

Development and Characterization of Semi-IPN Silver Nanocomposite Hydrogels for Antibacterial Applications

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Abstract - Sodium carboxymethyl cellulose/poly (*N*-isopropylacrylamide-co-2-acrylamido-2-methylpropane sulfonic acid) semi-interpenetrating polymer network (semi-IPN) hydrogels were prepared by using free radical polymerization technique. Silver nanoparticles were loaded into the semi-IPN hydrogel by *in situ* reduction of silver nitrate with sodium borohydrate at room temperature. The formation of silver nanoparticles in the hydrogels were characterized by using UV-visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), thermo gravimetric analysis, X-ray diffractometry, scanning electron microscopy, and transmission electron microscopy techniques. SEM images showed clearly the formation of group of silver nanoparticles with size range of 10–20 nm. Transmission electron microscopy study further supported the results. The semi-IPN silver nanocomposite hydrogels reported here might be a potentially smart material in applications of antibacterial activity.

Keywords: Sodium carboxymethyl cellulose, AMPS, NIPAM, silver nanoparticles, Antibacterial activity.

I. INTRODUCTION

Hydrogels are three-dimensional polymeric networks fabricated from polymers, stabilized through physical or chemical crosslinking. They absorb large quantities of water without losing their structural integrity [1]. Since they mimic body tissues and respond to external stimuli, they are made important and promising forms of biomaterials for various applications including tissue engineering, controlled drug release devices, biosensors, and mechanical actuators [2–4]. Due to the presence of water solubilizing groups, such as –OH, –COOH, –CONH₂, –CONH–, and –SO₃H, these hydrogels show higher hydrophilicity. The three-dimensional network of hydrogel provides relative stability to its structure. Their swollen state results from a balance between the dispersing forces acting on hydrated chains and cohesive forces that do not prevent the penetration of water through the network [5]. Based on these properties the hydrogels have been used recently as templates for production of metallic nanoparticles. Hence the design and development of metal nanoparticles dispersed in polymer matrix have attracted potential applications in various fields like electrical, optical, or mechanical properties [6, 7] making them valuable for applications in areas like optics [8], photo imaging and patterning [9], electronic devices [10], sensors

and biosensors [11–13], catalysis [14, 15], and antibacterial and antimicrobial coatings [16]. Silver nanoparticles (Ag NPs) have attracted considerable interest in biological studies because of their ease of preparation, good biocompatibility, and relatively large surface area [17, 18]. Ag NPs have many important applications in biomedical fields, sensors, and filters [19]. Additionally, silver is a potential antibacterial agent [20] and is thus used as a sterilizer for removing bacteria from drinking water [21, 22]. For economic and efficient use of silver, silver nanoparticle composites have been developed and tested for antimicrobial activity.

Nanocomposite polymer hydrogels may be defined as crosslinked three-dimensional polymer networks swollen with water or biological fluids in the presence of nanoparticles. The design and development of such materials containing metallic nanoparticles have scientific and technological research interests in recent years due to their unique and versatile properties [1–5]. These properties lead to potential applications in the field of numerous physical, biological, biomedical, and pharmaceutical sectors [6–13] as well as optical, electrical, chemical, and data storage [14–18]. These properties are known for silver in the form of ions, colloidal particles, nanoparticles, metallic silver, and silver compounds, and many works study their use to inhibit the proliferation of microorganisms for medical [19–21], food packaging [22, 23], and water treatment [24, 25] applications. Generally silver ions, as heavy metals, lead to the inactivation of proteins reacting with thiol groups (–SH) on the membrane of bacteria causing the microbial cell death [26–28].

The biological activity of silver, especially the antibacterial property, is size dependent [29]. Thus silver nanoparticles should be small enough to pass through the cell membrane. Silver ions kill micro organisms instantly by blocking their respiratory enzyme systems, while having no negative effect on human cells. Although nanocomposites containing metal NPs have elegant features, the homogeneous dispersion of metal NPs is not easy using a simple process because of their high surface free energy, which may cause agglomeration. Therefore, preparation of such nanocomposites with desired

properties (i.e., Ag NPs with convenient size) is an important issue. Thus various strategies have been employed to prepare nanocomposites containing silver nanoparticles with controlled size. One such effective approach reported by Wang et al. [30–32] is the *in situ* reduction of metal ions in the hydrogel networks. In this method the functional groups of the hydrogel network can act as an anchoring agent for the metal ions before *in situ* reduction.

