

## DYE ADSORPTION, ANTIOXIDANT ACTIVITY AND ANTIMICROBIAL STUDIES OF POLY (NTB-co-AM/AMPSNa) ZnO NANOCOMPOSITE HYDROGELS

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### ABSTRACT

This article describes the synthesis of ZnO nanocomposite hydrogels based on N-tert-butyl acrylamide, acrylamide and 2-acrylamido-2-methylpropane sulphonate (AMPSNa) monomers via free-radical polymerization. A required amount of monomers with N,N'-methylenebisacrylamide (MBA) crosslinker and Ammonium persulphate initiator were dissolved in methanol/water (3:1) and ZnO nanoparticles dispersed in the medium, then the polymerization was carried out at 60 °C. The synthesized ZnO nanocomposite hydrogels were characterized by FT-IR, SEM, XRD and TGA analysis. The AMPSNa content varied from 0.1 to 0.7g to study the influence of AMPSNa on swelling. The results indicate the equilibrium swelling increased with increasing amount of ionic monomer. SEM image reveals the presence of ZnO nanoparticles in the polymer matrix. XRD analysis indicates that the hydrogels are amorphous in nature. TGA of hydrogels showed double stage decomposition and are stable up to 300 °C. Methylene blue dye adsorption capacity of hydrogels exhibits 82.05 % at lower content of AMPSNa. The adsorption isotherm study showed Freundlich isotherm and the hydrogels favour multilayer adsorption. DPPH radical scavenging activity exhibited antioxidant property of hydrogels. The hydrogels are active against some selected microorganisms.

**KEY WORDS :** ZnO nanocomposite hydrogels, SEM, XRD, Swelling behavior, DPPH, Freundlich isotherm

### INTRODUCTION

Hydrogels are three-dimensionally cross linked polymer network having hydrophilic groups and it has the capacity to absorb more amount of water, saline and physiological solutions. Hydro gels are widely used in agriculture, biomedical, tissue engineering, biosensors, drug delivery and dye effluent treatment, because of their high swelling rate (Laftah *et al.*, 2011; Hoare and Kohane 2008; Van *et al.*, 2011; Paulino *et al.*, 2011; Yadollahi and Namazi 2013 and Yadollahi *et al.*, 2014). It is well-known that metal oxide (ZnO, CuO, Ag<sub>2</sub>O)

nanoparticles are used as sensors, solar cells, antimicrobial agent and UV protective film. Since metal oxide nanoparticles with more surface area can cause molecular mobility, relaxation behaviour and thermo- mechanical properties of the cross linked polymer, when the metal oxide nanoparticles were present in the polymer network (Espitia *et al.*, 2012 and Williams *et al.*, 2013). Normally thermo responsive hydro gels are playing an important role in drug releasing behaviour of the loaded drugs from the polymeric network. The thermo responsive hydro gels were also used in controlled drug release, tissue engineering and sensors. The main purpose of

intercalation/ incorporation of metal oxide nanoparticles in the polymer network is to sustained drug release, eco-friendly and low cost (Perelshtein *et al.*, 2013 and Shafei *et al.*, 2011). Recently, Carboxymethylcellulose /ZnO nanocomposite hydro gels were synthesized and demonstrated as good antimicrobial agents. ZnO Nanocomposite hydro gels were synthesized by the reduction of  $Zn^{2+}$  by adding NaOH in the preformed polymer network. It was noticed that the reduction of  $Zn^{2+}$  could not be achieved completely because of the presence of carboxyl ate group present in the network (Yadollahi *et al.*, 2015). The addition of NaOH not only reduces the  $Zn^{2+}$  but also neutralize the carboxylate as COONa which leads to agglomeration of ZnO nanoparticles. The agglomeration of ZnO nanoparticles may reduces the antibacterial activity. To avoid the agglomeration of nanoparticles in the network, it is better to intercalate ZnO during the course of polymerization, because polymer solution itself acting as capping agent. Carboxymethyl cellulose (CMC)/ZnO nanocomposite hydrogels were also used for dye removal applications (Jabin *et al.*, 2019). The CMC based ZnO hydrogel exhibited 89.40% of cationic dye removal efficiency. Now a days metal oxide based nanocomposite hydrogels were used as a better/alternate adsorbent materials for the removal of heavy metals and dye molecules because of low cost and reusability. The polymeric materials containing functional groups such as carboxylic acid, sulphonic acid, amine, hydroxyl and amide can trap and bind the adsorbate molecules and make it as effective adsorbent (Singh and Singhal, 2015; Tomar *et al.*, 2007; Ghahfarrokhi *et al.*, 2015; Hosseini *et al.*, 2016; Zhang *et al.*, 2006; Jafari *et al.*, 2015 and Huang *et al.*, 2019). For example, polymeric materials containing acrylic acid / acrylamide/with some anionic functional groups were used as an adsorbent for removal of methylene blue dye molecules (Singh *et al.*, 2012 and Bharathi and Pazhanisamy 2018). The review of

literatures, motivated us to synthesize N-tert-butylacrylamide based ZnO nanocomposite hydrogels in order to evaluate swelling behavior, antimicrobial and antioxidant activities. Herein we described the synthesis of poly (N-tert-butylacrylamide –co-acrylamide/AMPSNa) ZnO nanocomposite hydrogels via free radical crosslinked polymerization. The synthesized ZnO nanocomposite hydrogels were characterized by FT-IR spectroscopy, SEM and XRD analysis. The swelling behaviour was studied using gravimetric method distilled water at room temperature. Methylene Blue dye was used to study the dye adsorption behaviour. Antimicrobial activity of hydro gels was investigated using selected microorganisms. The DPPH free radical scavenging method was adopted to study antioxidant activity.

