Research Paper Chemistry

Dye adsorption studies of Poly (N-tert-amylacrylamide -co –Acrylamide / AMPS Na) Nanocomposite Hydrogels

*B.A.Brundha **P.Pazhanisamy

* Department of Chemistry, Sir Theagaraya College, Chennai-600 021, India.

** Department of Chemistry, Sir Theagaraya College, Chennai-600 021, India.

ABSTRACT

Poly (N-tert-amylacrylamide -co –acrylamide / AMPS Na) 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. The Nanocomposites Hydrogels were prepared via in situ polymerization using Organo modified MMT (O-MMT) Nano clay. The content of nano clay plays an important role in swelling rate. The surface morphology indicated that the rod shaped nano particles were distributed in the polymer matrix. The nanocomposite hydrogels showed up to 95% removal efficiency towards Methylene Blue dye adsorption study.

Keywords : Hydrogels, Dye adsorption study, XRD ,SEM analysis

Introduction

Polymeric hydrogels play an important role in the treatment of wastewater. Hydrogels are cross-linked hydrophilic polymers that are swollen in water usually to equilibrium. Hydrogels have considerable applications and have been used extensively in different fields including chemical separation [1], drug delivery [2] and controlled release in agriculture [3]. One of the polymeric hydrogels is super absorbent that are loosely cross-linked hydrophilic polymers that can absorb, swell and retain aqueous solutions up to hundred times of their own weight [4-8]. Because the super absorbent hydrogels have ionic functional groups, they can absorb and trap ionic dyes such as MB from wastewaters [5]. But these polymers have several limitations and always exhibit mechanically weak, brittle properties and low porosity [9]. Thus, many potential applications of conventional polymeric hydrogels have been restricted or abandoned because of their limitations. In past several years some attempts have been done to modify the properties of super absorbents by incorporation of nano or micro particles of inorganic materials such as montmorillonite [10-12], kaolin [13,14], mica [15], sercite [16], bentonite [17] and laponite clay [15] into polymer networks . Incorporation of these mineral powders not only reduces costs but also improves the properties (such as swelling ability, gel strength, mechanical and thermal stability) [17]. In the present study, we aimed to synthesis a novel Nanocomposite Hydrogels based on N-tert-amylacrylamide. Terpolymerization of Hydrophobic and Hydrophilic monomers to make Hydrophobic and hydrophilic interaction followed by the addition of ionic monomer Sodium salt of 2-acrylamido-2-methyl-1-propanesulphonate acid via free radical polymerization using crosslinker (Methylenebisacrylamide) at 60°C.

Experimental

Preparation of Hydrogels

Free-radical crosslinking copolymerization was carried out in methanol /water mixture as the polymerization solvent, at 60^{0}C in the presence of APS as initiator and MBA as crosslinker. Aqueous solution containing NTA (0.5g), AM (0.5g) , 0.045g MBA 0.005 g APS , AMPS Na (0.1,0.2, ,0.30, and 0.40 g) were prepared in methanol water mixture . The content of OMMT nanoclay was also varied. After bubbling nitrogen for 15 min, the contents were placed in thermostatic water bath at 60^{0}C and the polymerization was conducted for 1 day. After the reaction, the hydrogels were cut into pieces 3-4 mm long. The extracted hydrogels were dried in vacuum oven at 50 ^{0}C to constant weight for further use.

Swelling behavior

The swelling characteristics were measured by immersing weighed samples of dry hydrogels in double distilled water. The degree of swelling (Ds%) most commonly described as swelling ratio is expressed as increase in weight / gm of dried hydrogel after keeping in contact with water for selected period of time.

$$(Ds\ \%) = [(W_s\text{-}W_d/W_d)] \times 100 \quad \text{---------- (1)}$$

SEM Analysis

The Micro structure of Hydrogels were studied by Scanning electron Microscopy hydrogels were performed using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification.

