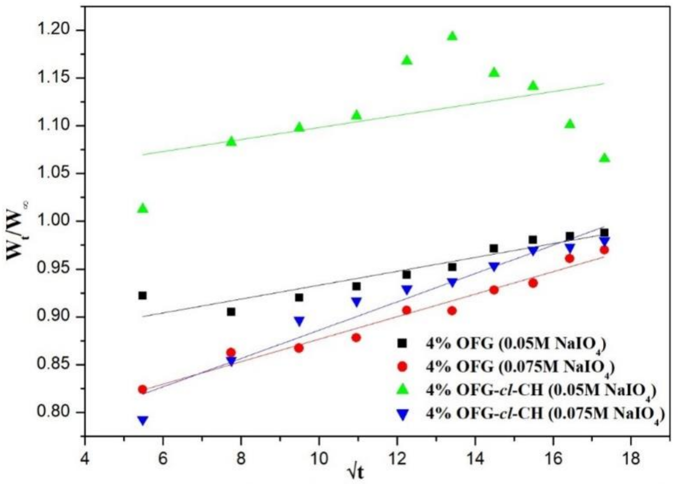

Fig.9.3: Plot of W_t/W_∞ with **√t** for oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked **(OFG-*cl*-CH)** hydrogel as a function of oxidant .

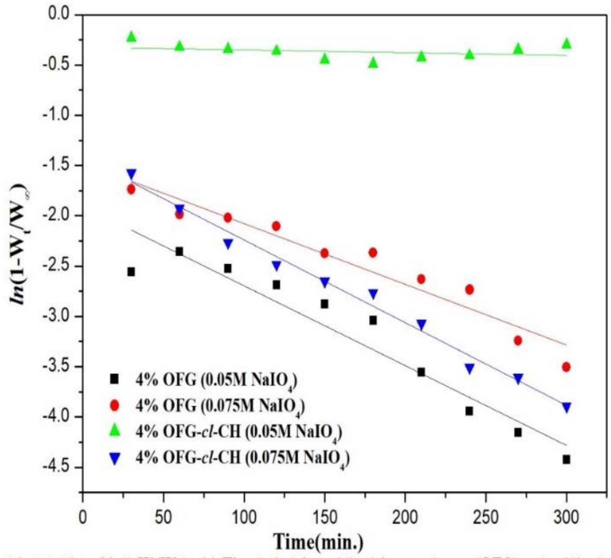

Fig.9.4: Plot of $ln(1-W_t/W_\infty)$ with **Time(min.)** for oxidized fenugreek gum **(OFG)** and oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of amount of oxidant.

Swelling profile of optimized OFG and OFG-*cl*-CH matrix have also been evaluated at 0.9% NaCl to check the suitability of functionalized gel for biological systems (Figure 13.1 and Figure 14.1). Fenugreek gum have more swelling in brine solution than chitosan but ultimately in both fenugreek gum and protein chitosan there is decrease of swelling percentage because swollen hydrogel shrinks in the presence of electrolytes. In the present study, swelling behaviour of oxidized fenugreek gum (2% and 4% FG) cross linked with chitosan (OFG-*cl*-CH) has been studied in 0.9% NaCl brine solution. For OFG, maximum swelling obtained was 130.90% for oxidized FG having composition 2% fenugreek gum oxidized with 0.05M sodium periodate. Maximum swelling of about 155.45%have been obtained for OFG-*cl*-CH network prepared from 4% fenugreek gum oxidized with 0.075M sodium per iodate and minimum 66.30% was observed for OFG-*cl*-CH synthesized from 2% fenugreek gum oxidized with 0.05M $NaIO_4$.The decrease in the swelling percentage for (OFG-*cl*-CH) synthesized with 2% FG oxidized with 0.05M $NaIO_4$ has been observed due to the phenomenon of ex-osmosis as even the swollen hydrogel network shrink in the presence of electrolytes.