## EXPERIMENTAL

### Materials

Acrylamide (AM) was purchased from Merck. Ammonium per sulphate (APS), N,N'-methylenebisacrylamide (MBA), 2-acrylamido-2-methylpropane sulphonic acid (AMPS) and ZnO nanoparticles were supplied by Sigma Aldrich. The ionic monomer AMPSNa was prepared by neutralization of 2-acrylamido-2-methylpropanesulphonic acid (AMPS) by sodium hydroxide. N-tert-butylacrylamide (NTB) was prepared by a reaction of t-butyl alcohol and acrylonitrile in presence of Sulphuric acid at 3 °C.

### Preparation of Zinc Oxide Nanocomposite Hydrogels

The Zinc oxide nanocomposite hydrogels were prepared by free radicals cross-linking copolymerization. Monomers NTB (0.5g), AM (0.5g) and AMPSNa (0.1, 0.3, 0.5 and 0.7 g) were added to the well-dispersed ZnO nanoparticles solution followed by addition of APS (0.05 g) as initiator and MBA (0.05 g) as a crosslinker in 3:1 methanol-water

**Table 1.** Synthesis of poly(NTB-co-AM/AMPSNa) ZnO nanocomposite hydrogels

NTB	Monomers (g)		Cross Linker MBA (g)	ZnO (g)	Initiator APS (g)	Medium MeOH/H <sub>2</sub> O (3:1) (ml)
	AM	AMPSNa				
0.500	0.500	0.100	0.050	0.050	0.050	20
0.500	0.500	0.300	0.050	0.050	0.050	20
0.500	0.500	0.500	0.050	0.050	0.050	20
0.500	0.500	0.700	0.050	0.050	0.050	20

mixture at room temperature. They were purged with nitrogen gas for 20 minutes then heated to 60 °C in a thermostatic water bath for a period of 24 hours. The synthesized nanocomposite hydrogels were dried at 50 °C.

### Characterization of ZnO nanocomposites hydrogels

ZnO nanocomposites were blended with potassium bromide (1:200 proportions) as pellets and subjected to FTIR analysis and the spectrum was recorded in wave number ranging from 400 to 4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$  in Bruker TENSOR 27- FTIR instrument. The surface morphology of the dried samples were investigated using SEM (JEOL- JSM-6390) operated at an accelerating voltage of 10 kV. For EDX analysis, nanocomposite hydrogels were dried on a carbon coated copper grid and examined under SEM equipped with thermo EDX attachment. The pattern of X-ray diffraction of the samples were performed by an X-ray diffractometer (PANalytical X-pert PRO),  $\text{Cu-K}\alpha$  radiation at 40kV, 30 mA at a scanning range of  $2\theta = 10-80^\circ$  and a scan rate of  $2^\circ/\text{min}$ . Thermogravimetric analysis was used to investigate the thermal stability and cross-link densities of the prepared hydrogels. The thermograms were recorded on a Perkin Elmer-7 instrument at a heating rate of  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$  protection over a temperature range from room temperature to  $800^\circ\text{C}$ .

### Swelling Behavior

In order to investigate the swelling behavior, the swelling tests of ZnO nanocomposite hydrogels were carried out by placing the dry hydrogels in water at room temperature. The water intake of dry hydrogel was determined by weighing the hydrogels after wiping gently with tissue paper at particular time intervals. The percentage swelling of the samples was determined by applying the following equation,

$$\text{DS \%} = \frac{W_s - W_d}{W_d} \times 100 \quad \dots (1)$$

$W_s$  is the weight of the swollen gel at a given time and  $W_d$  is the weight of the dry gel. DS% is the degree of swelling.

### Kinetic study of ZnO Nanocomposite Hydrogels

$$F_{\text{swp}} = Kt^n \quad \dots (2)$$

where  $K$  is the swelling constant,  $t$  is the time and  $n$  is swelling exponent.

### MB dye adsorption study

Adsorption experiments were carried out by batch mode technique because of its simplicity. A weighed quantity of dry hydrogel (100 mg) was immersed in methylene blue dye solution (20 mg, 20 mL) at room temperature. The amount of MB adsorbed was measured spectrophotometrically at 663 nm at predetermined time intervals in periodically taken solution samples which were again placed in the same vessel so that the liquid volume was kept constant. The adsorption capacity  $Q$  (mg of dye per g of polymer) of hydrogel was calculated by using the following expression:

$$Q_{(\text{mg/g})} = (C_i - C_e) V/m \quad \dots (3)$$

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 hydrogel used (g). The removal efficiency (RE %) of hydrogels was calculated using the following expression.

$$\text{RE \%} = (C_i - C_t / C_i) \times 100 \quad \dots (4)$$

where  $C_i$  and  $C_t$  are the initial and equilibrium concentration of the MB dye solution, respectively.

### Antioxidant activity

For determination of antioxidant property of ZnO hydrogels was studied by DPPH radical scavenging method using spectrophotometer at 517nm. The ability of scavenge DPPH radical was evaluated by using the following equation as follows

$$\text{DPPH scavenging activity (\%)} = \frac{\text{Abs}_{\text{control}} - \text{Abs}_{\text{sample}}}{\text{Abs}_{\text{control}}} \times 100 \quad \dots (5)$$

Where,  $\text{Abs}_{\text{control}}$  is the absorbance of DPPH radical + methanol;  $\text{Abs}_{\text{sample}}$  is the absorbance of DPPH + sample /standard.

