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Zincoxide Nanocomposite Hydrogels of Poly (N-tert-amylacrylamide –co –N-VinylPyrrolidone) Poly (N-tert-butylacrylamide –co –N-VinylPyrrolidone) Poly (N-cyclohexylacrylamide –co –N-VinylPyrrolidone)-Synthesis and Characterisation

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Abstract: ***In this study, we synthesiseda chains of Poly (N-tert-amylacrylamide –co –N-VinylPyrrolidone) ZincOxide nanocomposite hydrogel (Poly(NTA-NVP)ZnO), Poly (N-tert-butylacrylamide –co –N-VinylPyrrolidone) ZincOxide nanocomposite hydrogel (Poly(NTB-NVP)ZnO), Poly (N-cyclohexylacrylamide –co –N-VinylPyrrolidone) ZincOxide nanocomposite hydrogel (Poly(NCA-NVP)ZnO), by a free-radical polymerization using Azo- bis- iso -butyronitrile(AIBN) and N,N´-methylene-bis-acrylamide (MBA) initiator and cross-linking reagent respectively. These ZincOxide Nanocomposite hydrogels were characterized by Fourier transfom infrared Spectroscopy , X-ray diffraction and SEM analysis.Drug, Protein loading and the release behaviour were studied using UV Visible spectroscopy. The swelling nature of the hydrogel was studied by gravimetric method.***

Keywords: copolymerization; hydrogel; swelling; free radical polymerization.

1. Introduction

Nanotechnology is progressing field with its use in Science and Technology for the purpose of developing thingsat the nanoscale level . ZincOxide nanoparticles are understood to be biosafe and eco-friendly.Zinc oxide has attained more attention in various areas such as optical, piezoelectric, magnetic, gas sensing properties and antimicrobial agents.

In this work, we prepared a set of ZincOxide nanocomposite hydrogels by in situ polymerisation of N-tert- amylacrylamide, N-VinylPyrrolidone (NVP), N-tert-butylacrylamide, N-VinylPyrrolidone (NVP), N-cyclohexylacrylamide, N-VinylPyrrolidone(NVP),using AIBN as free radical initiator and N,N' –methylenebisacrylamide (MBA) as cross linker. These ZincOxide Nanocomposite hydrogels were characterized by Fourier transform infrared Spectroscopy, X-ray diffraction and SEM analysis.Swelling behavior of the obtained hydrogels were evaluated.

2. Experimental

Preparation of ZincOxide Nanocomposite Hydrogels–(Poly (NTA-NVP) ZnO), (Poly (NTB-NVP) ZnO), (Poly (NCA-NVP) ZnO).

The ZnO Nanocomposite hydrogel were prepared by free radical copolymerization of NTA, NVP in the presence of MBA as crosslinker and AIBN for initiating the polymerisation system. Aqueous solution containing a weighed amount of NTA, NVP, MBA, AIBN were dissolved in methanol–watermixture(3:1)andfinalvolumewas made 10mLin a polymerization tube. A solution containing 10mg of ZincOxide nanoparticle was added with constant stirring. After bubbling nitrogen for 15 min, the contents were placed in thermostatic water bath at 65^0C and the polymerization was conducted for 1 day. The prepared hydrogels were air-dried followed by vacuum drying. Similarly Poly (N-Tert-butylacrylamide-co-N-VinylPyrrolidone) ZIncOxide nanocomposite hydrogels and Poly (N-Cyclohexylacrylamide-co-N-VinylPyrrolidone)ZincOxide nanocomposite hydrogels were also prepared.

Characterization FTIR Spectra of ZnO Nanocomposite Hydrogel

The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule .The following characteristic bands were identified. The peak at 3478 cm^{-1} is due N-H stretching and a peak at 1592 cm^{-1} corresponds to C=O. Two bands at 1359, 1118 cm^{-1} represent the C-N and C-H bonding respectively. There was only new band at 485 cm-1 specific for stretching vibration of ZnO group. The Peaks at 1217 and 1389 cm^{-1} are corresponding to [-C(CH3)3] groups of NTB.

