Swelling characteristic behavior, Antioxidants and Antimicrobial activities of Hydroxyethyl acrylate based gold nanocomposite hydrogels

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Abstract

In the present study describes, the synthesis of poly (NTA-co-AM/HEA) gold nanocomposite hydrogels and are prepared by free radical copolymerization using ammonium per sulfate as an initiator and N, N′-methylene bis acryl amide as the cross-linker. The synthesized nanocomposite hydrogel was characterized by FTIR spectroscopy, XRD, SEM and TGA analysis. The swelling behavior, and dye adsorption studies antioxidant activity and antimicrobial activities were investigated. It was found that 0.1 g of HEA containing hydrogel showed the higher removal efficiency than the other feed content of HEA. The 0.5g of HEA content hydrogel showed the maximum of 52.65% of antioxidant activity by DPPH method. At higher content of HEA containing gold nanocomposite hydrogels exhibited excellent activities for both the antibacterial and antifungal activities towards the selected microorganisms.

Keywords:

Gold Nanocomposite Hydrogels; TGA analysis; SEM analysis; Antimicrobial Activities

1. Introduction

Hydrogels with metal / metal oxide nanoparticles in their polymer matrix showing wide application such as higher mechanical properties, dye adsorption, heavy metal adsorption, immobilization of enzyme, denaturing of protein solution, tissue engineering controlled drug delivery etc. Mostly metal/ metal oxide intercalated hydrogels exhibit stimuli response behavior like P^H, temperature, electrolyte-controlled drug release and swelling/ deswelling, light. Due to the presence of ionic group in the polymer matrix enhances the equilibrium swelling because of hydrophilic/ hydrophobic interaction, degree of crosslinking, degree of ionization and interaction of counter ions. The swelling behavior of acrylamide-based hydrogels can be enhanced by substituting alkyl groups in the acrylamide monomer [1]. For example N-cyclohexylacrylamide based gold nanocomposite hydrogel showed increased swelling behavior with increasing amount of ionic monomer (AMPSNa) [2]. Hydrophilic groups containing hydrogels are best biomaterials and resemble with natural living tissues. Therefore, the usage of hydrogels are as actuators, artificial skins [3]. Kayalvizhy et al, reported the protein adsorption, anthelmintic and antioxidant activity of AMPS-TEA ionic Liquid based hydrogels. These hydrogels are effective against parasitic infections and showed 89.44% of antioxidant activity [4].

Usually, metal nanoparticles like, Ag, Au, Cu are active against microorganism. When the nanoparticles are incorporated in the polymer matrix, antibacterial activity [14] and antioxidant activity [15] were increased. Dalaran et al, reported the removal of acidic dye (Indigo carmine) using MMT nanoclay containing 2-Hydroxyethyl methacrylate hydrogels. The dye adsorption with 1%weight ratio showed more adsorption behavior than at 4% of MMT [7]. Hydrogels of HEMA and BA exhibited super absorbency in water and organic solvent than the hydrogels of HEMA with DM&EMA monomers [8]. 2-Hydroxylethylmethacrylate based microgels used as a model drug carrier towards Lidocaine and Methylene Blue. But the drug releasing behavior of the microgels are affected by interactions of drug and microgel [9]. Blood protein adsorption of poly(2-Hydroxyethylmethacrylate-co-acrylonitrile) hydrogel was studied, which demonstrate the adsorption of protein and antithrombogenicity increased with increasing amount of HEMA[10]. The drug delivery system of starch grafted poly(acrylicacid-co-2-hydroxyethylmethacrylate) hydrogel against 5-fluorouracil was studied [11]. The drug releasing behavior is faster at P^H level of 7.4 than at lower level of P^H, because of shrinkage of hydrogel occurs at lower level (P^H=1.2). Due to the nontoxicity, biodegradable of 2-hydroxyethyl methacrylate, the hydrogel based on HEMA is used as soft contact lenses. The HEMA hydrogel resulted controlled solvent diffusion and follow to Fickian- II mechanism. A novel biodegradable gold nanocomposite hydrogel of acrylamide and wheat protein isolate is used as antibacterial agent [12]. According to the literature, works are reported on 2-hudrogelethyl methacrylate and very few works on hydroxyethyl acrylate-based gold nanocomposite hydrogels.

Therefore, we aimed /focused on the to synthesize the hydroxyethyl acrylate gold nanocomposite hydrogels.In this present investigation, we described/report the synthesize of poly(N-tert-amylacrylamide-co-acrylamide/hydroxyethyl acrylate) gold nanocomposite hydrogels via free radical polymerization.The swelling & swelling kinetics of the gold nanocomposite hydrogels were evaluated. The DPPH method used to study the antioxidant activity of the hydrogels.

2. Experimental

2.1.Materials

Hydroxy ethylacrylate (Aldrich) was used as received. Methylene blue dye was supplied by Merck and MB was the analytical reagent grade and is used as received. The $HAuCl_4 \cdot 3H_2O$ solid is hygroscopic purchased from Aldrich.

2.2. Synthesis of Gold nanoparticles (GNP/AuNPs)

Dissolved 1.0 g $HAuCl_4 \cdot 3H_2O$ in 250 mL distilled water to make a 10.0 mM stock solution of gold(III) ions that can be kept for years if stored in a brown bottle. Dilute 25 mL of stock to 250 mL to make the 1.0 mM concentration for this experiment **[2].** About 0.5 g $Na_3C_6H_5O_7 \cdot 2H_2O$ (sodium citrate) dissolved in 50 mL distilled water and 20 mL of 1.0 mM $HAuCl_4$ added to a 50 mL beaker or Erlenmeyer flask on a stirring hot plate. A magnetic stir bar is added and bring the solution to a rolling boil. To the rapidly-stirred boiling solution, quickly add 2 mL of a 1% solution of trisodium citrate dihydrate, $Na_3C_6H_5O_7 \cdot 2H_2O$. The gold sol gradually forms as the citrate reduces the gold (III). Remove from heat when the solution has turned deep red or 10 minutes has elapsed. The presence of a colloidal suspension can be detected by the reflection of a laser beam from the particles.

2.3. N-tert-amylacrylamide (NTA)

The monomer N-tert-amylacrylamide was prepared by the reaction of t-amyl alcohol with acrylonitrile. Colourless solid of N-tert-amylacrylamide formed was recrystallized in warm dry benzene. Percentage of yield and melting point of the white crystals of NTA obtained was analyzed **[1].** The monomer was confirmed by both ^{1}H-NMR and ^{13}C-NMR spectroscopy.

2.4. Synthesis of Poly(N-tert-amylacrylamide -co -Acrylamide/Hydroxy ethylacrylate) gold nanocomposite hydrogel

The hydrogel were prepared by free radical copolymerization of NTA, AM and HEA in the presence of MBA as crosslinker and APS for initiating the polymerization system. Aqueous solution containing a weighed amount of NTA (0.5g), AM (0.5g), MBA (0.050g), APS (0.050g) and certain amounts of HEA (0.00, 0.10, 0.30, 0.50g) were dissolved in methanol – water (3:1) mixture and final volume was made 10mLin a polymerization tube. A solution containing 10mg of gold nanoparticle was added with constant stirring. After bubbling nitrogen for 15 min, the contents were placed in thermostatic water bath at 60^0C and the polymerization was conducted for 1 day. The prepared hydrogels were air-dried followed by vacuum drying.