### Antimicrobial Studies

The bacterial culture medium was used agar medium which consists of 2.0g of beef extract, 17.5g of casein hydrolysate, 1.5g starch and 17.0g agar dissolved in 1 liter of distilled water and pH adjusted to neutral. The contents were autoclaved at 15 lbs pressure at  $121^\circ\text{C}$  for 15 minutes. The sterilized media were poured into 100mm Petri dishes. After 30 minutes, the culture medium was inoculated with the test organisms. Petri dishes containing 20 mL Muller Hinton medium were seeded with 24 hours culture of bacteria and fungi

and spread well with sterile swabs. Wells were cut and 20  $\mu$ L (100 mg) of the sample along with standard antibacterial and antifungal agents containing disc was placed on to an agar plate. Amikacin and ketoconazole were used as a standard antibacterial and anti fungal agents respectively. DMSO was used as a control. The plates were then inoculated at 37° C for 24 hours. The zone of inhibition was measured and expressed in millimetre.

## RESULTS AND DISCUSSION

The synthesis of ZnO nanocomposite hydrogels are depicted in scheme-1.

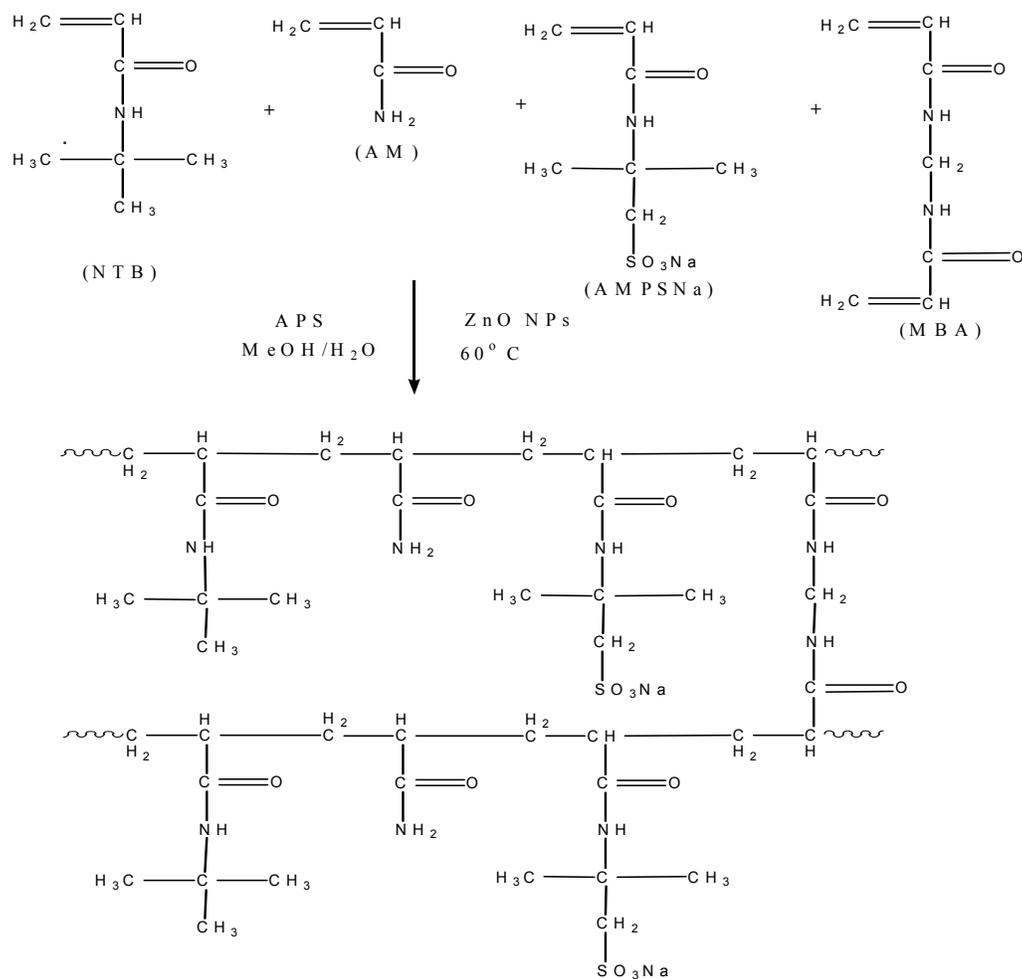
### FT-IR spectral Characterization

The FT-IR spectrum of poly (NTB-co-AM/AMPSNa) ZnO nanocomposite hydrogel is shown in Fig. 1. A broad peak corresponding to NH

stretching of NTB was observed around 3468.6  $\text{cm}^{-1}$ . The peak observed at 1663.7  $\text{cm}^{-1}$  corresponds to C=O stretching of NTB. The characteristic peak at 1542.9  $\text{cm}^{-1}$  corresponds to NH bending vibration of amides. The peak at 2978.9  $\text{cm}^{-1}$  is due to C-H stretching of the polymer backbone. The peak at 1117.8  $\text{cm}^{-1}$ , 1044.6  $\text{cm}^{-1}$  and 622.5  $\text{cm}^{-1}$  corresponds to asymmetric stretching of  $-\text{SO}_2$ , symmetric stretching of the  $-\text{SO}_2$  group and C-S stretching of AMPSNa respectively. The IR absorption at 473.1  $\text{cm}^{-1}$  corresponds to ZnO stretching confirms the incorporation of ZnO into the polymer matrix. The above IR spectral analysis confirmed the presence of all monomeric units in the crosslinked hydrogel.