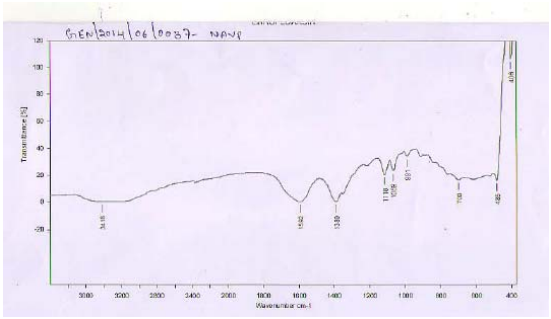

Figure 1: FT-IR Spectra of Poly (NTA-NVP) ZincOxide Nanocomposite Hydrogel

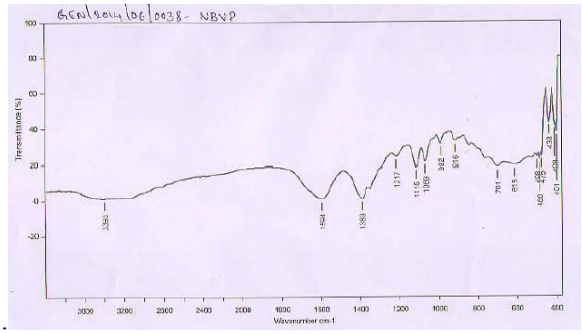

Figure 2: FT-IR Spectra of Poly (NTB-NVP) ZnO Nanocomposite Hydrogel

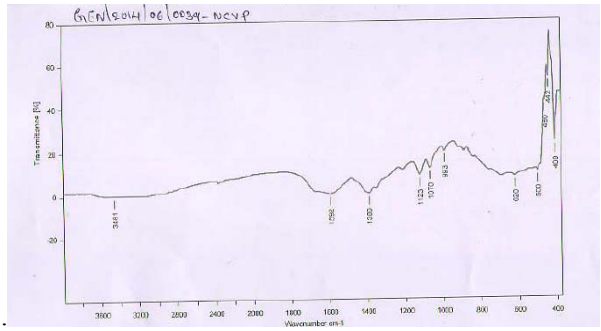

Figure 3: FT-IR Spectra of Poly (NCA-NVP) ZnO Nanocomposite Hydrogel

Scanning Electron Microscope (SEM)

Images for the ZincOxide Nanoparticle and ZincOxide Nanocomposite hydrogels were recorded using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification. SEM / EDAX were used to study the internal or cross morphology of the nanocomposite hydrogel. The image indicates the ZNPs are spherical in shape Zinc Oxide Nanocomposite hydrogels distributed uniformly throughout the polymer matrix.