Usually, carboxylic acid groups can be used as a transient anchoring agent for attaching silver cations to polymer hydrogels, and the silver ion is reduced with sodium borohydride to form nanoparticles [33]. This method of preparation depends on the number of functional groups present to stabilize the silver ions, but the nanoparticles are dispersed within the hydrogel matrix. One successful approach that has been employed is the reductive process in homogeneous matrices. In this approach the previously formed crosslinked polymer's swollen with a solution of silver salts and reducing agent, and then reduction takes place within the polymer matrix [34].

This paper focuses on the current design and use of cellulose-based hydrogels (NaCMC/poly(NIPAM-co-AMPS)), which usually couple their biodegradability with a smart stimuli-sensitive behavior. Sodium carboxymethyl cellulose (NaCMC) is an ionic ether of the cellulose with many major commercial applications. It is a highly water soluble anionic polysaccharide that is widely used in pharmaceuticals, cosmetics, and food industry [35–37]. Then 2-acrylamido-2-methyl-propane sulfonic acid is basically a strong acid [38], which can act as a good hydrophilic monomer, and therefore its copolymers have super swelling properties [39]. In this work we report the results obtained for sodium carboxymethyl cellulose/poly(N-isopropylacrylamide-co-2-acrylamido-2-methylpropane sulfonic acid) (NaCMC/ poly(NiPAM-co-AMPS) semi-IPN hydrogels designed as a new antimicrobial biomaterial. Silver containing NaCMC/ poly(NIPAM-co-AMPS) samples were characterized for their structural characteristics, swelling, UV-Vis, FTIR,

TGA, X-RD, and SEM as well as by their antimicrobial performances.

II. EXPERIMENTAL

A. MATERIALS

Acrylamido methyl propane sulphonic acid (AMPS) was purchased from Aldrich Chemicals. Sodium carboxymethyl cellulose (NaCMC) was purchased from HiMedia chemicals, India. N-isopropylacrylamide, N,N-methylene bisacrylamide (MBA), Ammonium persulfate (APS), and N, N,N',N''-tetra methyl ethylenediamine (TEMED) were purchased from S.D. Fine Chemicals, India. Silver nitrate (AgNO_3), Sodium borohydride (NaBH_4) were purchased from Aldrich Chemicals. All chemicals were used without further purification, and double distilled water was used for the preparation of all solutions for this study.

B. Preparation of Semi-IPN Silver Nanocomposite Hydrogels

NaCMC/poly (NIPAM-co-AMPS) semi-IPN hydrogels were synthesized by employing free radical polymerization using N,N'-methylenebisacrylamide as crosslinker and ammonium persulfate/N,N,N',N''-tetramethyl ethylenediamine as redox initiating pair. 1 gm of NiPAM and 0.1 gm of NaCMC were dissolved in 3 ml of distilled water in a 250 ml beaker under constant stirring. To this solution, 1 gm of AMPS was added as comonomer followed by the addition of 0.1 gm of MBA as hydrophilic crosslinker and 0.1 gm of APS and 0.2 ml of TEMEDA as an initiating pair. After the addition of the reactants, the temperature of the system was raised to 50°C for 2 hrs. After the reaction has been completed, the formed hydrogel was immersed in distilled water at room temperature for 24 hours to remove the unreacted materials present in the hydrogel network. Finally, the hydrogel was dried at room temperature for 2 days. Similarly, other hydrogels were prepared by the above procedure. Hydrogels prepared along with their different feed compositions are presented in Table 1