Table 1. Preparation of hydrogels by varying amount of Hydroxy ethylacrylate

S.No	Wt. of NTA (g)	Wt. of AM (g)	Wt. of HEA (g)	Wt. of APS (g)	Wt. of MBA (g)	Methanol/ Water (3:1)	Wt.of gold Nanoparticle (mg)
1	0.500	0.500	0.1	0.050	0.050	10	10
2	0.500	0.500	0.3	0.050	0.050	10	10
3	0.500	0.500	0.5	0.050	0.050	10	10

2.5. Characterization

Gold nanoparticles exhibit a distinct optical feature commonly referred to as localized surface plasmon resonance (LSPR), that is, the collective oscillation of electrons in the conduction band of gold nanoparticles in resonance with a specific wavelength of incident light. The absorbance measurements were made over the wavelength range of 250-700 nm using UV-Visible spectrophotometer (UV-1601 PC, Shimadzu, Japan; H14 grating. 1 cm path length quartz cuvettes were used. It was cleaned before each use by sonicating them for 5 min in deionized water and then rinsing with deionized water.

2.6. Surface morphology

The surface morphology of the freeze-dried monomers and gold nanocomposites was studied by Scanning Electron Microscopy with Energy-Dispersive X-ray spectroscopy (EDS). Surface morphology was performed using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification. To prepare samples for SEM, the swollen gold nanocomposites were freeze-dried and then sputter coated with gold. Energy-Dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of a sample.

2.7. Thermogravimetric analysis

Thermogravimetric analysis was used to investigate the thermal stability and crosslink densities of the prepared nanocomposite hydrogels. The TGA thermograms were recorded on a PerkinElmer-7 at a heating rate of 10^0C/min under N_2 protection over a temperature range from room temperature to 800^0C.

2.8.X-ray diffraction studies

The X-ray diffraction studies of the gold nanocomposite hydrogels were carried out using a BRUKER diffractometer (Germany), model D8 Advance, employing rotting Cu anode.

2. 9. Swelling measurements (Gravimetric Method)

The swelling characteristics were measured by immersing weighed samples of dry gold nanocomposite hydrogels in double distilled water and in Methylene blue dye solution. The excess surface water in the swollen gel was removed by blotting and then the swollen gel was weighed. The swollen gel was blotted several times till three consecutive weights are same within limits of experimental error of 1%. All measurements were performed thrice and the reported values are average of at least three individual measurements.

The degree of swelling (Ds) or percentage of swelling (%S) most commonly described as swelling ratio is expressed as increase in weight / gm of dried gold nanocomposite hydrogel after keeping in contact with water for selected period of time **[3, 4].**

$$\boldsymbol{Ds}\ \% = \frac{\boldsymbol{M_t - M_0}}{\boldsymbol{M_0}} \times \mathbf{100} \quad \text{---------- (1)}$$

Where W_t is the weight of the swollen gel at a given time and W_d is the weight of the dry gel.

2. 10.Equilibrium water content

The water absorbed by Am/ AmPSNa is quantitatively represented by the equilibrium water content (EWC), where

$$\mathbf{EWC} = \frac{\boldsymbol{M_t - M_0}}{\boldsymbol{M_t}} \quad \text{---------- (2)}$$

Here M_t is the mass of the swollen gel at time t (equilibrium), and M_o is the mass of the dry gel at time 0.

2. 11. Diffusion studies in water and methylene blue

Analysis of the mechanisms of diffusion in swellable polymeric systems has received considerable attention in recent years because of important applications of swellable polymers in biomedical, pharmaceutical, and agricultural engineering. The following equation **[5]** is used to determine the nature of diffusion of water and methylene blue into nanocomposite hydrogels:

$$\mathbf{F_{swp}} = \frac{\boldsymbol{M_t}}{\boldsymbol{M_\infty}} = \boldsymbol{Kt^n} \quad \text{---------- (3)}$$

Where F is the fractional uptake at time t, M_t and M_∞ denotes the amount of solvent or dyes diffused into the gel at time t and infinite time (at equilibrium), respectively.

2.12. Adsorption of Methylene blue

A weighed quantity of dry gold nanocomposite hydrogels (0.1g) with different composition was immersed in enough methylene blue (25ppm, 20ml) and kept at 37^0C.The amount of MB adsorbed was measured periodically (λ:661.6nm) by using spectrophotometer-106, Systronics instrument at 661nm. The adsorption capacity (Q) and removal efficiency (RE %) of the dye by the gold nanocomposite hydrogels with different composition was calculated by using the following expression:

(1) The adsorption capacity Q (mg dye per g polymer) of Nanocomposites was calculated by using the following expression:

$$\boldsymbol{Q}\ \left(\frac{\boldsymbol{mg}}{\boldsymbol{g}}\right) = (\boldsymbol{C_i} - \boldsymbol{C_e})\ \frac{\boldsymbol{V}}{\boldsymbol{m}} \quad \text{---------- (4)}$$

Where C_i and C_e are the initial and equilibrium concentrations of the dye in the solution, respectively (mg/l), V is the volume of the solution added (l) and m is the amount of Nanocomposites used (g) **[9, 10].**

(2) The Removal efficiency (RE %) of Nanocomposites was calculated by using the following expression:

$$\boldsymbol{RE}\ \% = \left(\frac{\boldsymbol{C_0 - C}}{\boldsymbol{C_0}}\right)\ \boldsymbol{X}\ \mathbf{100} \quad \text{---------- (5)}$$

Where C_0 and C are the initial and equilibrium concentration of the MB dye solution, respectively **[11].**

2.13. Antioxidant Activity

The free radical scavenging capacity of the GNH was determined using DPPH **[14].** DPPH solution (0.004%w/v) was prepared in DMSO. GNH was mixed with DMSO to prepare the stock solution. The conc of this solution was 10mg/100mL or 100µg/mL. This solution was taken in 5 test tube & by serial dilution with same solvent was made the final volume of each test tube up to 10mL whose conc was then 20 µg/mL, 40 µg/mL, 60 µg/mL, 80 µg/mL & 100 µg/mL respectively. Freshly prepared DPPH solution (0.004%w/v) was added in each of these test tubes and after 10min, the absorbance was taken at 520nm using spectrophotometer. Ascorbic acid was used as a reference standard and dissolved in distilled water to make the stock solution with the same conc. 10mg/100mL. DMSO was used as blank.Percentage scavenging of the DPPH free radical was measured using the following equation.

$$\%\ \text{DPPH radical scavenging} = \frac{\text{Absorbance of control} - \text{Absorbance of test sample}}{\text{Absorbance of control}} \text{ X } 100 \quad \text{------ (6)}$$

2.14. Antimicrobial studies

In vitro antibacterial activity studies were carried out by using the fresh nutrient method to investigate effect of the synthesized polymers against the microorganisms *Staphylococcus aureus, Bacillus substilis* (Gram +ve), *Escherichia coli, Salmonella paratyphi* (Gram –ve) species were used to analyse the antibacterial activity. *Candida albicans, Aspergillus Niger, Monoscus purpures* were used to analyse the antifungal activity. For the antibacterial and antifungal assays, the compounds were dissolved in Dimethyl sulfoxide (DMSO). Further dilutions of the compounds and standard drugs in the test medium were prepared at the required quantities of 50 and 200 ppm concentrations with fresh sabouraud's broth. The minimum inhibitory concentrations (MIC) were determined using the two fold serial dilution technique. *Ciprofloxacin* and *Clotrimazole* were used as control drugs. The data on the antimicrobial activity of the compounds was replicated twice and the data as MIC expressed in ppm.

3. Results and Discussion

The schematic representation of gold nanocomposite hydrogel synthesis is shown in Figure 1.