### SEM and EDX analysis

SEM image of ZnO nanocomposite hydrogel is depicted in Fig. 2a. The SEM analysis indicated that the ZnO nanoparticles are spherical in shape which are uniformly dispersed in the polymer matrix. A



**Scheme 1.** Schematic representation of poly (NTB-co-AM/AMPSNa) ZnO nanocomposite hydrogels.

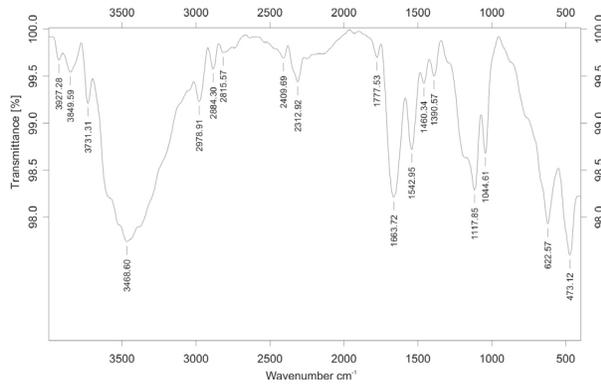


Fig. 1. FT-IR spectrum of poly (NTB-coAM/AMPSNa) ZnO nanocomposite hydrogel

typical EDX spectrum of ZnO hydrogel is given in Fig. 2(b). The signals at 1.0 (L $\alpha$ ) and 8.6 (K $\alpha$ ) keV confirm the presence of Zinc particles in the nanocomposite polymer matrix. In addition to the above signals, the presence of other elemental peaks of the polymer indicates the incorporation of zinc oxide into polymer matrix.

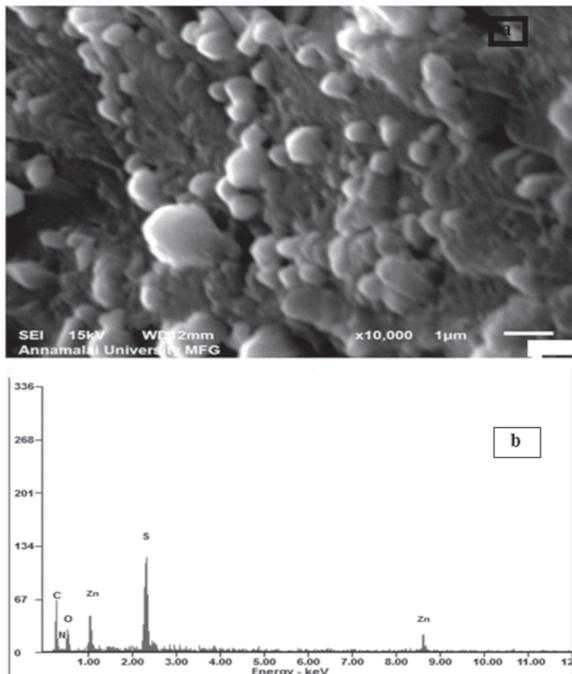


Fig. 2. (a) SEM image and (b) EDX spectrum of poly (NTB-co-AM/AMPSNa) ZnO nanocomposite hydrogel

### XRD analysis

The XRD pattern of ZnO nanocomposite hydrogel is shown in Fig. 3 and the 2  $\theta$  values are in range of 10 to 70°. It is also observed that 2 theta values about

34°, 37°, 39°, 44°, 64° and 68° planes of zincates phase of ZnO nanoparticles in ZnO nanocomposite hydrogels. A wide peak between 15 to 30° is due to the polymer networks. The peaks of ZnO nanoparticles are overlapped with broad peak. The XRD analysis exhibited the nanocomposite material is more amorphous in nature and attributes to the loss of degree of crystallinity.

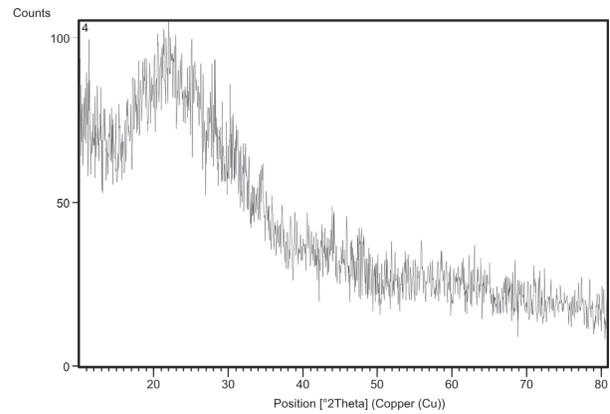


Fig. 3. XRD pattern of poly (NTB-co-AM/AMPSNa) ZnO nanocomposite hydrogel

### Thermogravimetric analysis

A typical thermogram of poly(NTB-co-AM/AMPSNa) ZnO anaocomposite hydrogel is presented as Fig. 4 and degradation values are listed in Table 2. The TGA analysis showed the zinc oxide nanocomposite hydrogels were thermally stable up to 280 °C. The initial weight loss at 140 °C is due to the evaporation of water in free State and in the inter layers of the polymeric hydrogel. The next stage at 300°C is due to the decomposition of amide group. The stage at starting at around 370°C shows the breakdown of polymer skeleton. The final decomposition ends at 440 °C. The residual weight is due the decomposed hydrogel residues (25%). The residual weight is due the decomposed