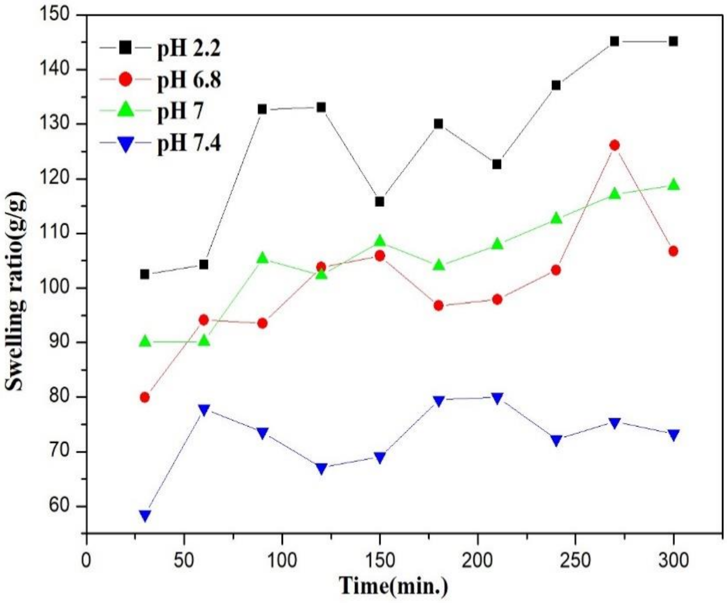

Fig.10.1:Swelling ratio of fenugreek gum **(FG)** as a function of pH.

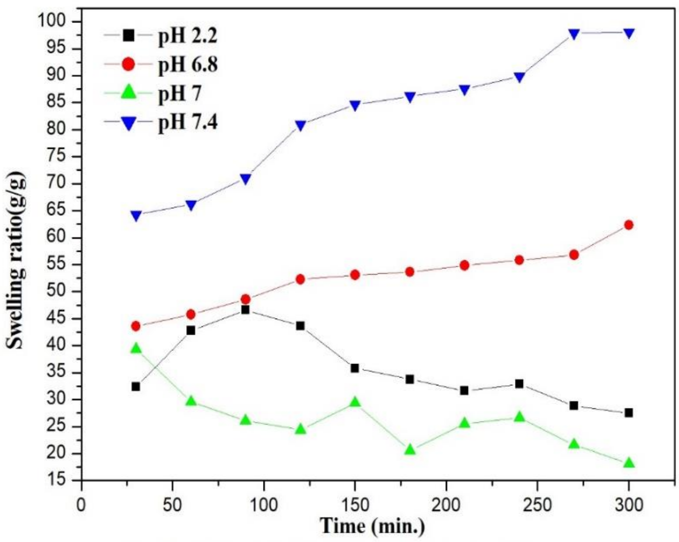

Fig.10.2: Swelling ratio of chitosan **(CH)** as a function of pH.

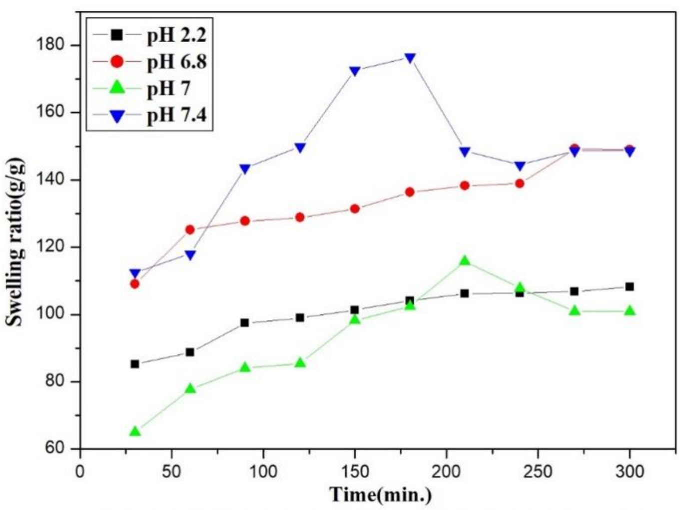

Fig.11.1: Swelling ratio of oxidized fenugrek gum **(OFG)** as a function of pH.

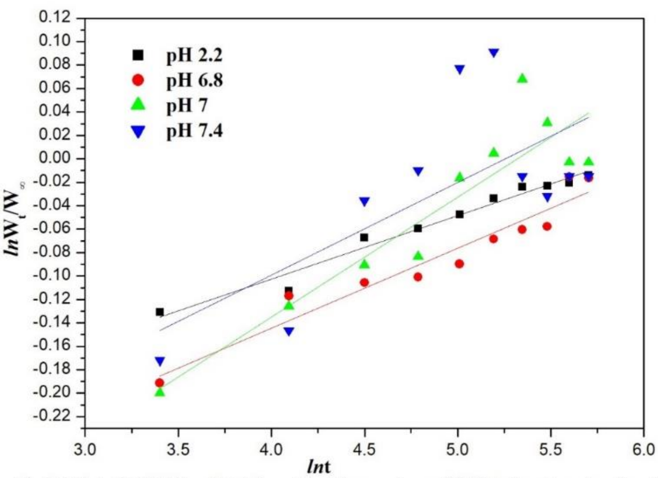

Fig.11.2:Plot of lnW_t/W_∞ with **ln t** for oxidized fenugreek gum **(OFG)** hydrogel as a function of pH.