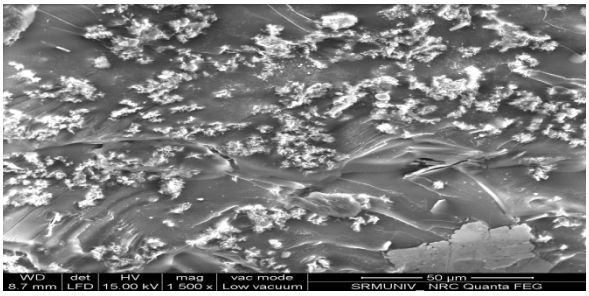

Figure 4: SEM image of Poly (NTA-NVP) ZincOxide Nanocomposite Hydrogel

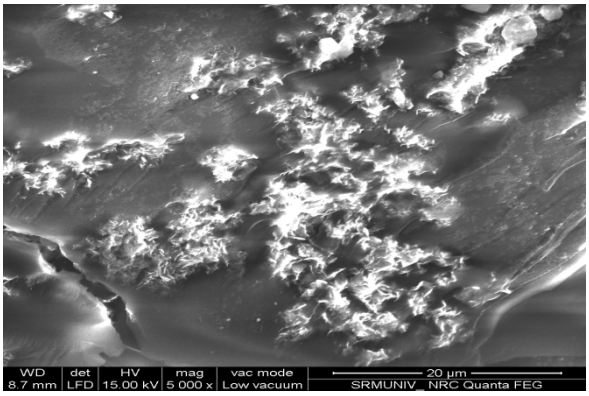

Figure 5: SEM image ofPoly (NTB-NVP) ZincOxide Nanocomposite Hydrogel

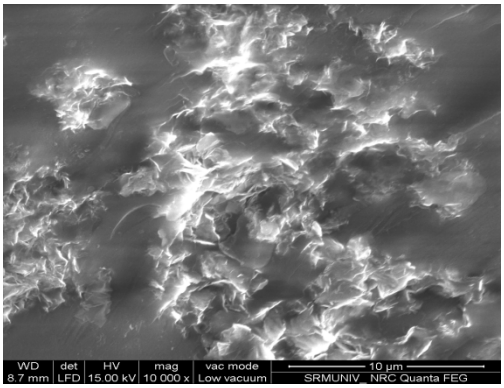

Figure 6: SEM image ofPoly (NCA-NVP) ZincOxide Nanocomposite Hydrogel

EDAX spectrum of ZNP Hydrogel

SEM/EDAX micro analysis was employed to determine the constitution of the ZincOxide nanoparticles dispersed in the hydrogel matrix. The representative EDAX spectrum showing well-resolved peaks for Zinc, carbon, oxygen which are the elements present in the ZincOxide nanocomposite hydrogel.

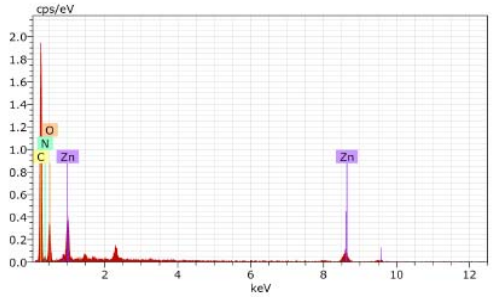

Figure 7: EDAX image of Poly (NTA-NVP) ZincOxide Nanocomposite Hydrogel

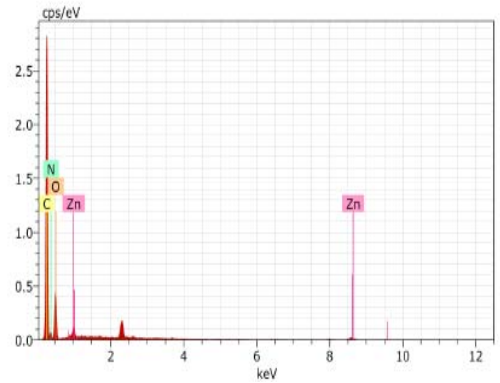

Figure 8: EDAX image ofPoly (NTB-NVP) ZincOxide Nanocomposite Hydrogel

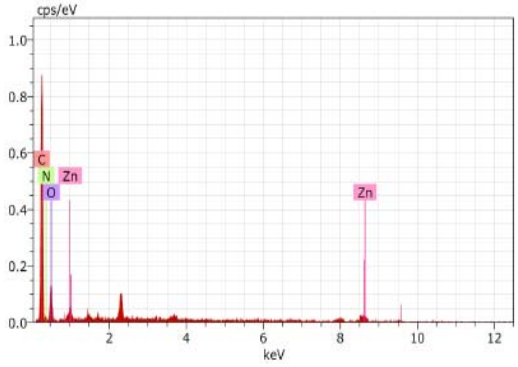

Figure 9: EDAX image ofPoly (NCA-NVP) ZincOxide Nanocomposite Hydrogel

X-ray Diffraction (XRD)

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

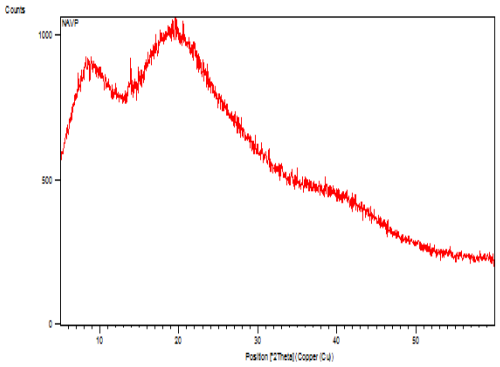

Figure 10: X-ray diffraction pattern of ZnO nanocomposite (NTA-NVP) hydrogel

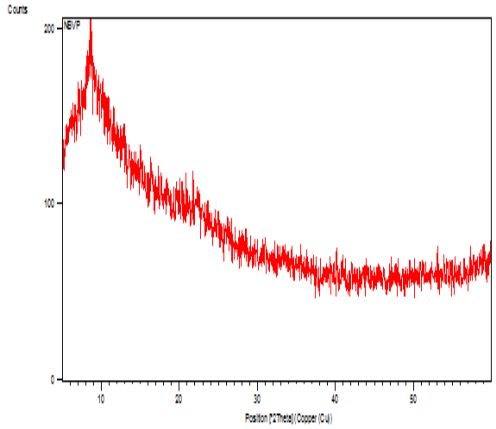

Figure 11: X-ray diffraction pattern of ZincOxide nanocomposite (NTB-NVP) hydrogel