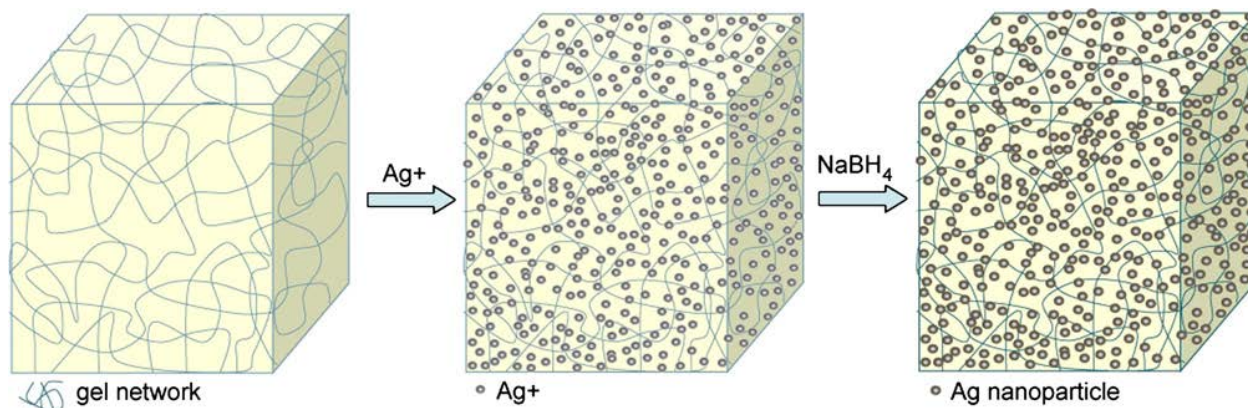


FIG. 1.1: Schematic representation of Silver nano composite preparation.

S.NO	Sample	NIPAM	NaCMC	AMPS	MBA	APS	TEMEDA	Water
1	CAN 1	0.5	0.05	0.5	0.1	0.05	0.1	8
2	CAN 2	0.5	0.1	0.5	0.1	0.05	0.2	8
3	CAN 3	0.5	0.15	0.5	0.1	0.05	0.2	8
4	CAN 4	0.5	0.05	0.6	0.1	0.05	0.2	8
5	CAN 5	0.5	0.05	0.7	0.1	0.05	0.2	8
6	CAN 6	0.5	0.5	0.5	0.5	0.5	0.5	8
7	CAN 7	0.5	0.5	0.5	0.025	0.5	0.5	8

TABLE 1: Various formulation parameters used in the preparation of the hydrogels.

The loading of silver nanoparticles into the hydrogel networks has been performed using the following procedure. Accurately weighed dried copolymeric hydrogels were swelled in double distilled water for 3 days. Then swollen copolymeric hydrogels were transferred into another beaker containing 50 ml of aqueous 5 mm AgNO₃ solution and then allowed to equilibrate the hydrogel for 24 hours to absorb the silver salt. During this process, most of the silver ions were loaded into free network spaces of hydrogel. These hydrogels with absorbed silver nitrate were finally transferred into a beaker containing 50 ml of 10 mm NaBH₄ aqueous solution and kept for 2 hours to reduce the silver ions, the hydrogel was turned into brown color, which confirms the formation of silver nanoparticles in copolymeric hydrogel matrix.

C. Swelling studies

Fully dried semiIPN hydrogels, silver nanocomposite hydrogels were accurately weighed and equilibrated in distilled water at 25^o C and 37^o C for 3 days. The equilibrium swelling capacity or swelling ratio (Q) of the hydrogels was calculated by employing

$$Q = W_e / W_d$$

Where W_e is the weight of swollen hydrogel and W_d is the dry weight of the semi IPN hydrogel.

D. Characterization

UV-visible spectra of semiIPN hydrogel silver nanocomposites (10 mg in 1 ml of distilled H₂O) were characterized using (Lab India UV 3000+) UV-Visible spectrophotometer; Fourier transform infrared spectroscopy (FTIR) spectral measurements were performed using Perkin Elmer (model Impact 410, Wilsconsin, MI, USA) spectrophotometer. The samples were finely grounded with KBr to prepare pellets under a hydraulic pressure of 600 dynes/m² and spectra were scanned between 4000 to 500 cm⁻¹. TGA (Model-SDTQ600, USA) analysis was performed for pristine

PAV-PC and PPSNC. Analysis of the samples was performed at heating rate of 10 °C/min under N₂ atmosphere at a purging rate of 100 mL/min.