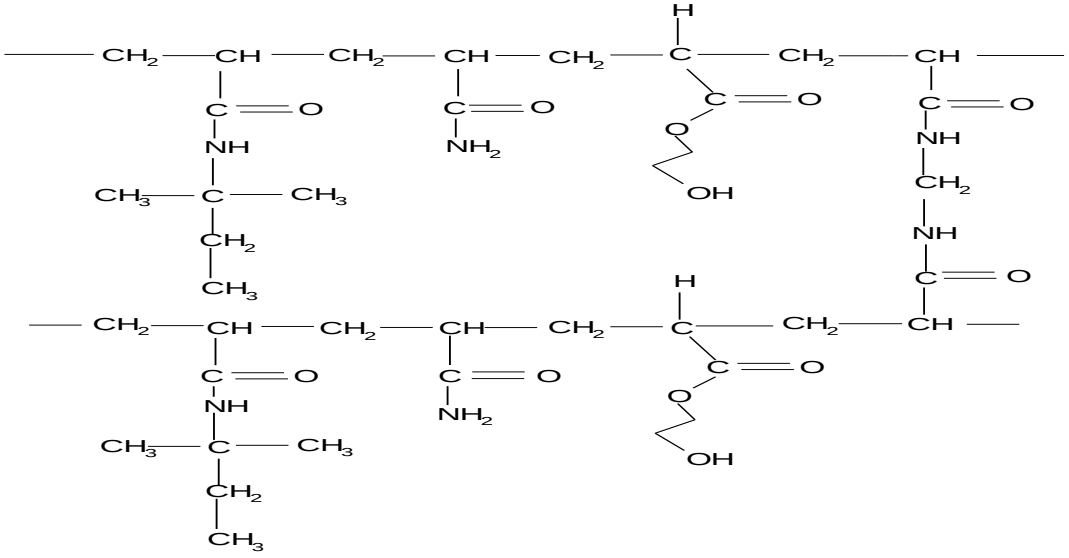


Figure 1. Schematic representation of poly (N-tert-amylacrylamide-co-acrylamide /Hydroxy ethylacrylate) gold nanocomposite hydrogel

3.1. FTIR spectral analysis

The FTIR spectrum of poly (NTA-co-AM/HEA) gold nanocomposite hydrogel is shown in Fig.1 .The peak corresponding to NH stretching of NTA was observed at 3301 $cm^{-1}$and 1537 cm^{-1} corresponding to $C=ONH_2$ of AM unit. The peaks for the C=C was observed at 1652 cm^{-1} and 1652 cm^{-1} corresponding to carbonyl (C=O stretching) of NTA and HEA unit. The peak at 2963 cm^{-1} corresponds to the aliphatic C-H stretching and -CH_2- peak is at 1444 cm^{-1} of HEA. Ester group of HEA can be seen at 1735 cm^{-1}. The characteristic peat at 550 cm^{-1} represents the incorporation of Au NPs in the polymer matrix.

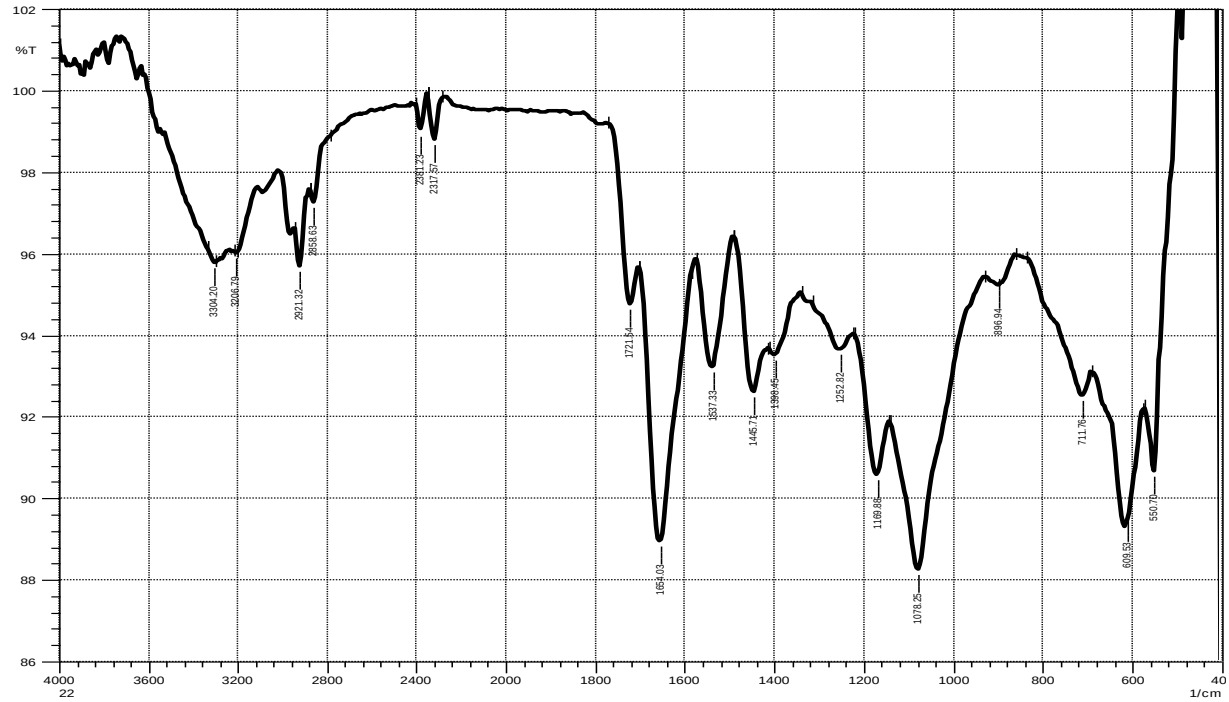


Figure 2. FTIR spectrum of poly (N-tert-amylacrylamide-co-acrylamide /Hydroxyethyl acrylate) gold nanocomposite hydrogel

3.2. SEM analysis of poly (NTA-co-AM/HEA) gold nanocomposite hydrogel

SEM images of poly (NTA-co-AM/HEA) GNH are shown in Fig.3. The SEM analysis indicated that gold nanoparticles are not only spherical but also number of tetragonal crystal shapes. During the in situ polymerization of hydrogel, some unreduced Au^{3+} ions are getting reduced as AuNPs. From the analysis, we can conclude that the monomers are also play an important role in the formation gold nanoparticles.

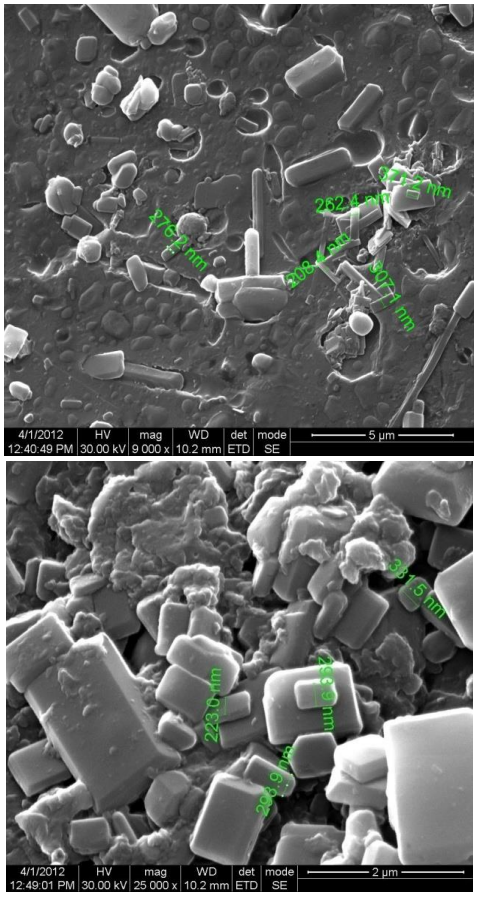


Fig.3. SEM images of poly (NTA-co-AM/HEA) GNH

3.4. XRD Studies

X-ray diffraction patterns of poly (NTA-co-AM/HEA) gold nanocomposite hydrogel is shown in Fig.4. Some diffraction peaks at 2θ: 22 and 45 are clearly seen and can be indexed as the gold nanoparticles. The wide peak conforms more amorphous and less crystallinity. It showed that the more the amorphous in the matrix more will be the swelling. It was clear that the regular crystal structure of gold was partly destroyed and the gold platelets were intercalated and dispersed in the nanocomposite hydrogel matrix.

