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Swelling Behavior of Poly (N-Cyclohexylacrylamide-Co-Acrylamide/Sodium Acrylate) Gold Nanocomposite Hydrogels

KEYWORDS

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ABSTRACT *Poly (N-cyclohexylacrylamide –co-acrylamide / AcNa) Gold nanocomposite Hydrogels were synthesized by free-radical copolymerization in Water/Methanol medium using Ammonium persulfate (APS) as the initiator and N,N-methylenebisacrylamide (MBA) as a crosslinker at 600C. Because of abundance of the hydrophilic groups of AcNa causes an improvement in the swelling characteristics of the hydrogel . Kinetics of swelling of hydrogels follows non-Fickian character. The Surface Morphology of Gold Nanocomposite hydrogels indicates that the GNPs are spherical in shape and are distributed uniformly throughout the polymer matrix. X-ray diffraction pattern showed that the nanocomposite material is more amorphous and less crystalline in nature.*

Introduction
Hydrogels represent polymeric networks capable of absorbing large quantities of water, but remain insoluble due to chemical or physical crosslink between individual polymeric chains [1]. Recently, there is a great deal of interest concerning the production of nanoparticles in the hydrogel networks since they have enormous valuable applications in bio-related fields [2]. Indeed the design and development of nanoparticles and nanostructural materials have opened a new era for constructing well designed nanostructures that have been considered as a novel class of materials for catalytic, optical, electronic and biomedical application. Polymer nanocomposite containing metal nanoparticles can be prepared by several methods. Methods used for preparation comprise mechanical mixing of a polymer with metal nanoparticles [3], the in situ polymerization of a monomer in the presence of metal nanoparticles and the in situ reduction of metal salts or in a polymer [4] . Copolymeric hydrogel networks are composed of two or more different monomer species with at least one hydrophilic component, arranged in a random, block or alternating configuration along the chain of the polymer network. The copolymeric hydrogel networks are generally covalently or ionically crosslinked structures, which are not water soluble. Hydrogels can swell to profitable rates when placed into an appropriate environment, which means a specific pH, temperature, electric field, light, pressure or specific molecule [5 – 11]. Several researchers have studied the swelling of pH-sensitive hydrogels and the influence of this parameter in chemical, biological and physiological systems [12] .Hydrogels exhibiting pH-sensitive swelling behavior have been usually swollen from ionic networks that can contain acidic or basic pendant groups. When these groups are ionized, a swelling osmotic pressure inside the material is built up, and fixed charges are trapped in the gel. As a result of the electrostatic repulsion, the uptake of solvent in the network is increased [13-16]

In the present study, we have synthesized gold nanocomposite hydrogels by in situ polymerization of N-cyclohexylacrylamide, Acrylamide and Sodium acrylate (AcNa) using ammonium persulphate as free radical initiator and N,N' –methylenebisacrylamide (MBA) as cross linker. Swelling behavior and swelling kinetics of the obtained hydrogels were evaluated. Distribution of gold nanoparticles within the polymer matrix was studied through their characterization using SEM analysis.

Experimental
Materials
Acrylamide (AM, Merck) was recrystallized from acetone/ethanol mixture. Ammonium persulphate (APS), Acrylic acid and Sodium hydroxide were supplied from Aldrich. The crosslinker N,N'-methylene-bis-acrylamide(MBA) was used as received.

Acrylonitrile
Acrylonitrile was first washed with 5% NaOH solution in water to remove the inhibitor and then with 3% Orthophosphoric acid solution in water to remove basic impurities. Then the Acrylonitrile was washed with double distilled water and dried over andhydrous $CaCl_2$. The acrylonitrile was then distilled in an atmosphere of Nitrogen at reduced pressure. It was then collected in a clean dry amber colour bottle and kept in the refrigerator at 5^{O} C.

Preparation of N-cyclohexylacrylamide
The monomer N-cyclohexylacrylamide was prepared by the reaction of Cyclohexanol with acrylonitrile and recrystallized in warm dry benzene [17]. The white crystals have a m.p.115° C and the yield was 92%.