X-ray diffraction measurements were also carried out for the nanocomposites using A Siemens d 5000 (Germany) Powder X-ray diffractometer to know the crystallinity of the hydrogel. Thermal properties of semiIPN hydrogels were evaluated by using SDT-Q600 thermal system at heating range of 10^o C/min under N₂ atmosphere (flow rate 100 ml/min). Morphological variations of dry hydrogel, silver nanocomposite hydrogel were studied using JSM 6400 Scanning Electron Microscope (SEM) (Japan), operating at an acceleration voltage of 15 K volts coating with a thin layer of palladium gold alloy.

E. Antibacterial activity

To carry out antibacterial activity for these nanocomposites, nutrient agar medium was prepared by using peptone(5.0), beef extract (3.0 g), and sodium chloride (NaCl) (5.0 g) in 1000 ml distilled water and the pH was adjusted to 7.0 and agar (15.0) was added to the solution. The agar medium was sterilized in a conical flask at a pressure of 15 lbs for 30 min. This nutrient agar medium was transferred into sterilized petri dishes in a laminar air flow. After solidification of the media, bacillus culture was streaked on the solid surface of the media. To this inoculated petri dish, one drop of gel particle solution (20 mg/10 ml distilled water) was added using 50 ul tip and incubated for 2 days at 37^oC in the incubation chamber.

III. RESULTS AND DISCUSSIONS

The concept of producing nanoparticles in the networks of hydro-, micro-, and nanogel systems was recognized as most important approach due to its direct applicability in various biomedical applications and in this way a number of composite systems were evaluated (Bajpai et al., 2007).

3.1. SWELLING STUDIES

In this study, N-isopropylacrylamide and AMPS were copolymerized in the presence of NaCMC to obtain NaCMC/poly (NIPAM-co-AMPS) semi-IPN hydrogels, where the NaCMC chains are randomly distributed throughout gel networks. The special interest in choosing NaCMC as an interpenetrating polymer in hydrogels is due to its viscosity increasing, binding, protecting, reducing, stabilizing, and disintegration properties [40], that is widely used in pharmaceutical applications. The main criterion in selecting AMPS as a comonomer in the preparation of hydrogel is due to the presence of sulphonic acid groups, which are highly water attractive in nature and thereby increase the water absorbing capacity. Hence the hydrogels swell more as the AMPS concentration increases.

Figure 2 shows the swelling studies of various formulations of semi-IPN pure hydrogels and their silver loaded hydrogels. For all these formulations the order of swelling capacity for semi-IPN hydrogels was found to be greater than the silver nanocomposite hydrogels. From Figures 1(a) and 1(b) it is observed that as the amount of NaCMC and AMPS weight ratio increased, the swelling ratio also increased. This can be attributed due to the presence of polar groups ($-OH$, $-CONH_2$, $-COO^-$, Na^+ , and SO_3H) in polymeric chains. The presence of the ionic groups in polymer chains results in increasing of the swelling ratio because the ionic groups are more strongly solvated than the nonionic groups in the aqueous medium. The effect of crosslinker concentration on the swelling behavior of semi-IPN hydrogels was studied by varying the amount of crosslinker content 0.02–0.12 gm. In Figure 1(c) as the crosslinker concentration is increased the swelling ratio decreased this is because the higher the concentration of crosslinker, the higher is the extent of crosslinking in the polymer network and decrease diameter of pores of resultant hydrogels leading to solvent mobility, and then less will be the swelling ratio. Similar observations have been reported in the literature [41–44].