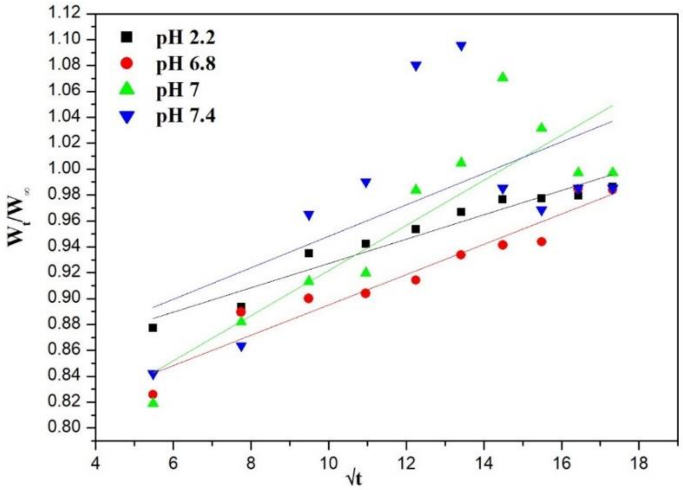

Fig.11.3:Plot of W_t/W_∞ with **√t** for oxidized fenugreek gum**(OFG)** hydrogel as a function of pH.

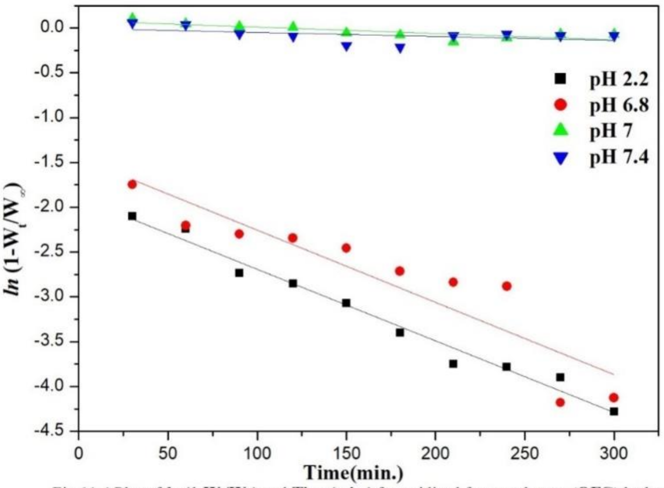

Fig.11.4:Plot of ***ln*** **(1-W_t/W_∞)** and **Time(min.)** for oxidized fenugreek gum (**OFG**) hydrogel as a function of pH.

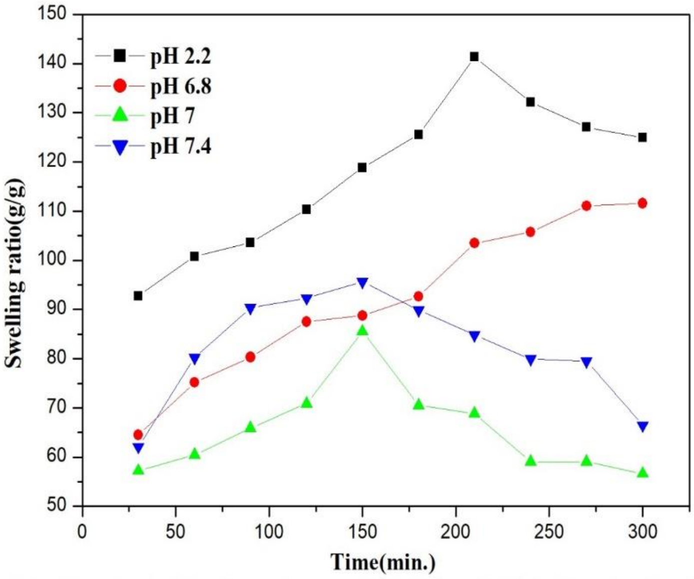

Fig.12.1:Swelling ratio of oxidized fenugreek gum crosslinked chitosan**(OFG-*cl*-CH)**as a function of pH.