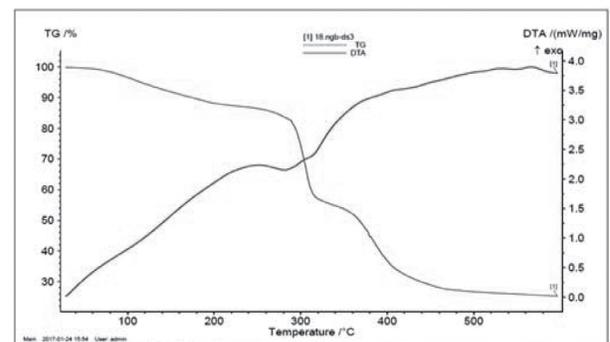


Fig. 4. Thermogram of poly (NTB-co-AM/AMPSNa) ZnO nanocomposite hydrogel

**Table 2.** Thermal behaviour of poly (NTB-co-AM/ AMPSNa) ZnO hydrogels

Weight of AMPSNa (g)	Initial weight loss	Decomposition Temperature (°C) (% weight loss)		Residual weight %	FDT (°C)
		Stage 1	Stage 2		
0.1	140 °C (12%)	295 °C (20%)	370 °C (26%)	26%	425
0.3	140 °C (12%)	300 °C (22%)	380 °C (24%)	26%	425
0.5	140 °C (12%)	300 °C (25%)	370 °C (26%)	27%	425
0.7	140 °C (12%)	300 °C (26%)	380 °C (27%)	28%	425

FDT: Final decomposition Temperature

hydrogel residues (about 25% at 600 °C). All the zinc oxide nanocomposite hydrogels were showed almost same behavior.

### Swelling behavior

Swelling behaviour of ZnO nanocomposite hydrogels are depicted in Fig. 5a and it observed that the swelling ratio increases with increasing amount of AMPSNa up to 0.5g of AMPSNa. The increase of swelling ratio with increase of AMPSNa, due to increase in hydrophilicity and decrease in crosslink density (Tomar *et al.*, 2007). But, when the content of AMPSNa was 0.7g the swelling ratio decreased it may be attributed that the formation of more number of hydrophilic (AMPSNa) chains in the network. Due to the formation of denser

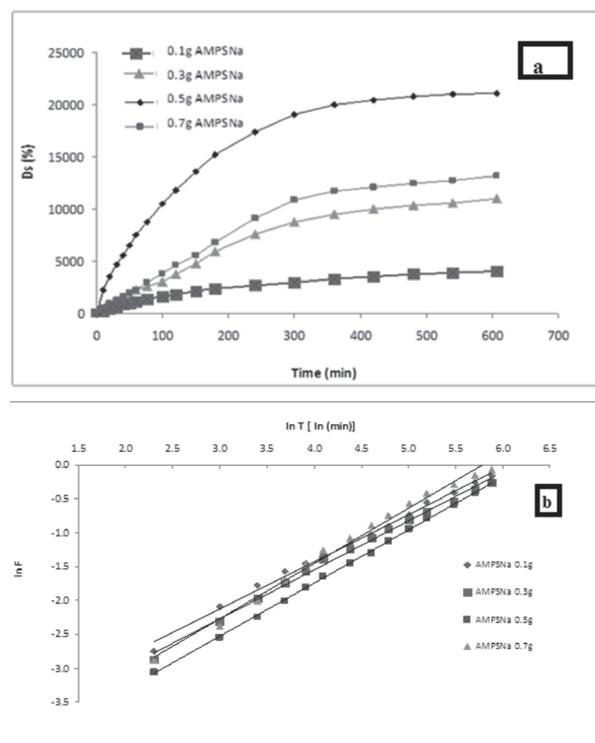
network, the penetration of water molecules in to the hydrogel became difficult, thereby the absorption capacity got reduced (Bajpai *et al.*, 2002). The Fig. 5b. indicates the plots of  $\ln F$  against  $\ln T$  gives a straight line whose slope is “n”, and the values are listed in Table 3 which is equal to 0.91, 0.75, 0.87 and 0.61. These values of “n” is in the range between  $0.50 < n < 1.00$  which indicates that the diffusion is non-Fickian. In the non-Fickian diffusion mechanism, diffusion and relaxation are said to be isochronal effective (Kayalvizhy and Pazhanisamy, 2016).

**Table 3.** Maximum swelling and diffusion parameters ZnO nanocomposite hydrogels

Weight of AMPSNa (g)	Max. Ds %	‘n’	Intercept “k”
0.1	4023	0.9133	- 5.4446
0.3	11002	0.7554	- 4.4422
0.5	13184	0.8736	- 5.2548
0.7	21062	0.6121	- 3.5753

### Adsorption studies of Methylene Blue dye on ZnO nanocomposite hydrogels

The adsorption behaviour of dye molecules are mainly due to two reasons, firstly the interaction between positively charged dye molecules and negatively charged active functional groups present in the network and secondly electrostatic force of attraction due to formation of coordinate bonds. The adsorption of ZnO nanocomposite hydrogels with respect to contact time are presented in Figure 6. The effect of dosage of hydrogel (0.1g AMPSNa) on removal dye molecules are listed in Table 4. From the table it is observed that the removal efficiency of dye was increased with increasing amount of hydrogel and it was achieved to 82.05%. The dye removal efficiency of hydrogels are increased with increasing amount of AMPSNa content from 0.1 to 0.7 g which have more number of active sulphonate



**Fig. 5.** (a) Swelling behaviour of ZnO nanocomposite hydrogels in water and (b) Plot of  $\ln F$  Vs  $\ln T$

groups to adsorb MB molecules by electrostatic force of attraction.