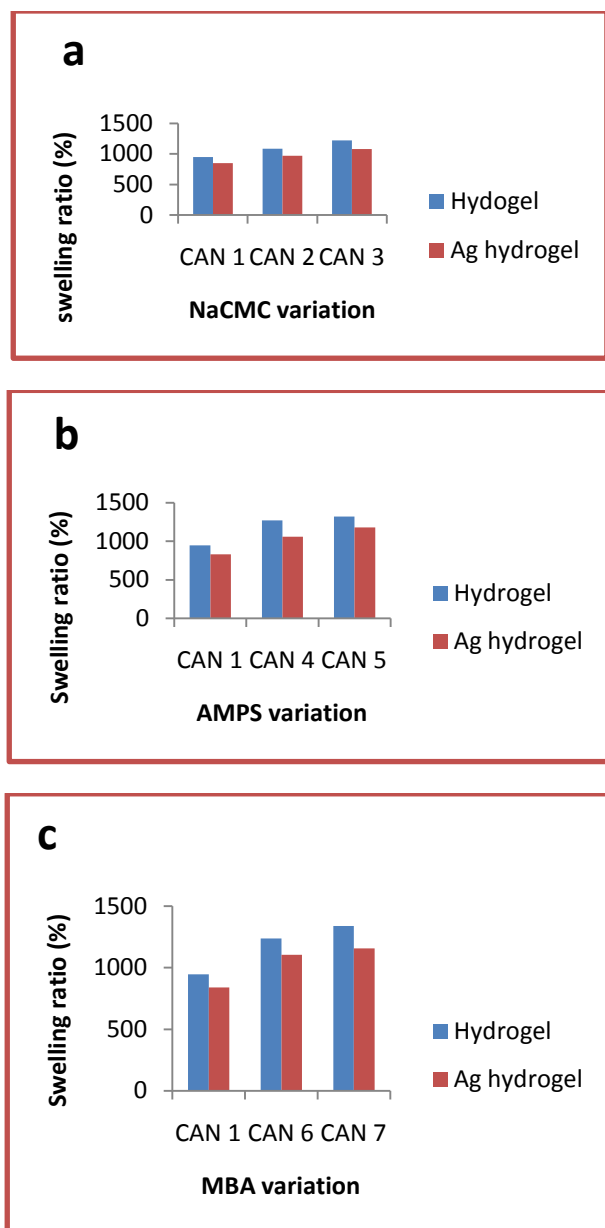


FIGURE.2. Swelling studies of hydrogel and silver nanocomposite hydrogel with NaCMC variation (a), AMPS variation (b) and MBA variation (c)

3.2. UV-VISIBLE SPECTROSCOPY

Generally in silver nanoparticles the conduction band and valence band lie very close to each other in which electrons move freely. These free electrons give rise to a surface Plasmon resonance (SPR) absorption band [45-47] (380–500 nm range) occurring due to the collective oscillation of electrons of silver nanoparticles in resonance with the light wave of UV-Vis spectroscopy. The formation of silver nanoparticles in semi-IPN hydrogel networks can be expected in our spectral analysis. Figure 3 illustrates the absorption spectra for hydrogel loaded with Ag^+ ions in the range of 300 nm and silver nanocomposites in the range of 380–500 nm. A significant improvement in the absorption peak ($\lambda_{max} = 420$ nm) was observed due to the surface Plasmon resonance (SPR) effect. However, there is no peak observed in pure semi-IPN hydrogel. This spectral analysis confirmed the formation of silver nanoparticles in the semi-IPN hydrogel networks.