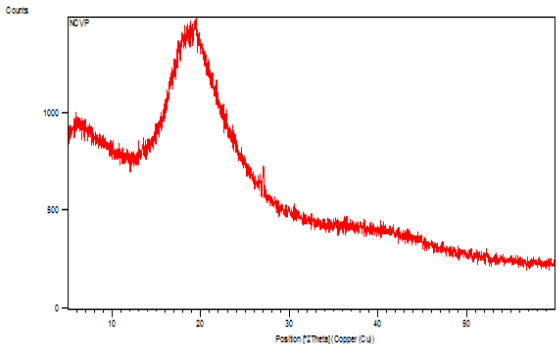

Figure 12: X-ray diffraction pattern of ZincOxide nanocomposite (NCA-NVP) hydrogel

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

$\%S = (M_t - M_0)/M_0$ -------(1)

Swelling behavior of ZincOxide nanocomposite hydrogels in different pH

Dynamic and equilibrium swelling coefficients of cross-linked hydrogels were determined in 0.05 M USP phosphate buffer solutions of pH 2.7,3.5,4.2,5.1,6.8 with constant ionic strength maintained. Dried hydrogels were soaked to swell in a solution of different pH. For dynamic swelling, swollen gels removed, dried and weighed at different time intervals.

Table 1: Swelling behavior of Poly (NTA-NVP) ZincOxide nanocomposite hydrogels in different pH

pH	2.7	3.5	4.2	5.1	6.8
Dyanamic swelling Coefficient	0.87	1.0	1.1	1.46	1.74
Equlibrium swelling coefficient	0.46	0.5	0.52	0.59	0.63
Diffusional Exponent n	0.551	0.551	0.552	0.552	0.551

Table 2: Swelling behavior of Poly (NTB-NVP) ZincOxide nanocomposite hydrogels in different pH

pH	2.7	3.5	4.2	5.1	6.8
Dyanamic swelling Coefficient	0.90	1.05	1.85	2.05	2.65
Equlibrium swelling coefficient	0.47	0.51	0.64	0.67	0.72
Diffusional Exponent n	0.61	0.60	0.58	0.59	0.62

Table 3: Swelling behavior of Poly (NCA-NVP) ZincOxide nanocomposite hydrogels in different pH

pH	2.7	3.5	4.2	5.1	6.8
Dyanamic swelling Coefficient	0.50	0.93	0.9	1.0	1.2
Equlibrium swelling coefficient	0.33	0.47	0.48	0.5	0.54
Diffusional Exponent n	0.53	0.55	0.55	0.54	0.55

Analysis of drug release pattern

Peppas model $M_t/M_\infty = Kt^n$ (12)

where M_t/M_∞ is the fraction of drug released at time "t", K is a constant incorporating the structural and geometric characteristics of the gels and "n" is the release exponent or diffusional exponent. When n = 0.5, order of release is Fickian, n = 1 responds to a case II transport, while 0.5<n<1 corresponds to a diffusion mechanism that is non-Fickian .

Drug Loading and Release

50ml of 100 ppm (drug) Chloramphenicol solution was used for loading the Nanocomposite hydrogels. Prepared gels were dried and weighed. Drug solution was added to the nanocomposite hydrogelsand maintained away from sunlight. The swollen nanocomposite hydrogels were removed from the drug and wiped. Then the absorbance was measured during different time intervals using UV-Vis spectrometer. Dried gels were added with the pH solution of 4.2 and kept for a day. The release of the drug was obtained by the measured absorbance of UV visible spectrometer.