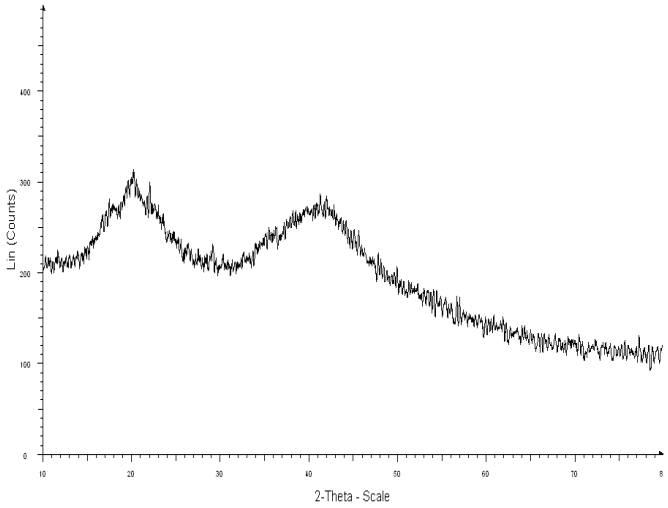


Fig.4. X-ray diffraction patterns of poly (NTA-co-AM/HEA) GNH

3.5. TGA of poly (NTA-co-AM/HEA) gold Nano composite hydrogel

The TGA curve of poly (NTA-co-AM/HEA)GNH is given in Fig.5. The initial weight loss of the gold nanocomposite hydrogel containing 0.3g of HEA is 15.8%. The initial weight loss is due to the evaporation of free water and inter layered water present in the sample. The first stage and the second stage are attributed to the thermal decomposition of the amide group of NTA and the decomposition of crosslinker respectively.

The final stage [FDT] is due to the breakdown of the polymer backbone. The residual weight (5.4) percentage indicates the charred content and the nanoparticles. From the data, we can conclude that 0.3g of HEA nanocomposite is stable up to 200^{O}C.

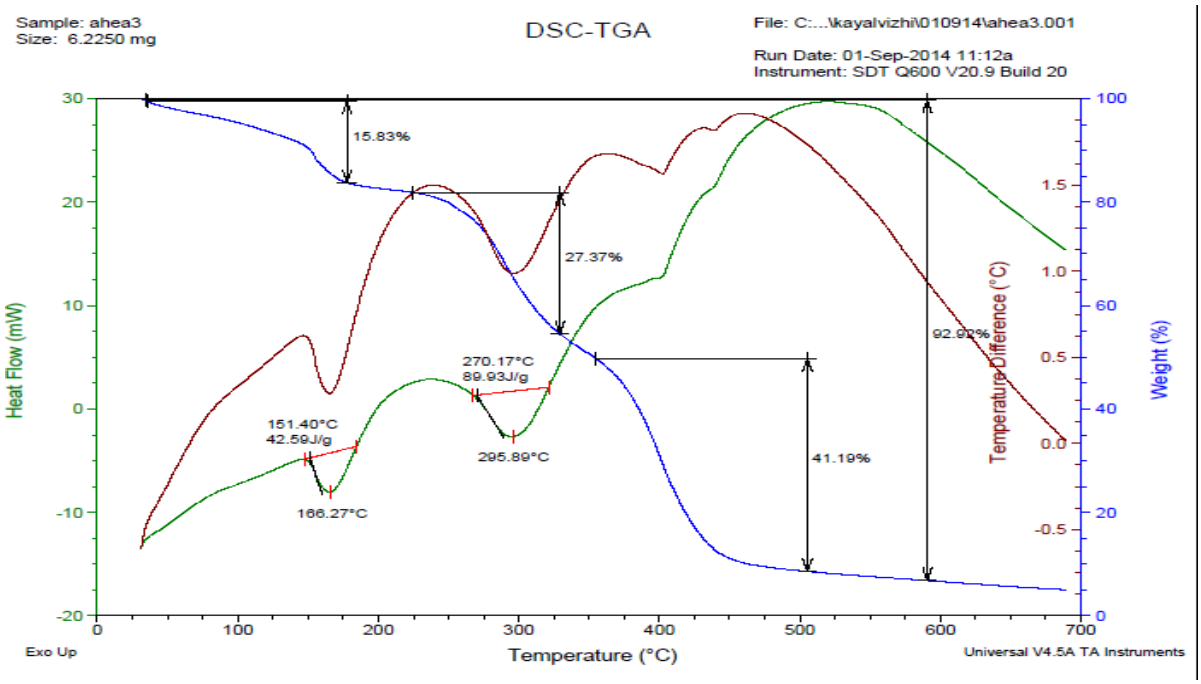
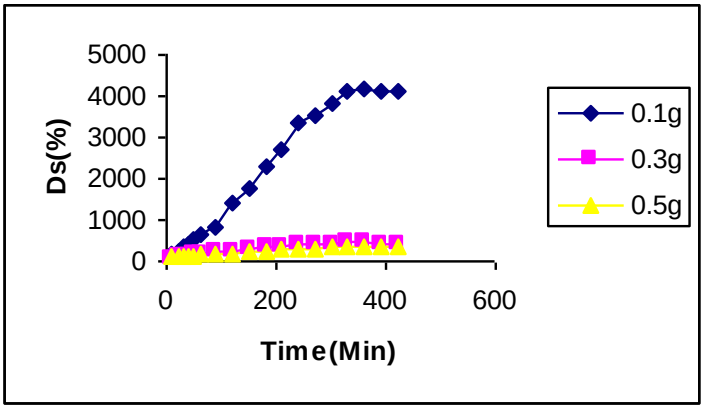


Fig.5. TGA curve of poly (NTA-co-AM/HEA) gold nanocomposite hydrogel

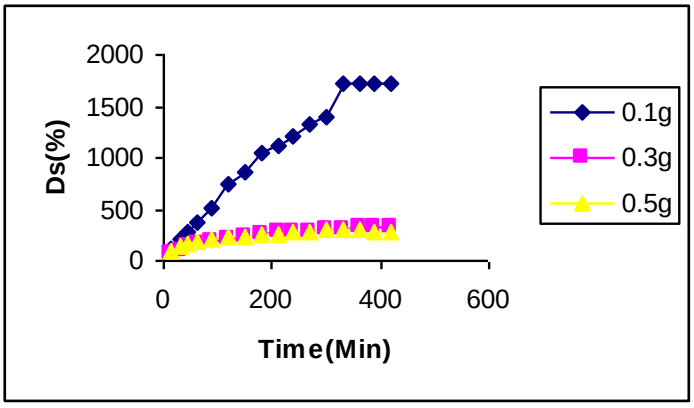
3.6. Swelling behavior of poly (N-tert-amylacrylamide-co-acrylamide / Hydroxy ethylacrylate) gold nanocomposite hydrogels

3.6.1. Swelling of hydrogels in water and in dye solution at room temperature

The swelling behavior of poly (NTA-co-AM/HEA) gold nanocomposite hydrogel at room temperature in water and dye solution is shown in Fig.6. The swelling behavior of hydrogel in water decreases with increasing amount of HEA may due to the presence of hydroxyl ethyl group. The same trend also occurs in dye solution but lesser in swelling than in water.