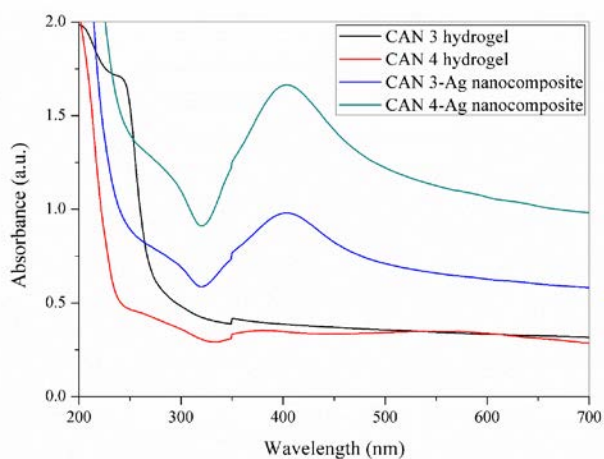


FIGURE.3. UV-visible spectra of CAN, CAN-Ag nanocomposite hydrogels

3.4 FOURIER TRANSFORMS INFRARED SPECTROSCOPY ANALYSIS:

The FTIR spectrum of poly(NIPAM), Poly(AMPS), Poly(NIPAM-co-AMPS) and NaCMC-g-Poly(NIPAM-co-AMPS) hydrogels is shown in FIGURE.4. The samples have shown characteristic peak at 3424 cm^{-1} due to N – H stretching of amide groups of acryl amide units present in the hydrogels.

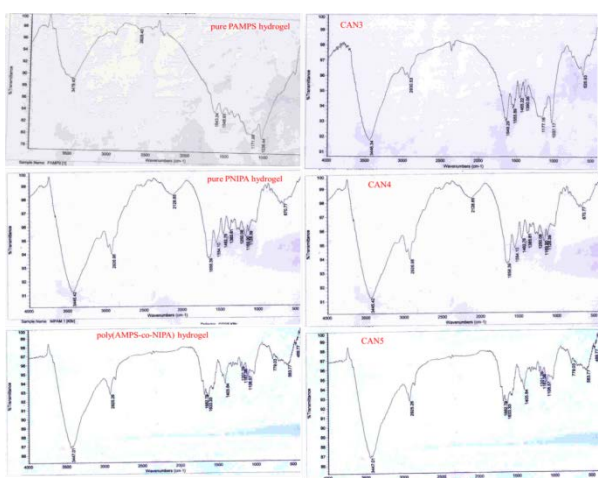


FIGURE.4. FTIR spectra of Poly(AMPS), Poly(NIPAM), Poly(NIPAM-co-AMPS) hydrogels and different CAN hydrogels

In the spectra of poly[NIPAM – AMPS] hydrogel some more characteristic absorption bands are observed at 1627.6 and 1545.7 cm^{-1} due to amide carbonyl group peaks of AMPS and NIPAM units, and secondary amide N – H deformation peak of hydrogel. The peaks at 1465.3 cm^{-1} indicates C – H bending of CH_2 groups and the peak at 1384.5 cm^{-1} indicating the vibration of the isopropyl group. The group at 1216.6 cm^{-1} , 1078.70 cm^{-1} , and 1016.3 cm^{-1} , are indicating the asymmetric and symmetric stretching of S – O bond of SO_3^- groups. An absorption band with multiple peaks in the $1150\text{--}1000\text{ cm}^{-1}$ range is attributed

to the ether bonds in the cellulose backbone. The ionized carboxyl groups (COO^-) show two absorption peaks at 1580 and 1410 cm^{-1} due to the symmetric and asymmetric stretching. Smaller peaks at 1321 and 1268 cm^{-1} can be assigned to the stretching vibrations at C=O and OH groups.

3.4. X-RD ANALYSIS

The crystallographic nature of the silver nanoparticles in hydrogels was investigated by X-ray diffraction. The X-ray diffraction of pure and silver nanocomposite semi-IPN hydrogels was illustrated in Figure 5. The diffractogram of semi-IPN hydrogel silver nanocomposites is assigned to diffraction at 2θ value about 38°C , 44°C , 65°C , 77°C , and 82°C to the brags reflections of (111), (200), (220), (311), and (222) lattice planes [48], are observed. These peaks are matched with the face centered cubic (FCC) structure of silver (JCPDS card file no. 04-0783). The intense peak represents to highly crystalline silver nanostructures formed in semi-IPN silver nanocomposite hydrogels. In pure hydrogel there is no peak observed; this is due to the absence of silver nanoparticles in pure semi-IPN hydrogel.