**Kinetic studies of ZnO nanocomposite hydrogels**

Adsorption kinetic models have been proposed to clarify the mechanism of adsorption from aqueous solution to on an adsorbent. The adsorption kinetics of methylene blue on ZnO hydrogels can be investigated either through pseudo first order

(Lagergren equation) or pseudo second order kinetics (Ho equation)

$$\log (q_e - q_t) = \log q_e - k_1 / 2.303 \times t \quad \dots (6)$$

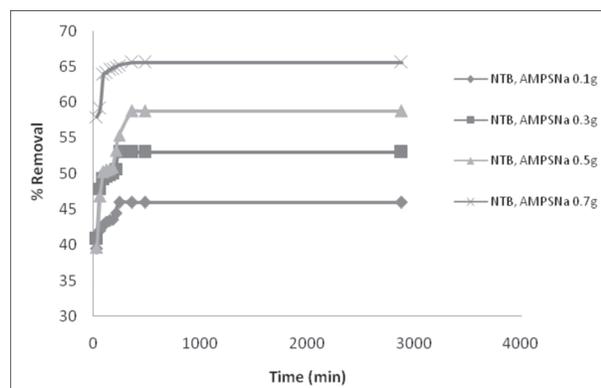
$$t / q_t = 1 / k_2 \cdot q_e^2 + 1 / q_e t \quad \dots (7)$$

The adsorption capacities  $q_t$  and  $q_e$  (mg /g) represents methylene blue ZnO nanocomposites at time  $t$  (min) and at equilibrium respectively.  $k_1$  is the rate constant of adsorption ( $\text{min}^{-1}$ ) and  $k_2$  is second-order constant. The kinetics data of first order and pseudo second order kinetics are determined by using equation (6) and (7) are listed in Table 5 and Table 6 and are shown as Fig. 8 a. and 8b. respectively. Between the first order and second order, second order kinetic model seems to best to describe the above adsorption system. The kinetics data of ZnO hydrogels indicated that the coefficients and calculated  $q$  values do not fit the pseudo-first-order model. The correlation coefficients ( $R^2 > 0.999$ ) value of second order kinetics was very close to unity. Moreover, the difference between calculated adsorption capacity ( $q_{e(\text{cal})}$ ) and experimental adsorption capacity ( $q_{e(\text{exp})}$ ) values of second order is very small. Therefore, the investigations of adsorption of dye molecules on ZnO hydrogels showed pseudo second order kinetics and it reveals that the adsorption was chemical adsorption (Singh and Singhal, 2015).

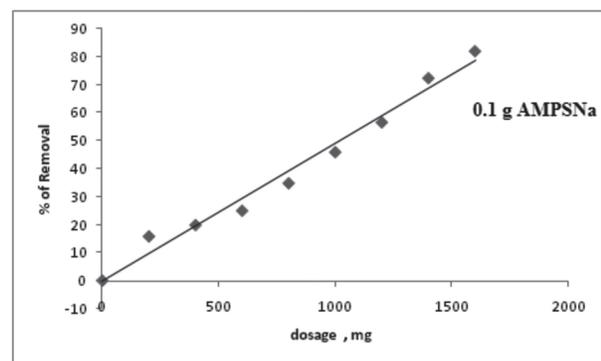
**Table 4.** Effect of ZnO nanocomposite hydrogel dose on the percentage removal of MB dye at pH 7.0.

Dose in mg	% Removal of MB dye
0	0
200	15.81
400	19.87
600	25.00
800	34.82
1000	45.94
1200	56.62
1400	72.43
1600	82.05

( $C_i = 20\text{mg/L}$ , Contact time = 2880 min).



**Fig. 6.** Effect of contact time on MB dye of ZnO nanocomposite hydrogels



**Fig. 7.** Effect of dose on MB dye adsorption of ZnO nanocomposite hydrogel

**Adsorption Isotherms of ZnO hydrogels**

Langmuir and Freundlich adsorption isotherms were used to determine the adsorption capacities and nature of adsorption in removal of MB dye molecules onto ZnO hydrogels. The Langmuir adsorption isotherm represents monolayer coverage of MB dye molecules on the outer layer of hydrogel at equilibrium. The adsorption capacities and Langmuir constants were calculated by the following linearized equation -8

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{(q_{\text{max}} \cdot b)} \quad \dots (8)$$

where  $C_e$  is the equilibrium concentration of dye molecules in solution;  $q_e$  is the amount of dye molecules adsorbed at equilibrium (mg/g);  $q_{\text{max}}$  is the maximum adsorption of dye molecules (mg/g);  $b$  is the Langmuir constant related to energy. The values of Langmuir constants and  $R^2$  (correlation coefficient) were obtained by plotting  $C_e/q_e$  vs  $C_e$  (Fig. 9a) and values are listed in Table 7. The  $R^2$  values indicate the applicability of adsorption