(a) In water



(b) In dye solution

Fig.6. Swelling behavior of poly(NTA-co-AM/HEA)gold nanocomposite hydrogel in water(a) and dye solution (b)

3.6.2. Effect of electrolytes

The swelling of hydrogels in NaCl and KCl are shown in Fig.7. Different concentration of NaCl have been used to see the effect of electrolyte concentration on swelling of nano composite hydrogel. The swelling decreased as the concentration of NaCl increased in the solution. It was due to the fact that an increased of the ionic strength of the solution leads to a decrease in the swelling ratio of the nanocomposites. The swelling of hydrogels and attributed to a charge screening effect of the additional cations causing a non-perfect anion-anion electrostatic repulsion. This led to a decrease in osmotic pressure difference between the composite network and the external solution.

The extent of swelling was more in the presence on NaCl than in KCl. Disruption and desolvation of the -C=O, H_2O hydrogen bonds allow attractive interchain hydrophobic interaction and hydrogen bonding to dominate. Thus the gel deswelled and contracts. The presence of Na+ and K^+ ions deswell the polymeric gel, being incapable of breaking strong attractive forces between the permanent charges of the polymeric backbone. Moreover, the smaller hydration sphere of bigger cation is able to penetrate the gel crosslinks where as the smaller ions (Na^+,K^+) with larger hydration sphere were unable to penetrate the gel network, thus deswells the gel.

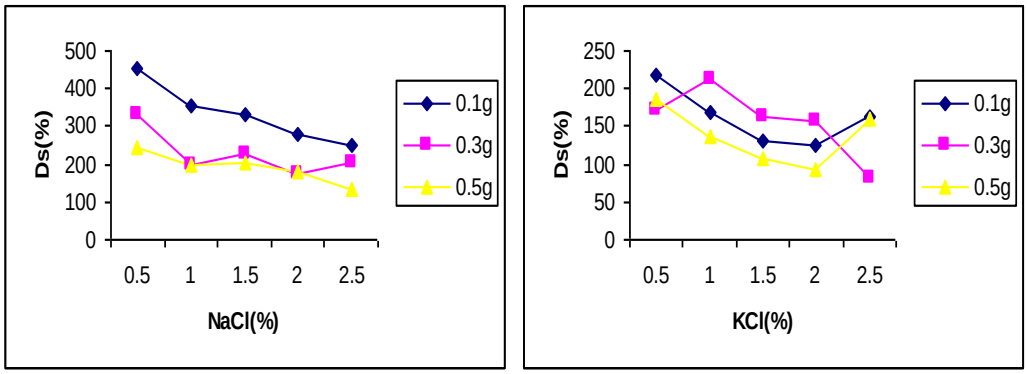


Fig.7.Swelling behavior of nanocomposites at different concentrations of NaCl and KCl

3.6.3. Diffusion studies

The following equation is used to determine the nature of diffusion of water into gold nanocomposite hydrogels:

$F=M_t/M_\infty=kt^n$ ---------- (3)

Where F is the fractional uptake at time t, M_t and M_∞ denotes the amount of solvent or dyes diffused into the gel at time t and infinite time(at equilibrium),respectively is a constant related to the network, and the exponent n is a number to determine the type of diffusion. The diffusion of water through polymer network is associated with the physical-chemical properties of the hydrogels. Plot of lnF Vs lnt curves of poly(NTA-co-AM/HEA) GNH in water and MB dye solution are given in Fig.8 and Fig.9 and the n-values are shown in Table 1 and Table 2.

The n values are characterized by both non-Fickian and Fickian diffusion. At higher content of HEA containing hydrogel follows non-Fickian and at lower content of HEA follows Fickian diffusion. In the Fickian diffusion, the mobility rate for the solution is smaller than the segmental relaxation rate of the polymer and in non-Fickian, the diffusion and relaxation rates are comparable.

Table 1. Maximum swelling and diffusion parameters of poly (NTA-co-AM/HEA) GNH in distilled water

S.No	Weight of HEA(g)	Maximum Ds (%)	n	k
1	0.1	4196.4	0.98	-2.51
2	0.3	453.0	0.54	-1.35
3	0.5	389.4	0.40	-1.09

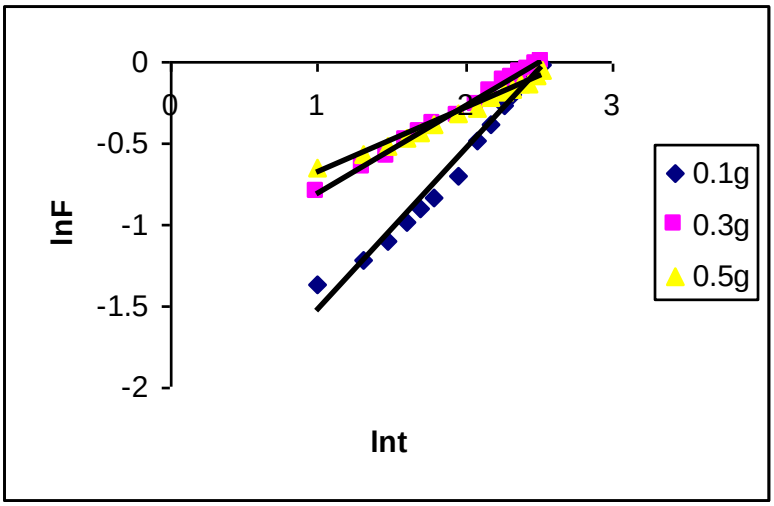


Fig. 8 . Plot of ln F Vs lnt of poly (NTA-co-AM/HEA) GNH in water

Table 2.Maximum swelling and diffusion parameters of poly (NTA-co-AM/HEA) gold nanocomposite hydrogel in MB Dye solution

S.No	Weight of HEA (g)	Maximum Ds (%)	n	K
1	0.1	1726.2	0.87	-2.20
2	0.3	320.9	0.45	-1.12
3	0.5	295.3	0.37	-0.90