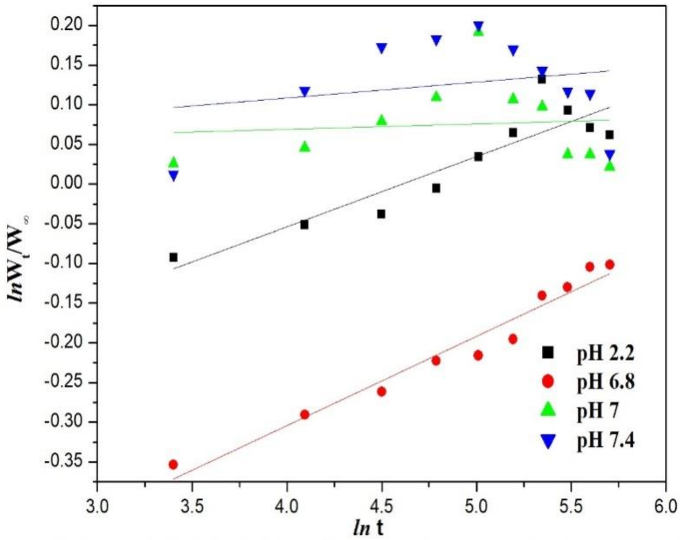

Fig.12.2:Plot of ***ln***W_t/W_∞ with ***ln*** t for oxidized fenugreek gum crosslinked chitosan**(OFG-*cl*-CH)**

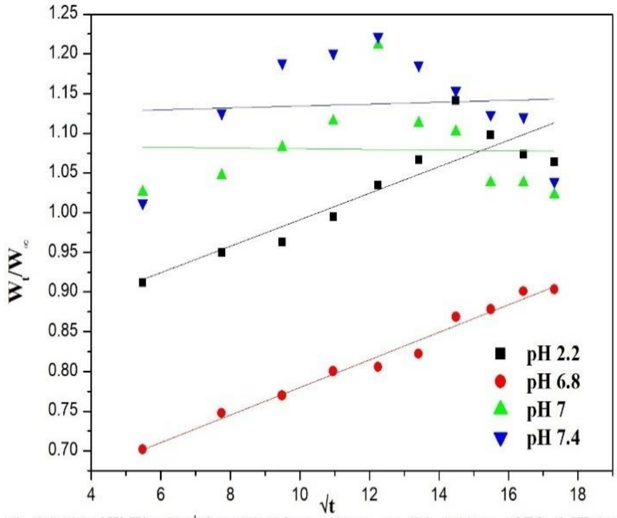

Fig.12.3:Plot of W_t/W_∞ with √t for oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of pH.

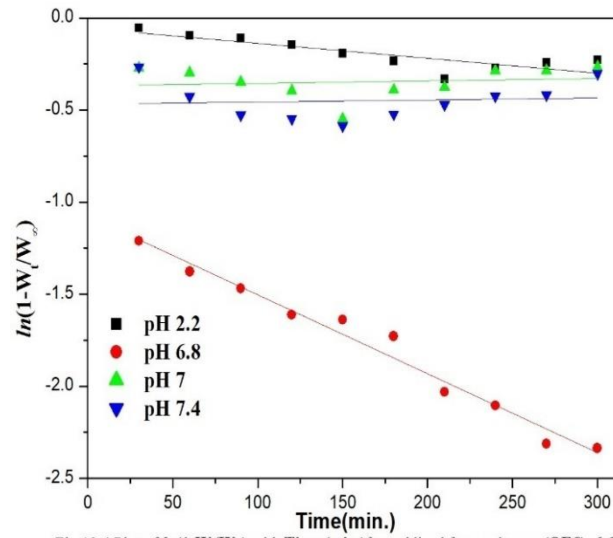

Fig.12.4:Plot of ***ln*(1-W_t/W_∞)** with **Time (min.)**for oxidized fenugrek gum **(OFG-*cl*-CH)** hydrogel as a function of pH.

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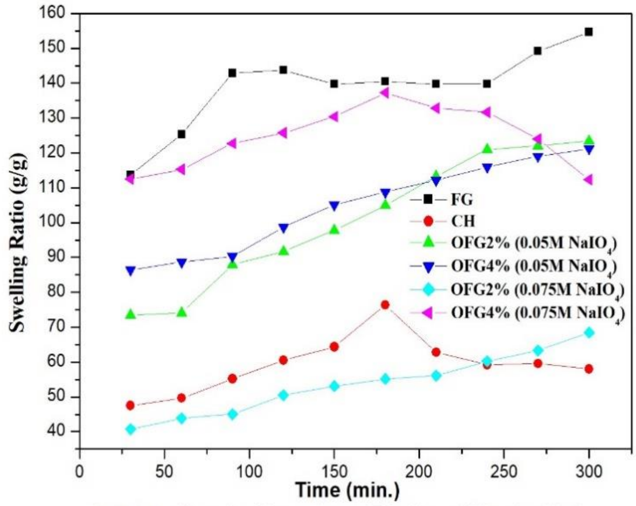

Fig.13.1: Swelling ratio of fenugreek gum **(FG)**,chitosan**(CH)** and oxidized fenugreek gum **(OFG)** as a function of 0.9% NaCl solution.