**Table 5.** First order kinetics of ZnO nanocomposite hydrogels

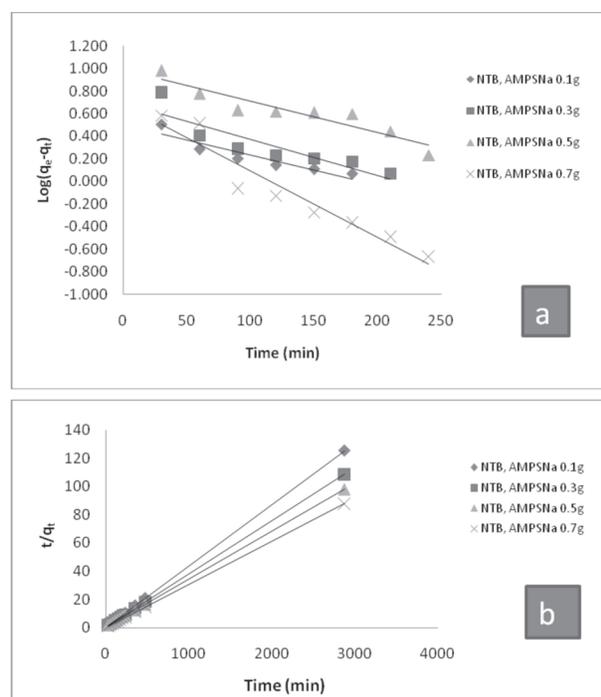
AMPSNa (g)	$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (cal)	$q_e$ (exp)	$\Delta q_e$	$R^2$ values	SSE %
0.1	-0.0060	3.13	22.97	19.84	0.862	7.4210
0.3	-0.0074	4.92	26.50	25.58	0.787	
0.5	-0.0064	9.70	29.38	19.68	0.871	
0.7	-0.0136	4.82	32.80	27.98	0.922	

[pH =7, Dose 100mg/20mL, Contact time =2880 mins]

**Table 6.** Second order kinetics of ZnO nanocomposite hydrogels

AMPSNa (g)	$k_2$ (g/mg.min)	$q_e$ (cal) (mg/g)	$\Delta q_e$	h	$R^2$	SSE %
0.1	0.000760	29.58	6.61	0.66	1.000	1.0661
0.3	0.000115	30.39	3.89	1.06	1.000	
0.5	0.001120	31.64	2.26	1.12	0.999	
0.7	0.011220	32.78	0.02	12.06	1.000	

[pH =7, Dose 100mg/20mL, Contact time =2880 mins]

**Fig. 8.** (a) First order kinetics (b) second order kinetics of ZnO nanocomposite hydrogels.

isotherm. Freundlich isotherm describes the non-ideal adsorption onto heterogeneous surface and multilayer adsorption of dye molecules. The linearized equation of Freundlich model is represented by equation -9.

$$\log(q_e) = 1/n \log(C_e) + \log K_f \quad \dots (9)$$

$q_e$  where  $C_e$  is the equilibrium concentration of

dye molecules in solution;  $K_f$  is the Freundlich constant. Plotting of  $\log(q_e)$  vs  $\log C_e$  gives a straight line whose intercept is  $K_f$  and slope is  $1/n$  and the values are listed in Table 8.

In this investigation, the  $R^2$  value of Freundlich is greater than Langmuir adsorption model which is very close to unity. The value of 'n' denotes the favourability of the adsorption, herein the 'n' values are equal to 1. As the Freundlich isotherm gave a better fit compared to Langmuir, it can be concluded that the surface of hydrogel is heterogeneously multilayered adsorption of dye molecules (Singh and Singhal, 2015).

### Antioxidant activity

The DPPH radical scavenging activities (%) in methanol extracts of the ZnO nanocomposite hydrogels are presented in Fig.10. When a DPPH solution is mixed with polymer solution acting as a hydrogen atom donor, a stable non-radical form of DPPH is obtained with the simultaneous change of the violet colour to pale yellow. Hence, DPPH has been used extensively as a free radical to evaluate reducing substances and is a useful reagent for investigating the free radical scavenging activities of compounds. The decrease in absorbance of DPPH radical caused by Zn O hydrogel is due to the reaction between them and the radical, results in the scavenging of the radical by hydrogen donation. It is visually noticeable a discoloration from purple to pale yellow. As the concentration of ZnO hydrogel increases the absorbance decreases and the inhibition percentage increases due to radical

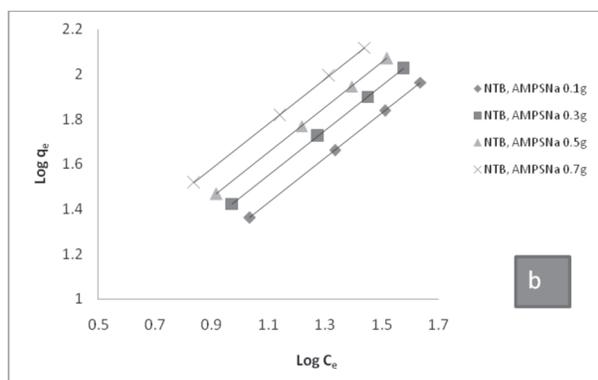


Fig. 9. (a) Langmuir and (b) Freundlich adsorption isotherm for the of MB dye on ZnO hydrogels

scavenging effect by donating electrons and hydrogen atoms.