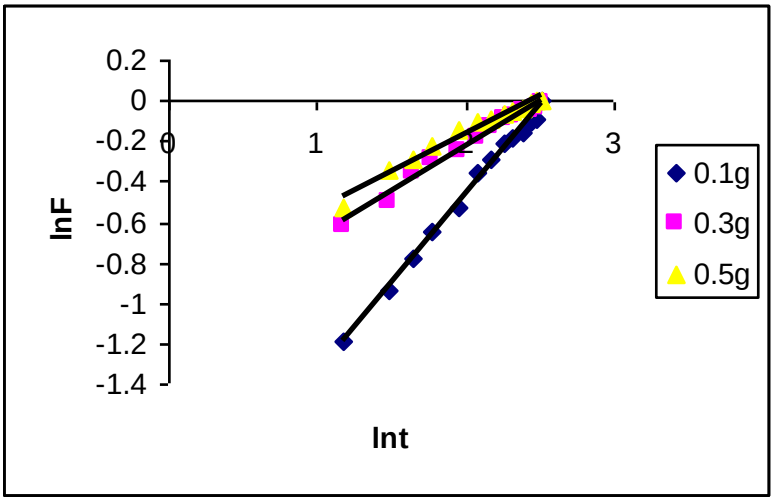


Fig.9. Plot of ln F Vs lnt of poly (NTA-co-AM/HEA) GNH in MB Dye solution

3.6.4. Adsorption capacity and dye removal efficiency of poly(NTA-co-AM/HEA)GNH

The adsorption curves of Hydrogels in MB dye solution are shown in Fig.10. The maximum adsorption capacity is about 312.2 for 0.1g of HEA, 070.9 for 0.3g of HEA 470.5 and 223.1 for 0.5g of HEA. After one day all nanocomposites showed dark color compared with the original composites. Also, the color of MB solution became colorless compared with the original solution. The cationic dyes like MB have electronegative atoms such as nitrogen and sulfur behave like hydrophilic groups and form hydrogen bonds with water.

The percentage of dye removed from solution for Nanocomposites are given in Table 3. The maximum Removal efficiency is about 65.3% for 0.1g of HEA, 17.9% for 0.3g of HEA 95.1 for and 47.8% for 0.5g of HEA. From the Table, it is noticed that maximum of 65.3% at 0.1g of HEA hydrogel, at higher content of HEA the removal efficiency decreases because of poor interaction of dye molecules [13].

Table 3. Removal efficiency and Adsorption capacity of poly (NTA-co-AM/HEA) GNH

S.No	Weight of HEA(g)	RE (%)	Q
1	0.1	65.3	312.2
2	0.3	17.9	070.9
3	0.5	47.8	223.1

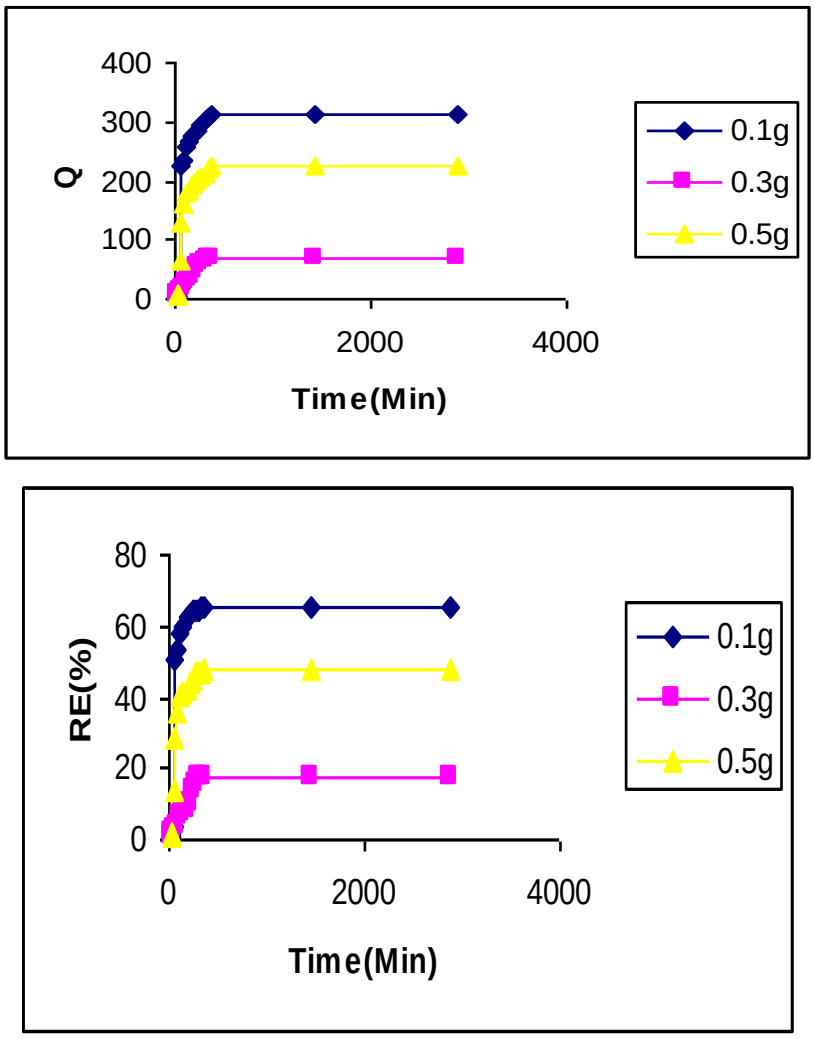


Fig.10. Removal efficiency and Adsorption capacity of Poly (NTA-co-AM/HEA) gold nanocomposite hydrogel

3. 7. Antioxidant activity of poly (NTA-co-AM/HEA) gold nanocomposite hydrogel

The scavenging effect of GNH is given in Table 4 and Fig.11. The percentage inhibition gets increased with increase in concentration of hydrogel. Though the DPPH scavenging ability of GNH was less than that of the commercially available Ascorbic acid, the study showed that the GNH have the ability of donating a proton and can serve as a free radical inhibitor, acting as primary antioxidants. From results, it is found that the gold nanocomposite hydrogels displayed strong antioxidant properties.

Table 4.Antioxidant activity of poly (NTA-co-AM/HEA) gold nanocomposite hydrogel

S.No.	Conc (µg/ml)	% of Activity	
		Test	Standard
1	20	4.9287	22.3788
2	40	16.8965	31.6429
3	60	30.9679	43.8248
4	80	43.8755	49.5285
5	100	52.6573	63.6762
	IC_{50}	76.7633	60.0976

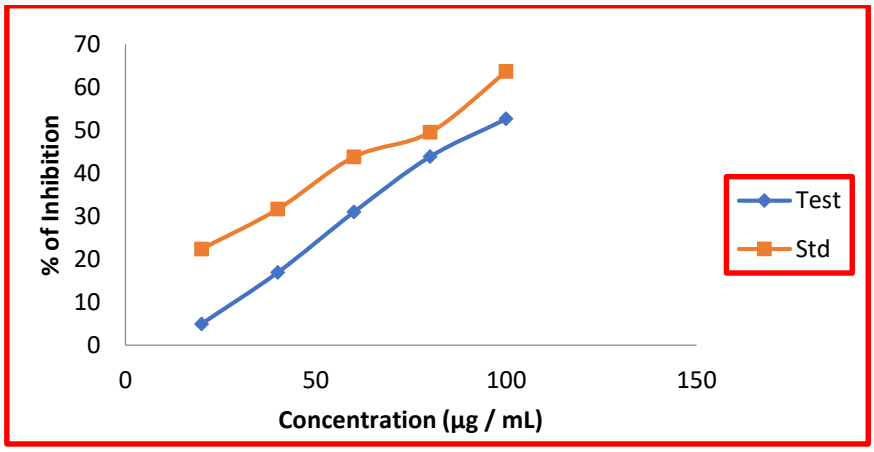


Fig.11.Antioxidant activity of poly (NTA-co-AM/HEA) gold nanocomposite hydrogel

3.8. Antimicrobial studies

3.8.1. Antibacterial activity

The zone of inhibition of hydrogels against the micro-organism *Staphylococcus aureus, Bacillus substilis* (Gram +ve), *Escherichia coli, Salmonella paratyphi* (Gram –ve) are listed in Table 5 and are shown in Figure 12 and 13.