Preparation of sodium acrylate (Ac Na)
Sodium acrylate was prepared by neutralizing the acrylic acid using Sodium hydroxide.

Preparation of Gold nanoparticles
About 1.0mM of $HAuCl_4$ was added to a 50mL Erlenmeyer flask on stirring in hot plate. To the rapidly stirred boiling solution, add 1% solution of trisodium citrate dihydrate. The gold solution gradually forms as the citrate reduces the gold (III) and removed from heat when the solution was turned to deep red in color.

Synthesis of Poly (N-cyclohexylacrylamide - co - Acrylamide / Sodium acrylate) Gold Nanocomposite Hydrogels

The hydrogels were prepared by free radical copolymerization of NCA, AM and Ac Na in the presence of MBA as crosslinker and APS for initiating the polymerization system. Aqueous solution containing a weighed amount of NCA, AM, MBA, APS and certain amounts of AcNa (0.00, 0.10, 0.30, 0.50g) were dissolved in methanol – water (3:1) mixture and final volume was made to 20mLin 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^{O}C and the polymerization was conducted for 1 day. The prepared hydrogels were air-dried followed by vacuum drying. The schematic representation of GNP Hydrogel is given below.

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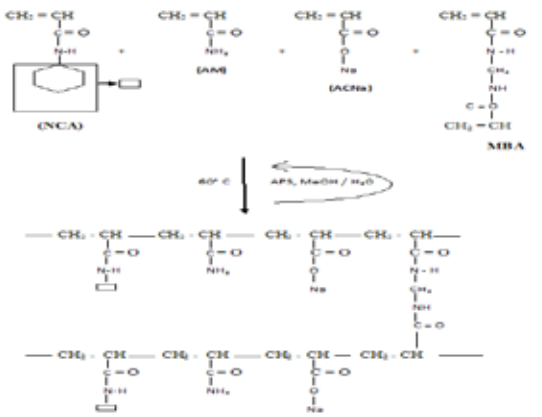

Scheme: Poly (NCA-co-AM/AcNa) Gold Nanocomposite Hydrogel

Experiments of Swelling and Diffusion
The swelling behavior of dried hydrogels were carried out by immersion in doubly distilled water at 25 ± 0.1 °C in a water bath. The water absorbed was determined by weighing the samples, after wiping, at various time intervals. Swollen gels weighed by an electronic balance.

Scanning Electron microscope (SEM)
Images for the Gold Nanoparticle and Gold Nanocomposite hydrogels were recorded using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification. SEM/EDAX was used to study the internal or cross morphology of the nanocomposite hydrogel. Before the measurements, the swollen nanocomposite hydrogel at 22^{0}C was firstly freeze-dried and then fractured and sputter coated with gold.

X-ray Diffraction (XRD)
XRD patterns of Gold nanocomposite hydrogel was measured using Riga-ku DMAX-2000 X-ray diffractometer with the Cu Kα radiation at a scanning rate of 2s-1 in 2 ranging from 10 to 80. The sample for XRD was supported on glass substrates.

Results and Discussion
^{1}H-NMR ($CDCl_3$),δ(ppm)

^{1}H-NMR spectra of the monomer N-cyclohexylacrylamide are shown in Fig.1 .The peaks observed at 1.2- 1. 9 ppm for cyclohexyl CH_2, 3.84 ppm for cyclohexyl methane, 5.59-6.28 ppm for vinyl protons and at 7.27 ppm for N-H proton

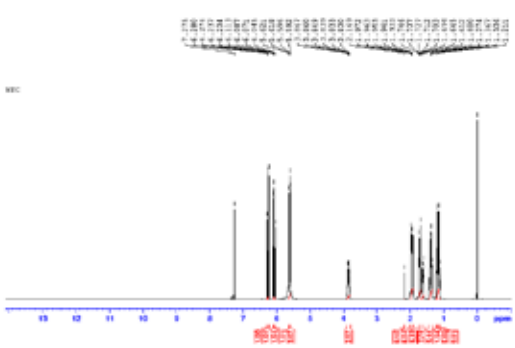

Fig.1. ^{1}H-NMR spectra of the monomer N-cyclohexylacrylamide
^{13}C-NMR ($CDCl_3$), δ(ppm)