**Antimicrobial activities of ZnO nanocomposite hydrogels**

Antibacterial as well as an antifungal activities of hydrogels are given as Fig. 11 and the zone of inhibition are listed in Table 9. The zones of inhibition of hydrogels with the bacterial species are

observed from the Table and the hydrogels are active against both *E.coli* and *Staphylococcus aureus*. Among the two fungal species ZnO nanocomposite

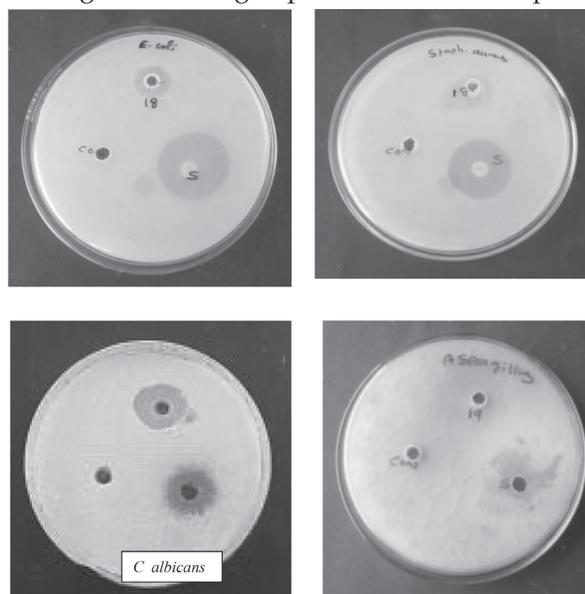


Fig. 11. Antimicrobial and antifungal response of ZnO nanocomposite hydrogel

Table 7. Langmuir adsorption isotherm for the of MB dye on ZnO hydrogels

AMPSNa (mg)	Temperature	Q <sub>m</sub> (mg/g)	b	R <sup>2</sup>
100	303	625.000	0.004	0.973
300	303	588.235	0.005	0.995
500	303	476.190	0.008	0.990
700	303	588.235	0.009	0.943

[pH = 7, Dose 100 mg/20 mL, Contact time = 2880 mins]

Table 8. Freundlich adsorption isotherm for the of MB dye on ZnO hydrogels

AMPSNa (mg)	Temperature (K)	n	K <sub>f</sub> (mg/g)	R <sup>2</sup>
100	303	1.000	2.1247	1.000
300	303	1.000	2.8190	1.000
500	303	1.000	3.5612	1.000
700	303	1.000	4.7676	1.000

[pH =7, Dose 100 mg/20 mL, Contact time = 2880 mins]

Fig. 10. Antioxidant activity of ZnO nanocomposite hydrogel

AMPSNa Content (g.ml <sup>-1</sup> )	Zone of inhibition (mm)			
	<i>Escherichia Coli</i>	<i>Staphylococcus aureus</i>	<i>Candida albicans</i>	<i>Aspergillus niger</i>
0.1	13	12	13	NI
0.3	14	13	14	NI
0.5	15	15	15	NI
0.7	16	16	15	NI
Control	NI	NI	NI	NI
Standard	17	16	15	15

NI: No inhibition.

hydrogels are active against *Candida albicans* only. These antimicrobial observations suggest for the destruction of the bacterial cells which could be due to reactive oxygen species such as singlet oxygen ( $^1O_2$ ), hydroxyl radicals (.OH),  $H_2O_2$  and liberation of  $Zn^{2+}$  resulting in inhibition of bacterial growth. Similarly, spore formation in *Candida albicans* was influenced by ZnO nanocomposite hydrogels. Due to this antimicrobial activity, it can be used in food packaging and in cosmetic materials (Bharathi and Pazhanisamy, 2018).

### CONCLUSION

ZnO nanocomposite hydrogels were synthesized by free-radical polymerization using NTA, AM, AMPSNa monomers, MBA cross-linker and ammonium persulphate initiator in Methanol/water (3:1) medium at 60°C. The ZnO nanoparticles were dispersed in the medium before polymerization reaction to get uniform distribution of nanoparticles in the polymer matrix. In the system, medium solution is acted as capping agent to avoid agglomeration of nanoparticles. FT-IR spectral analysis conformed the incorporation of monomeric units in the polymer chain network and incorporation of ZnO. Thermogravimetric analysis of hydrogels showed double stage decomposition, the first stage is due to scission in amide linkage and second stage is due to breakdown of polymer backbone and network collapse. The SEM and XRD analysis conformed the distribution of ZnO in the polymer network. The results of equilibrium swelling indicated that the equilibrium swelling increased with increasing amount of AMPSNa up to 0.5 g and then decreased. At higher content of AMPSNa, the penetration of water molecules became difficult due to denser network of hydrophilic group. In swelling, the hydrogel follow non-Fickian diffusion mechanism. Methylene blue dye adsorption studies of hydrogels indicates that the removal efficiency increased with increasing amount of AMPSNa, because of more number of anionic groups available to adsorb more cationic dye molecules. Moreover, the removal efficiency was enhanced by changing the dosage level of hydrogel (0.1g AMPSNa) and it is achieved to 82.05%. Adsorption kinetics of hydrogels follow pseudo second order and it reveals the adsorption is chemical adsorption. Investigation of adsorption isotherms on hydrogels, it follow Freundlich isotherm. The results of DPPH radical scavenging

activity showed 50.2% of antioxidant property. These hydrogels were more active against *E. coli* and *Staphylococcus aureus* bacteria rather Fungi. Based on the findings, the ZnO hydrogels can be used as adsorbent for dye removal, scaffold for Tissue engineering antimicrobial agents and antioxidant materials.

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