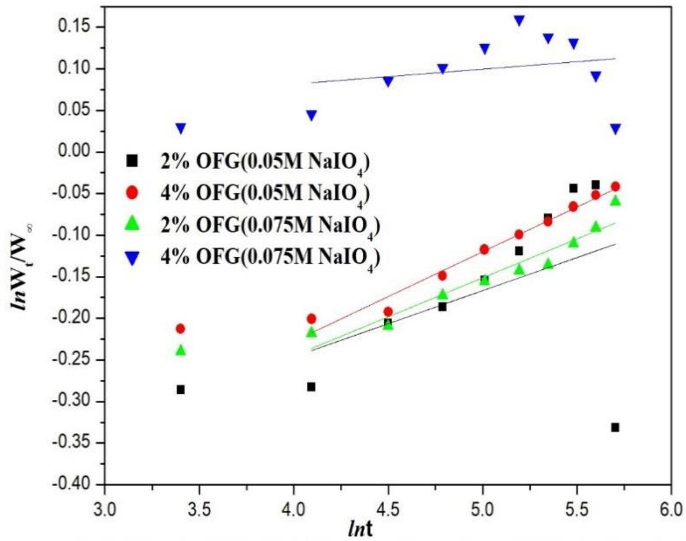

Fig.13.2:Plot of ***ln*** W_t/W_∞ with ***ln*** **t** for oxidized fenugreek gum **(OFG)** hydrogel as a function of 0.9% NaCl solution.

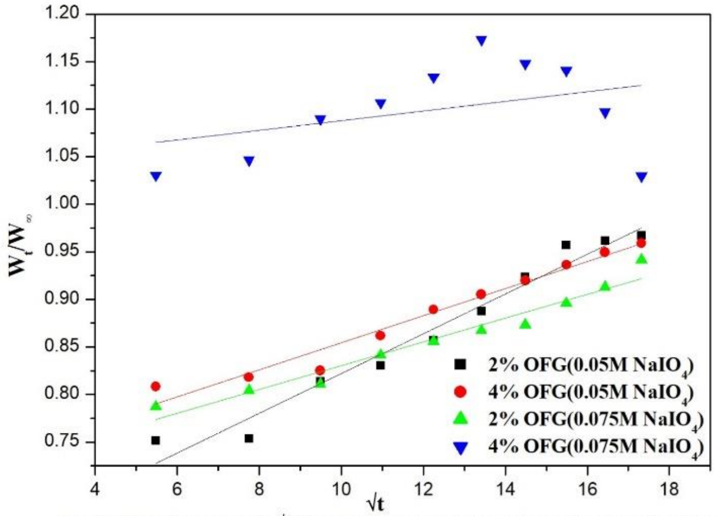

Fig.13.3:Plot of W_t/W_∞ with **√t** for oxidized fenugreek gum**(OFG)** hydrogel as a function of 0.9% NaCl solution.

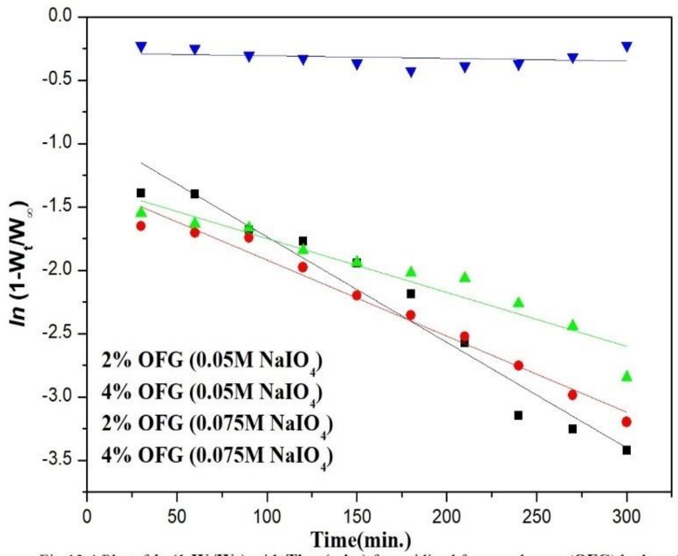

Fig.13.4:Plot of ***ln*** **(1-W_t/W_∞)** with **Time(min.)** for oxidized fenugreek gum (**OFG**) hydrogel as a function of 0.9% NaCl soluion.