Table 4: Drug Loaded and Released UV Absorbance of Zincoxide NANOCOMPOSITE HYDROGELS

Samples	UV absorbance of drug loaded samples	UV absorbance of drug released samples
Poly (NTA-NVP) ZnO hydrogel	0.638	1.511
Poly (NTB-NVP) ZnO hydrogel	0.524	1.511
Poly (NCA-NVP) ZnO hydrogel	0.246	0.705

Absorbance of loaded drug solution =1.886

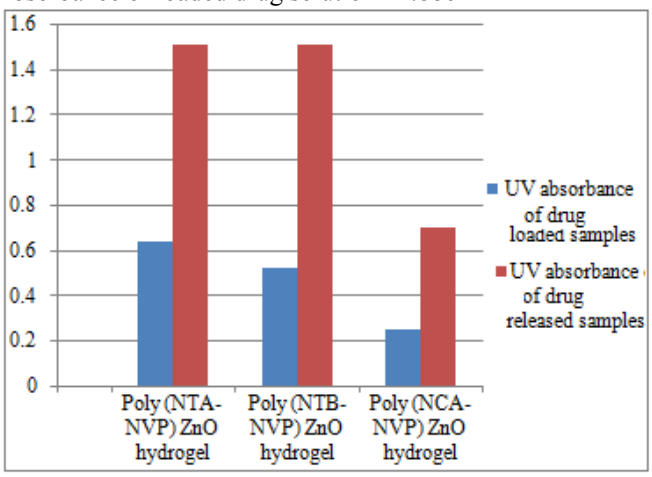

Figure 13: Drug Loaded and Released UV Absorbance

Protein Loading and Release

50ml of 100 ppm (BSA) Bovine –Serum-Albumin solution was used for loading the Nanocomposite hydrogels. Prepared gels were extracted, dried and weighed. Protein solution was added to the nanocomposite hydrogels then it was closed and stored away from direct sunlight. The nanocomposite hydrogels were swollen. The gel was removed from the drug and wiped. It was added with the required amount of solvent and stored, and then the absorbance was measured during different time intervals using UV-Vis spectrometer to determine the loading and release behavior of the hydrogel.

Table 5: UV Absorbance of Protein Loaded in ZincOxide Nanocomposite Hydrogels

+SAMPLES	UV absorbance of Protein loaded samples	UV absorbance of Protein released samples
Poly (NTA-NVP) ZnO hydrogel	0.252	1.307
Poly (NTB-NVP) ZnO hydrogel	0.260	1.329
Poly (NCA-NVP) ZnO hydrogel	0.291	1.766

Absorbance of loaded protein solution =1.911

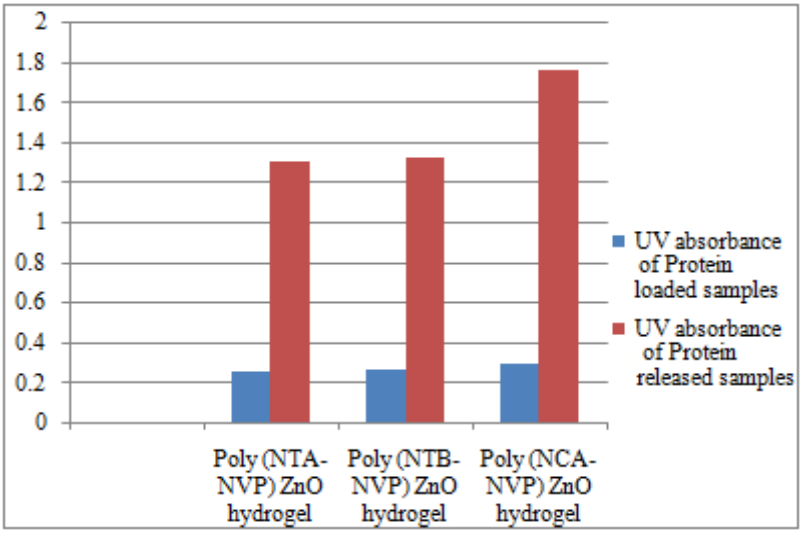

Figure 14: UV Absorbance of Protein Loaded in Zinc Oxide NANOCOMPOSITE HYDROGELS

3. Conclusion

X-ray diffraction studies indicated that ZincOxide nanocomposite hydrogels are micro-crystalline in nature. Swelling behaviour increases with the increase in pH of the solution. The diffusion of ZincOxide nanocomposite hydrogel systems has non-Fickian character. The drug loading is effectively observed in Poly (NTA-NVP)ZincOxide nanocomposite hydrogel and Poly (NTB-NVP)ZincOxide nanocomposite hydrogel. Protein loading is efficient in Poly(NCA-NVP).

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