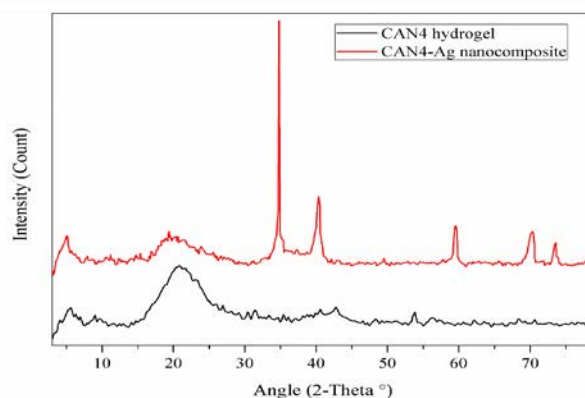


FIGURE.5. XRD pattern of the CAN4, and CAN4-Ag nanocomposite hydrogels

3.5. THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA is an important technique to study the formation and thermal stability of hydrogels and its Ag nanocomposite hydrogels. TGA curves of hydrogel and Silver nanocomposites are shown in FIGURE.6. The starting decomposition temperature of Ag nanocomposite hydrogel (195°C ($0.2679\% / ^\circ\text{C}$)) is more than that of plain hydrogel (170°C ($0.5327\% / ^\circ\text{C}$)). The weight loss observed in the case of pure hydrogel is 80% around 550°C where as the weight loss observed for silver nanocomposite hydrogel at this temperature is only 72%. So, a clear variation has been observed in TGA experiments, that silver nanocomposites exhibit excellent thermal stability than placebo hydrogels. The weight loss difference between the hydrogel and Silver nanocomposites is 5.32 % which represents the presence of silver nanoparticles (weight percent) in the semi IPNs.

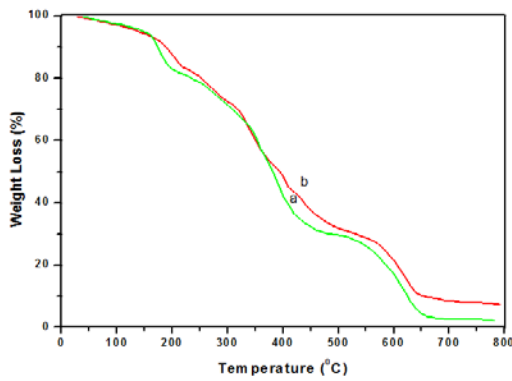


FIGURE.6. Thermo gravimetric analysis of pure hydrogel (a) and silver composite hydrogel (b)

3.6. SCANNING ELECTRON MICROSCOPY

The scanning electron micrographs of pure hydrogel and silver nanocomposite hydrogels were shown in Figure 7. The pure hydrogel showed branches and rough surface (Figures 7(a) and 7(b)), whereas silver nanocomposite hydrogels showed a shrunken surface (Figures 7(c), 7(d) and 7(e)) having uniform distribution of silver nanoparticles in size around 10–20 nm. However there is a pin point variation in the case of silver nanoparticles formed in the gel networks. This clearly indicates the formation of silver nanoparticles along with the polymer chains throughout the gel networks. It reveals that NaCMC polymeric chains control to lower particle size due to effective reduction and stabilization properties. It is quite common that the control or alignment of silver nanoparticles can be achieved by modifying the hydrogel network architectures (49).

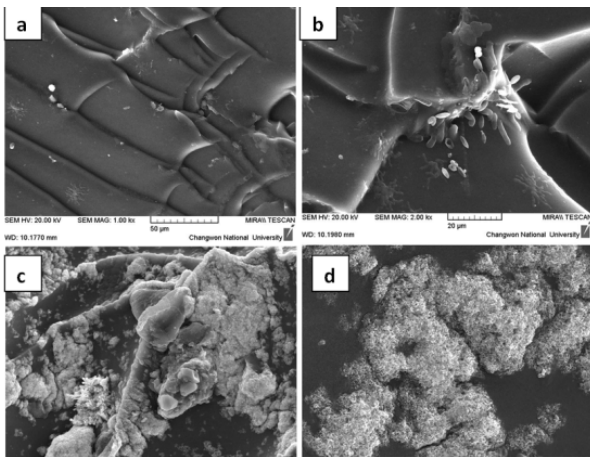


FIGURE.7. Scanning electron micrographs of pure hydrogel (a & b) and silver nanoparticle hydrogel (c and d)