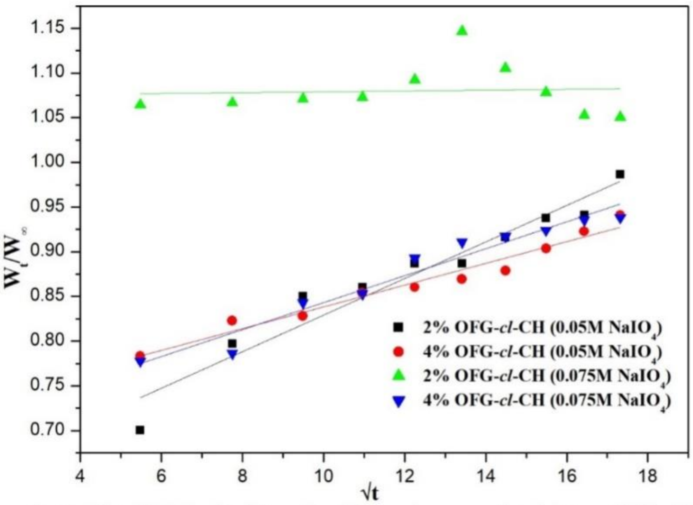

Fig.14.3:Plot of W_t/W_∞ with √t for oxidized fenugreek gum crosslinked chitosan **(OFG-*cl*-CH)** hydrogel as a function of 0.9% NaCl solution.

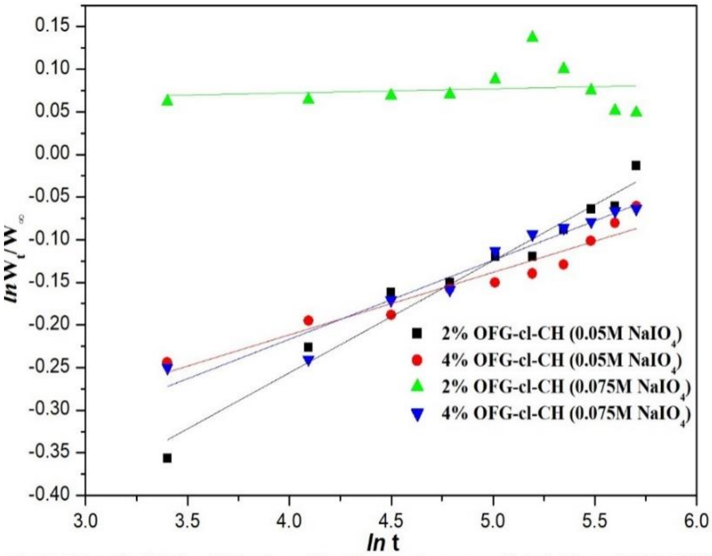

Fig.14.2:Plot of ***ln*** W_t/W_∞ with ***ln*** t for oxidized fenugreek gum crosslinked chitosan**(OFG-*cl*-CH)** hydrogel as a function of 0.9% NaCl solution.

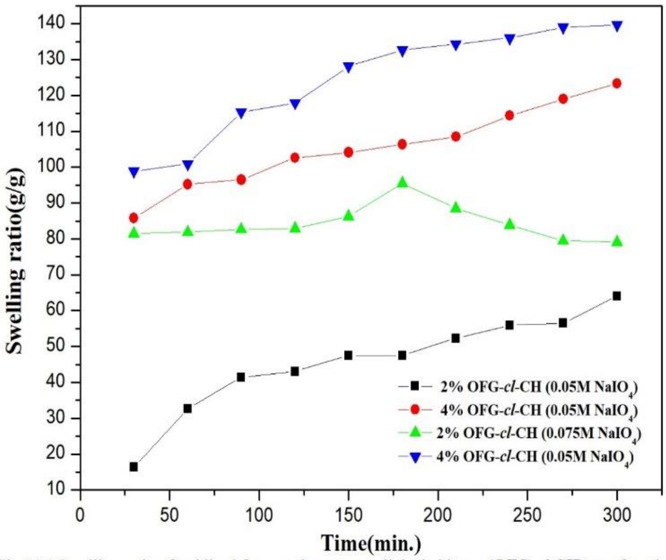

Fig.14.1:Swelling ratio of oxidized fenugreek gum crosslinked chitosan**(OFG-*cl*-CH)** as a function of 0.9% NaCl solution.