^{13}C-NMR spectra of the monomer N-cyclohexylacrylamide is shown in Fig.2. The characteristic group peak assignments are given as follows δ 164.80 (CH_2 = C(H)-CO-NH..); δ 132.93 (CH_2 =C(H)-CO-NH…);◦ 122.82 (CH_2=C(H)-CO-NH..) ; δ 49.82 (cyclohexyl- C_1); δ 32.84 (cyclohexyl- C_2); δ 26.19 (cyclohexyl- C_3) δ 26.17 (cyclohexyl- C_4)

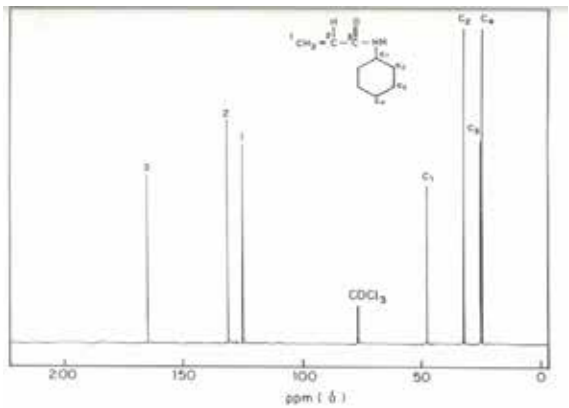

Fig.2. ^{13}C-NMR spectra of the monomer N-cyclohexylacrylamide

Preparation of Gold nanoparticles (GNP)
To characterize the surface morphology of gold nanoparticle SEM and energy dispersive X-ray (EDAX) were recorded. Figure 3 shows the SEM images and indicates the GNP are spherical in shape. EDAX of gold nanoparticle (Figure 4) was used to evaluate their elemental composition.

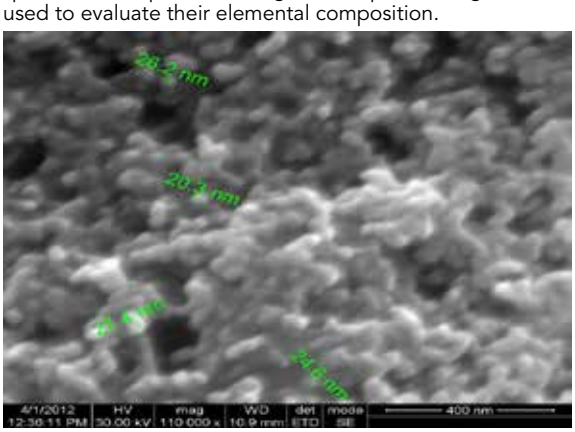

Fig.3 SEM image Gold nanoparticles

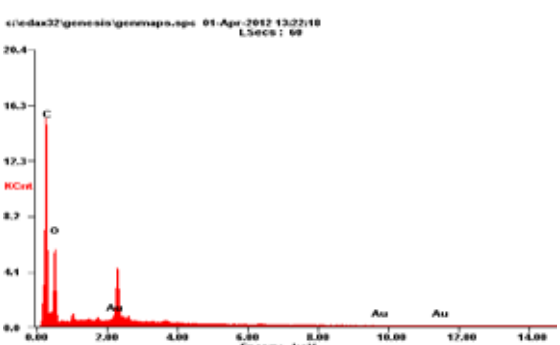

Fig.4. Energy Dispersive Analysis X-ray of GNP

Characterization
FTIR Spectra
Figure 5 shows the FT-IR spectra of the gold nanocomposite hydrogel and the spectra is given below. A broad peak corresponding to NH of NCA as well as NH stretching of acrylamide was observed around 3430 cm^{-1}. The peaks were also observed at 1662, 1500 cm^{-1} corresponding to C=O, C – C of NCA and 1541 cm^{-1} corresponds to C=O NH_2 of AM unit. The peak at 1723 cm^{-1} corresponds to C=O of -COONa. The

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peak at 1386 cm^{-1} is due to the C-N stretching of amide.