The zone of inhibition reveals that the antibacterial activity of the compound is specific to the microorganism. The data indicated that all hydrogels showed high inhibition values comparatively except *Escherichia coli.*

3.8.2. Antifungal activity

The results of the antifungal activity are shown in Table 6 and Figure 14 and 15. The zone of inhibition reveals that the antifungal activity of the compounds is specific to the microorganism examined.

The observation on the biological assay indicates that the antibacterial action due to all compounds have N,O groups which is of considerable chemotherapeutic interest. All the investigated compounds showed good activity. Therefore, these gold nanocomposite hydrogels may be used for biomedical applications.

Table 5. Antibacterial activity of poly (NTA-co-AM/HEA) gold nanocomposite hydrogel

S.No	Organisms	Zone of Inhibition(mm)			
		Std. Ciprofloxacin (10µg/disc)	Samples (100µg/disc)		
			0.1 g	0.3 g	0.5 g
1.	*Staphylococcus aureus*	19	23	20	24
2.	*Bacillus subtilis*	19	18	20	21
4.	*Escherichia coli*	22	17	15	16
5.	*Salmonella paratyphi*	25	21	20	24

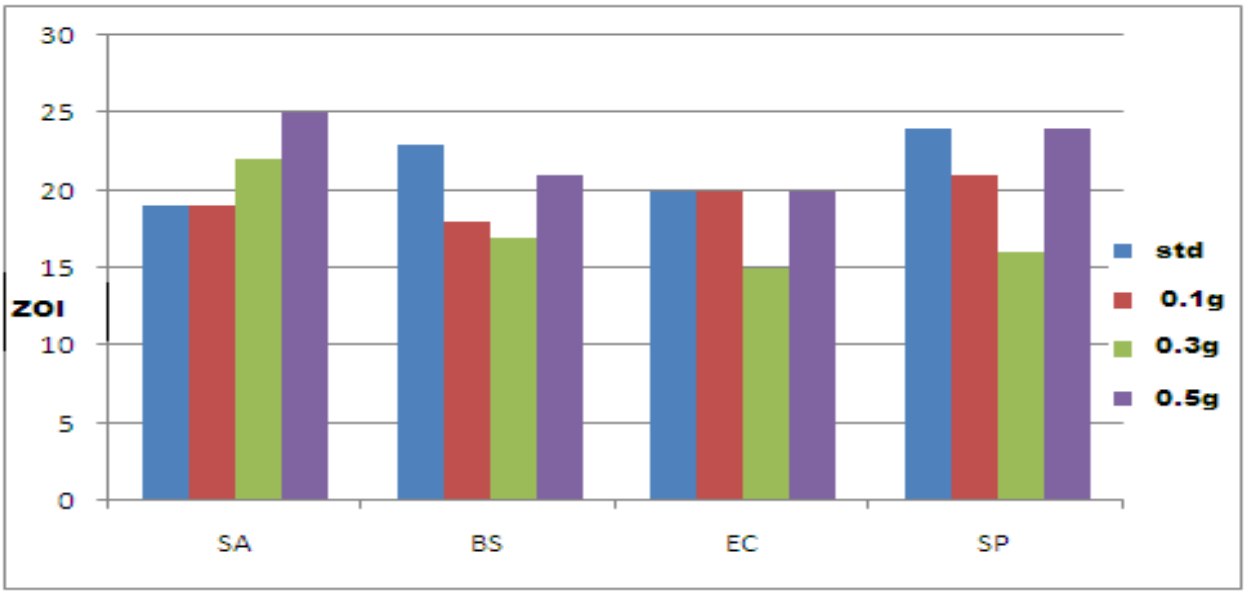


Figure 12. Graphical representation of Antibacterial activity of poly (NTA-co-AM/ HEA) gold nanocomposite hydrogel

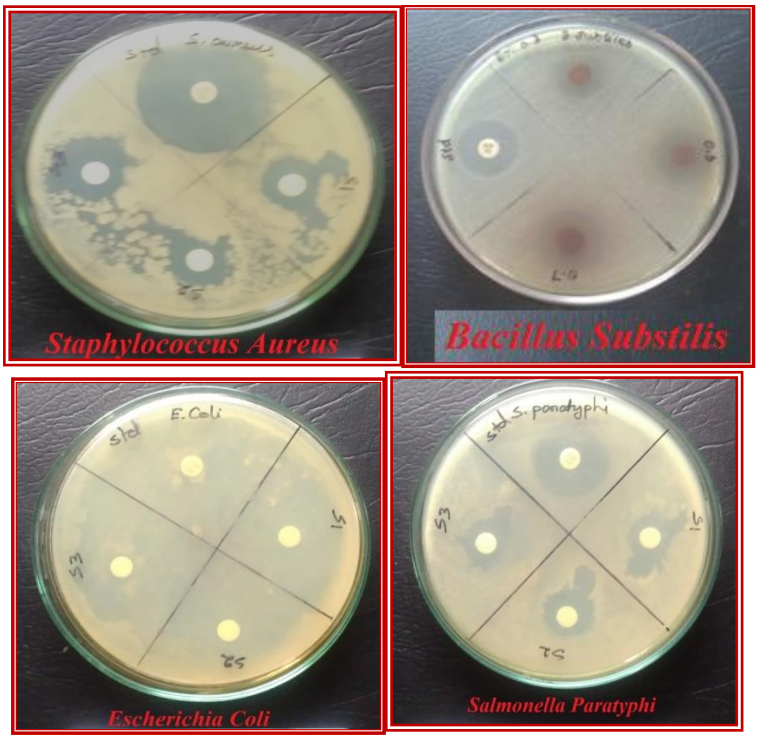


Figure 13.Antibacterial activity of poly (NTA-co-AM/HEA) gold nanocomposite hydrogel (S1:0.1g ; S2:0.3g; S3:0.5g)

Table 6. Antifungal activity of poly (NTA-co-AM/) gold nanocomposite hydrogel

S.No	Organisms	Zone of Inhibition(mm)			
		Std. Clotrimazole (10µg/disc)	Samples (100µg/disc)		
			0.1 g	0.3 g	0.5 g
1.	*Candida albicans*	38	28	24	32
2.	*Aspergillus niger*	32	30	35	38
3.	*Monoscus purpures*	41	32	25	36

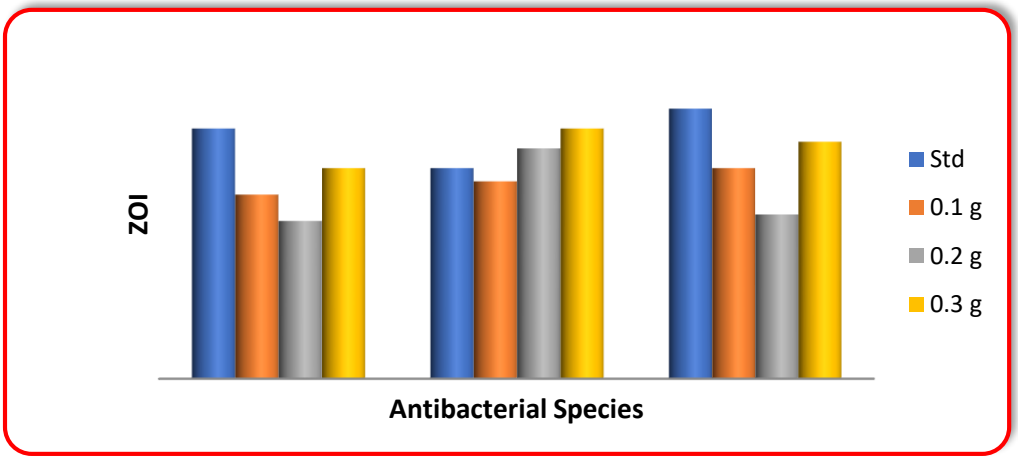


Figure 14.Graphical representation of Antifungal activity of poly (NTA-co-AM/ HEA) gold nanocomposite hydrogel