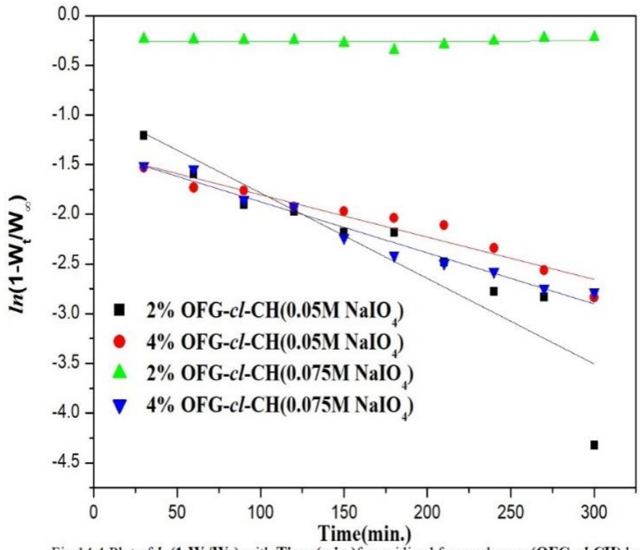

Fig.14.4:Plot of ***ln***(1-W_t/W_∞) with **Time (min.)**for oxidized fenugrek gum **(OFG-*cl*-CH)** hydrogel as a function of 0.9% NaCl solution.

Swelling kinetics of OFG and OFG-*cl*-CH matrix have also been evaluated using Ritger & Peppas equations. Diffusion constant (n) and gel characteristics constant (K) of OFG and OFG-*cl*-CH matrix at pH 2.2,6.8, 7.4 and 0.9%NaCl solution have been evaluated from the slope and intercept of the plot of *ln* W_t/W_∞ vs. *ln*t, and there values have been reported in table 4. Diffusion exponent was less than 0.5 for OFG, OFG-*cl*-CH Schiff base matrix in different swelling conditions. This shows pseudo-Fickian diffusion and its curves resemble with Fickian curves but with slower approach to equilibrium[54].Values of gel characteristic constant was found comparable for both OFG and OFG-*cl*-CH Schiff base matrix (Table 4). D_i and D_A for OFGand OFG-*cl*-CH as a function of backbone FG (2% and4%) and as a concentration of oxidant (0.05M and 0.075M) at pH7 at pH 2.2,6.8, 7.4 and 0.09% NaCl solutions have been calculated by equations (5)and(6) and observed by plot of √t vs W_t/W_∞(Figure 11.3,12.3,13.3, 14.3).The value of D_L have been evaluated by plotting the graph *ln* (1-W_t/W_∞) vs. time (t) as shown in Figure (11.4, 12.4, 13.4, 14.4). and results have been shown in table 5 and 6 respectively.At pH 2.2, 6.8, 7.4 and 0.9% NaCl, value of D_i have been obtained lower than that of D_L. At pH 2.2, D_i value is less than the D_L, when the backbone (2%FG) of polysaccharide gum is small. But when backbone of the polysaccharide gum increased the D_i have greater value than D_L at concentration of oxidizing agent, $NaIO_4$(0.05M&0.075M).Same trends have been obtained for OFG-*cl*-CH Schiff base, it means at lower backbone initial swelling is less than the latter stage at different concentration of oxidizing agent. At pH 6.8 expect 4% fenugreek gum oxidized with 0.075M $NaIO_4$, initial diffusion (Di) value is less than the D_L. At pH 6.8 for OFG-c*l*-CH the initial swelling is less than the latter stage. These swelling results depicts that functionalized polymeric matrix synthesized from oxidized fenugreek gum possess pH responsive behaviour and could be employed for drug uptake and release of pharmaceutical agents in biological systems.

TABLE-1: Diffusion exponent (n) and Gel Characteristic constant (k) of OFG and OFG-*cl*-Ch (Schiff's base) from Slope and intercept of plot *ln* t against *ln* W_t/W_∞ at pH 7 as a function of amount of backbone & concentration of oxidant.

S.No.	FG%	Conc.of $NaIO_4$ (M)	OFG		OFG-*cl*-Ch (Schiff's base)	
			Diffusion exponent(n)	Gel characteristic constant K×10	Diffusion exponent(n)	Gel characteristic constant K×10
1	2%	0.05M	0.10229	5.8	0.01922	9.89
2	4%	0.05M	0.03779	7.88	0.05345	8.63
3	2%	0.075M	0.0762	5.6	0.05684	6.15
4	4%	0.075M	0.06798	6.46	0.09173	5.86

TABLE 2: Diffusion coefficient for OFG (cm2min-1) Di, DA and DL as a function of amount of backbone & concentration of oxidant.