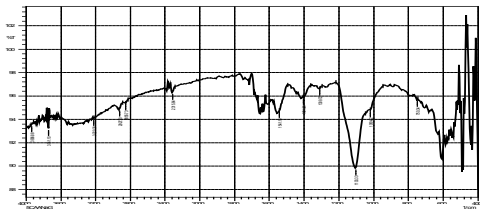


Fig.5. FTIR Spectra of Gold Nanocomposite Hydrogel

Swelling Behavior

Swelling experiments were carried out with a view of evaluation of the swelling capacity of the hydrogels under investigation in distilled water. Results of these experiments indicated that the increase in weight of the swollen hydrogels is directly related to the duration of swelling. The swelling behavior observed could be associated with absorption mechanism, which, in turn, is determined by the diffusion process.

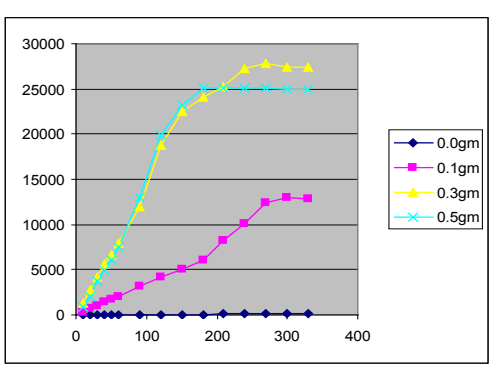
Swelling measurements

A fundamental relationship exists between the swelling of a polymer in a solvent and the natures of the polymer and the solvent. The percentage swelling (or mass swelling) is the most important parameter about swelling studies. The percentage swelling (%S) was calculated from the following equation

$$\%\, S = \frac{M_t - M_0}{M_0} \times 100$$

Where M_t is the mass of the swollen gel at time t, and M_0 is the mass of dry gel at time 0.

Figure 6 shows the effect of varying content of AcNa in the presence of gold nanoparticle on the swelling characteristics of the hydrogel at room temperature. The swelling is driven by repulsion of hydrophilic groups such as NH_2, C=0NH_2 and COO^- inside the network and osmotic pressure difference between the gels and the external solution. As the concentration of AcNa increases the swelling behavior also increases to certain extent (upto 0.3g) due to the additional osmotic pressure developed which expand the gel network further.



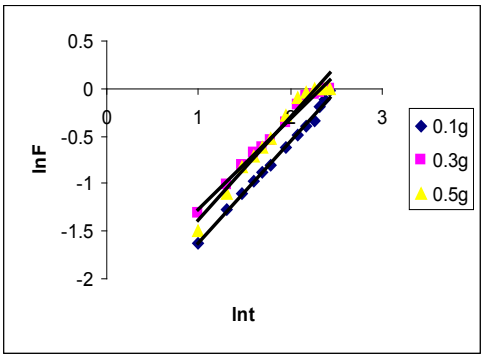


Fig. 6. Swelling Behavior of Poly(NCA-AM/ AcNa) Gold Nanocomposite Hydrogels

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

$$F = M_t / M_\infty = kt^n$$

Where F is the fractional uptake at time t, Mt 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. During the swelling, a non-Fickian process occurs; n values lie between 0.5 and 1.0.

Scanning Electron microscope (SEM)

The Surface Morphology of Gold Nanocomposite hydrogels (Figure 7) were studied by SEM analysis. The image indicates the GNPs are spherical in shape. Gold Nanocomposite hydrogels have the particle size between 41 to 56 nm and distributed uniformly throughout the polymer matrix.