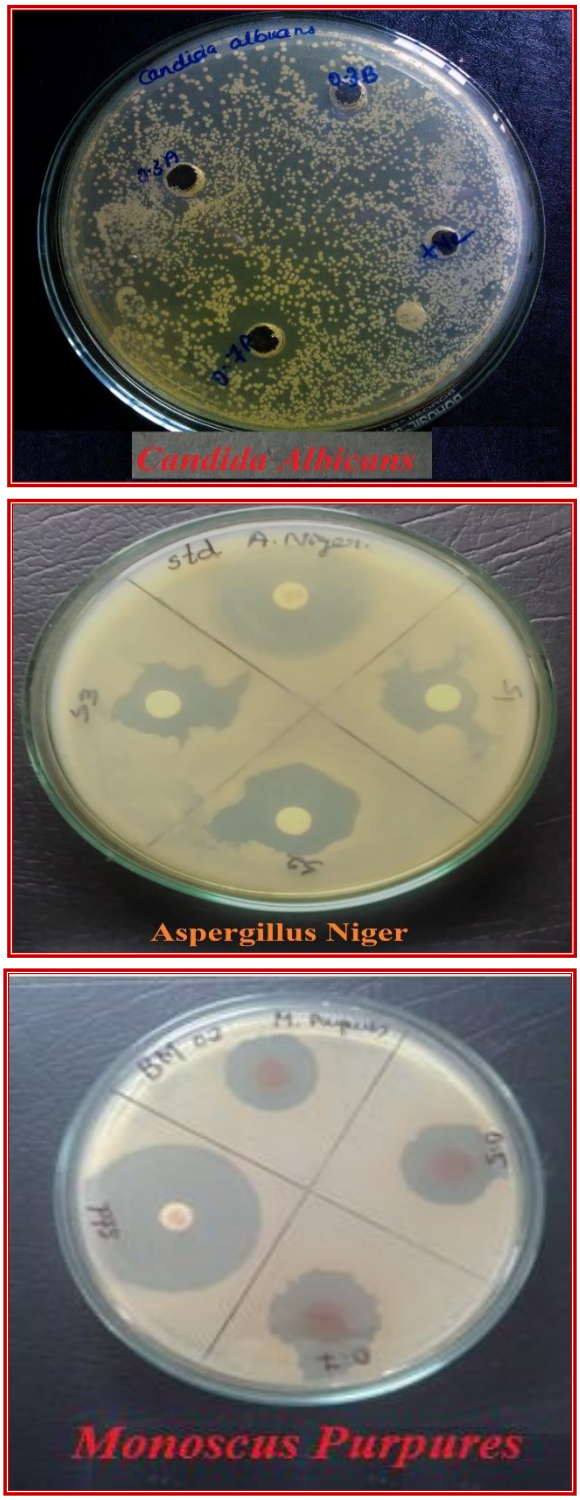


Figure 15. Antifungal activity of poly (NTA-co-AM/ HEA) gold nanocomposite hydrogel

4. Conclusions

The poly (N-tert-amylacrylamide -co-acrylamide/ HEA) gold nanocomposite hydrogels were synthesized by free-radical polymerization and the gold NPs were intercalated via in situ polymerization using the monomers at 60^0C. The synthesized hydrogels were characterized by FTIR, SEM, TGA analysis. The TGA study exhibited double stage decomposition, The first stage and the second stage are attributed to the thermal decomposition of the amide group of NTA and the decomposition of crosslinker respectively. The SEM analysis indicated that gold nanoparticles are not only spherical but also number of tetragonal crystal shapes. At 100μg/mL of concentration of hydrogel showed a good antioxidant and antimicrobial activities.

References

[1]A Tagri, Polyacrylamide based hydrogels: Synthesis characterization and applications, Int, J Pharm. Chem. Bio Sci., 4. 951-959(2014)

[2] E.kayalvizhy and P.Pazhanisamy, swelling behavior of Poly(N-cyclohexylacrylamide-co-acrylate AMPSNa)gold nanocomposite hydrogels, Internnational of Biological Macromolecules,86,721-727(2016).

[3] E.Kayalvizhy and P.Pazhanisamy, swelling behavior and antioxidant activity of Poly(N-tertazylacrylamide-co-Acrylamide/MPTMA Cl)gold nanocomposite hydrogels, Research Journal, of chemistry and Environment, 24(9), 28-36(2020).

[4] E.Kayalvizhy, M.S.Rajan, P.Pazhanisamy, BSA adsorptions, anthelmintic activity and swelling behavior of poly(N-cyclohexylacrlamide-co-AMPS-IL)hydrogel, Journal of - Molecular Liquids, 314, 113692(2020).

[5A. Bal ,F.E. Cepni , O. Cakir, I. Acar and G. Gudu , Synthesis and characterization of copolymeric and terpolymeric hydrogel-silver nanocomposites based on acrylic acid, acrylamide and itaconic investigation of their antibacterial activity against gram-negative bacteria, Brazilian J. Chem. Engg., 32(2), 509-520 (2015)

[6] H. Omidian , J.G .Rocca and K. Park ,Processing tough supramolecular hydrogels, J. Control Release, 102, 3-12 (2005)

[7] M, Dalaran, S.Erik, G.Guclu, T.B. Iyin and S.Ozgumus, Removal of acidic dye from aqueous solutions using poly(DYAEMA-AMPS-HEMA)terpolymer/MMT nanocomposite hydrogels, Polym. Bull., 63, 159-171(2009).

[8] X. Yang, Y.Fang, X.Li, K.Zhang, Y.Cui, B.Zhang and G.Yin, e-polymers, 14(5), 335-343(2014)

[9] Z. Nart and N.Kayaman-Apohan, Preparation, characterization and drug release behavior of poly(acrylicacid-co-2-hydroxylethylmethacrylate-co-2-acrylamide-2-methylppropane sulphuric acid)microgels, Polym. Bull 18.869-874(2010).

[10] A.K. Bajpai, Blood protein adsorption onto a Polymeric biomaterial of PEG and poly(2-Hydroxyethyl methacrylate-co-acrylonitrile) and evaluation of in vitro blood compatibility, Polym. Inter. 54, 304-315(2005).
[11] M.Sadeghi, synthesis of starch-g—poly(acrylic acid-co-2-hydroxyethyl methacrylate) as potential P^H sensitive hydrogel based drug delivery system, Tur. J. Chem., 35,723-733 (2011).
[12].T. Jayaramudu, G.M Raghaventra, K. Varaprasad, R. Sadiku and K.M.Raju, Development of novel biodegradable Au nanocomposite hydrogels based on wheat: for inactivation of bacteria, carbohydr. Poly., 2(2), 2193-2200(2013).
[13] P. Pazhanisamy , E.N. Hidayah ,Indra Sulania, poly(N-tert-amylacrylamide -co-Acrylamide/ Sodium acrylate) Fe_3O_4 Nanocomposite Hydrogels as polymer catalyst for the reduction of Methylene Blue Dye, International journal of Eco-Innovation in Science and Engineering, 3(2), 41-44 (2022).