Diffusion coefficient for OFG (cm^2min^{-1}) D_i, D_A and D_L at pH 7

S.N0.	FG %	Conc.of $NaIO_4$ (M)	pH	$D_i \times 10^5$	$D_A \times 10^3$	$D_L \times 10^5$
1	2%	0.05M	7	7.94	1.84	0.9
2	4%	0.05M	7	1	1.48	10.05
3	2%	0.075M	7	2.33	1.95	3.52
4	4%	0.075M	7	2.55	2	7.65

TABLE -3 Diffusion coefficient for OFG-*cl*-Ch (Schiff's base) (cm2min-1) Di, DA and DL as a function of amount of backbone & concentration of oxidant.

Diffusion coefficient for OFG-*cl*-Ch Schiff's base (cm^2min^{-1}) D_i, D_A and D_L at pH 7

S.N0.	FG %	Conc.of $NaIO_4$ (M)	pH	$D_i \times 10^5$	$D_A \times 10^3$	$D_L \times 10^5$
1	2%	0.05M	7	3.16	5.25	-2.19
2	4%	0.05M	7	6.23	5.16	-1.41
3	2%	0.075M	7	1.78	2.42	2.19
4	4%	0.075M	7	5.7	1.93	11.1

TABLE-4: Diffusion exponent (n) and Gel Characteristic constant (k) of OFG and OFG-*cl*-Ch (Schiff's base) from Slope and intercept of plot *ln* t against *ln* W_t/W_∞ at different pH and 0.9% NaCl

S.No.	FG%	Conc.of $NaIO_4$ (M)	Parameter	OFG		OFG-*cl*-Ch (Schiff's base)	
				Diffusion exponent(n)	Gel characteristic constant K×10	Diffusion exponent(n)	Gel characteristic constant K×10
1	2%	0.05M	2.2	0.05415	7.27	0.08849	6.66
2	2%	0.05M	6.8	0.06568	6.67	0.11244	4.71
3	2%	0.05M	7	0.10229	5.8	0.01922	9.89
4	2%	0.05M	7.4	0.07902	6.61	0.02	10.29
5	2%	0.05M	0.9% NaCl	0.07711	5.77	0.13153	4.58

TABLE 5: Diffusion coefficient for OFG (cm2min-1) Di, DA and DL at different pH and 0.9%NaCl solution.

S.N0.	FG %	Concentration of NaIO4 (M)	Parameter	$D_i \times 10^5$	$D_A \times 10^3$	$D_L \times 10^5$
1	2%	0.05M	2.2	1.73	1.93	10.11
2	2%	0.05M	6.8	2.61	2.26	10.21
3	2%	0.05M	7	7.94	1.84	0.9
4	2%	0.05M	7.4	2.89	2.25	10.56
5	2%	0.05M	0.9% NaCl	8.57	2.08	10.56

TABLE 6: Diffusion coefficient for OFG-*cl*-Ch (Schiff's base) (cm2min-1) Di, DA and DL at different pH and 0.9%NaCl solution.

S.N0.	FG %	Concentration of NaIO4 (M)	Parameter	$D_i \times 10^5$	$D_A \times 10^3$	$D_L \times 10^5$
1	2%	0.05M	2.2	5.45	5.67	0.93
2	2%	0.05M	6.8	5.9	2.11	5.42
3	2%	0.05M	7	3.16	5.25	-2.19
4	2%	0.05M	7.4	0.02	5.54	0.83
5	2%	0.05M	0.9% NaCl	7.88	1.48	8.03

4. Conclusions

In present scenario, there is a continuous interest in the modification of natural galactomannan fenugreek gum with the aim to have better materials for drug delivery systems. Fenugreek gum is a promising biodegradable natural polymeric material with therapeutic significance. In addition they are easily available, less expensive and nontoxic. Fenugreek gum could be exploited for different application through chemical modifications. In present study, we have functionalized FG with sodium per iodate (a selective oxidizing agent) and further functionalized with chitosan through self-crosslinking condensation mode to fabricate OFG-

cl-CH hybrid network. Functionalized gel matrix has been characterized through FTIR, XRD, FSEM, EDX and swelling study. Swelling kinetics has been evaluated as a function of reaction parameters and ionic strength of swelling medium to check their suitability as drug delivery agents. Oxidized fenugreek gum depicts less swelling than the fenugreek gum due to increase in crystallinity due to oxidation of gum. OFG and OFG-*cl*-CH Schiff base matrix represents pH responsive behaviour as confirmed by swelling kinetics and porous structure is confirmed by SEM analysis.OFG-*cl*-CHSchiff base polymeric networks follow pseudo-Fickian mechanism. Therefore new synthesised OFG-*cl*-CH Schiff base could be used further as potential drug delivery systems.

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Conflict of interest

The authors declare that there is no conflict of interests regarding the publication this article.

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