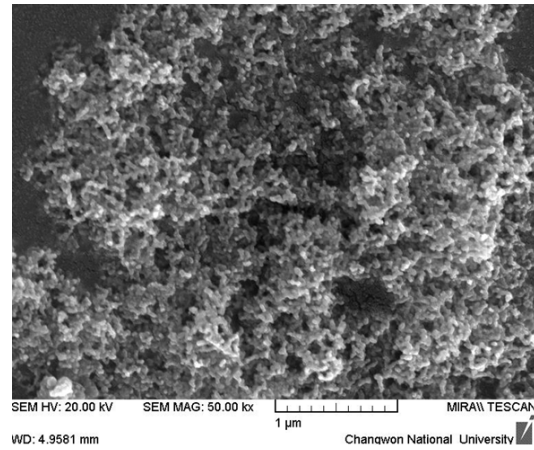


FIGURE.7(e). Scanning electron micrographs of silver nanoparticles inside hydrogel networks

3.7. ANTIBACTERIAL STUDIES

In this study the bacterial effect of silver nanocomposite hydrogels mostly depends on the size of particles and the swelling ratio, which have a direct interaction with the bacteria. Antibacterial studies of pure semi-IPN hydrogel and silver nanocomposite hydrogels were tested by paper disc method using *Bacillus subtilis* as shown in Figure 8. The results suggest that CAN-4, CAN-3, CAN-2, CAN-1 have an antibacterial activity against *Bacillus subtilis* (Gram +ve bacteria), while pure hydrogels were generally inefficient. The inhibition area follows the order SIPN-4 > SIPN-3 > SIPN-2 > SIPN-1. This behavior is expected for silver nanoparticles of small sizes (1–20 nm) and the same order is expected for swelling ratio. So that these silver nanoparticles could come out easily and could interact with lipid layer of cell membrane, thereby attaching to microbial DNA to prevent bacterial replication, which are responsible for inhibition of bacterial growth (50).

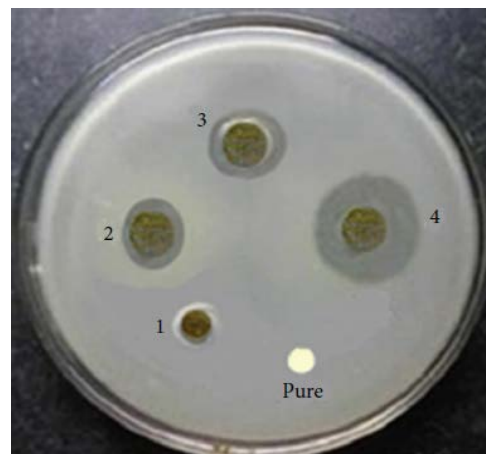


FIGURE.8. Antibacterial activity picture of silver nanocomposite hydrogels

IV. CONCLUSION

NaCMC/poly(NIPAM-co-AMPS) semi-IPN silver nanocomposite hydrogels were successfully prepared via a

free radical polymerization along with varying doses of polymer, comonomer, and crosslinking agent thereby reduction of silver ions into silver nanoparticles. The developed silver nanoparticles are well characterized by using different techniques to confirm the formation of silver nanoparticles and antibacterial activity on *Bacillus subtilis* bactericides. The swelling capacity of the resulting hydrogels was found to be directly related to NaCMC, AMPS, and MBA ratio used in the polymerization process. UV-visible spectra, thermal analysis, and XRD data revealed the formation of silver nanoparticles through examination of micrographs obtained using SEM. The developed silver nanocomposite hydrogels confirmed that small sizes and abundance of silver nanoparticles determine the antibacterial activity.

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