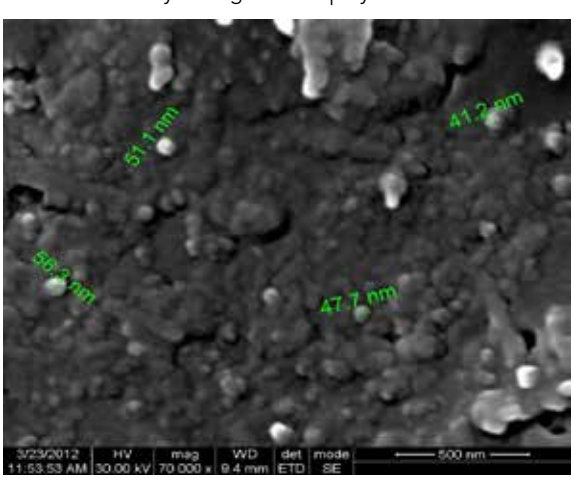


Fig.7. SEM image of Gold Nanocomposite

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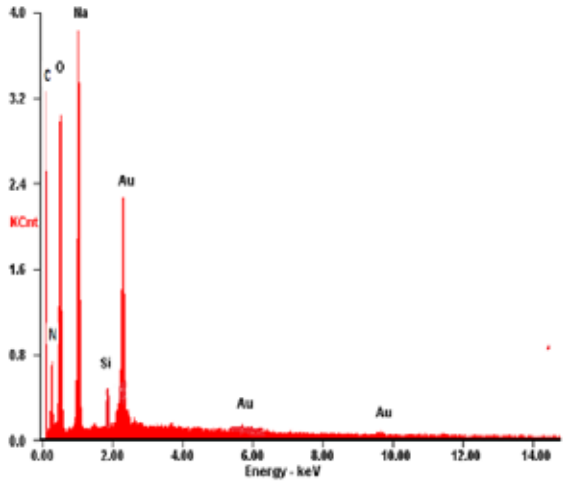

Fig.8. EDAX of GNP Hydrogel hydrogel

SEM/EDAX micro analysis was employed to determine the constitution of the gold nanoparticles dispersed in the hydrogel matrix. Energy dispersive analysis x-ray confirms the presence of gold nanoparticles in the hydrogel polymer matrix. The representative EDAX spectrum showing well-resolved peaks for gold, carbon, nitrogen, oxygen and sodium which are the elements present in the gold nanocomposite hydrogel. The observation of silicon in the EDAX spectra is due either to the thinness of gold layers or the interference of glass composition.

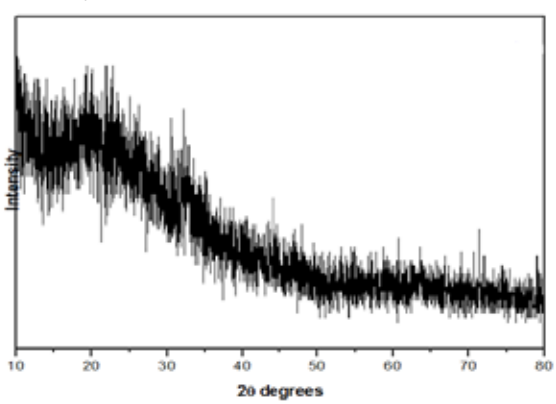

Fig.9. X-ray Diffraction (XRD)

The XRD of GNP Hydrogel is shown in Figure 9. X-ray diffraction pattern shows the GNP nanocomposite material is more amorphous and less crystalline in nature.

Conclusion

Gold Nanoparticles are prepared by reducing Hydrogen tetrachloro aurate using sodium citrate as reducing and capping agent. Surface Morphology was confirmed by SEM analysis. Particle size of the GNPs is between 20 - 27nm. Gold Nanoparticles are Spherical in shape. Their elemental compositions are evaluated by Energy dispersive analysis x-ray (EDAX). The Surface Morphology of Gold Nanocomposite hydrogels indicates that the GNPs are spherical in shape and distributed uniformly throughout the polymer matrix. Particle size of Gold Nanocomposite hydrogels is between 41 – 56 nm. X-ray diffraction pattern shows the nanocomposite material is more amorphous and less crystalline in nature. The swellability of the prepared hydrogel increases at higher concentrations of AcNa ratio in the matrix. Because of abundance of the hydrophilic groups of AcNa causes an improvement in the swelling characteristics of the hydrogel prepared. Kinetics of swelling of hydrogels was a non-Fickian character.

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