XRD Studies

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

Dye adsorption studies

A weighed quantity of dry nanocomposite hydrogel (0.1 g) with different composition was immersed in enough methylene blue (30 ppm) and kept at 34°C. The amount of MB adsorbed was measured spectrophotometrically (λ: 661.6 nm) in periodically taken solution samples and again placed in the same vessel so that the liquid volume was kept constant. The removal efficiency (RE %) of the dye by the hydrogels with different composition was calculated by

$$RE\% = [(C_o\text{-}C/C_o)] \times 100 \quad \text{-------- (2)}$$

where C_o and C are the initial and equilibrium concentration of the MB dye solution, respectively.

Results and Discussion

The schematic representation of the Hydrogel 3synthesis is shown below:

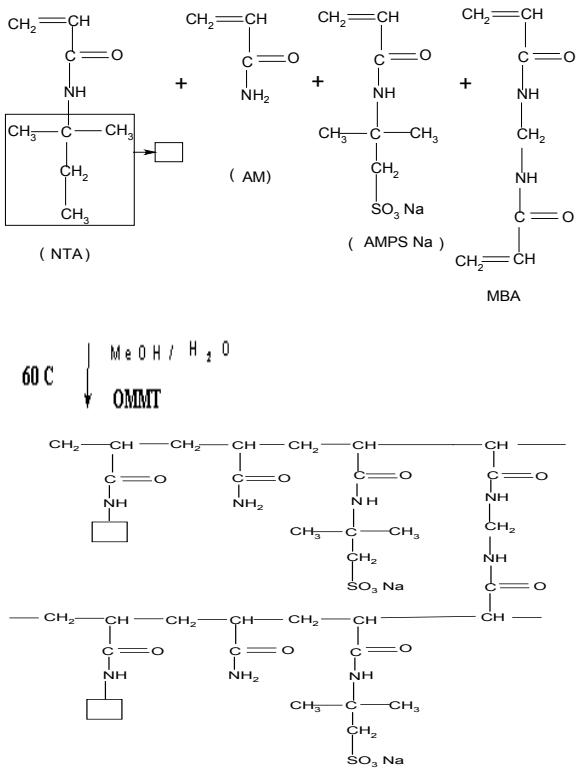

Figure 1. Poly(NTA-AM/AMPSNa) OMMT Nanocomposite Hydrogels

Swelling Behavior Nanocomposite Hydrogels

The degree of swelling of the nanocomposite hydrogels containing 0.3 g of AMPSNa is shown in Figure2. The swelling behavior of hydrogel containing 100mg of nanoclay is higher than the other. The incorporation of nano clay enhances the swelling rate to a particular extent (Figure 2). Therefore the content of nano clay also plays an important role for swelling rate.

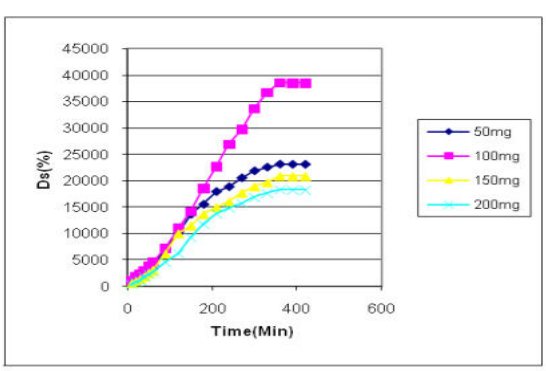

Figure 2. Swelling behavior of Poly(NTA-AM/AMPS-Na-0.3g) OMMT at room Temp.

Surface Morphology and XRD study

The Surface Morphology of Nanocomposite studied by SEM analysis. The SEM image of the nanocomposite Hydrogel was shown in Figure 3. The image indicates the presence of nanocomposite as nano rod shape. These nano rods were distributed uniformly throughout the polymer matrix. The XRD study indicates that all the nanocomposite hydrogels show more amorphous in state and less crystallinity.

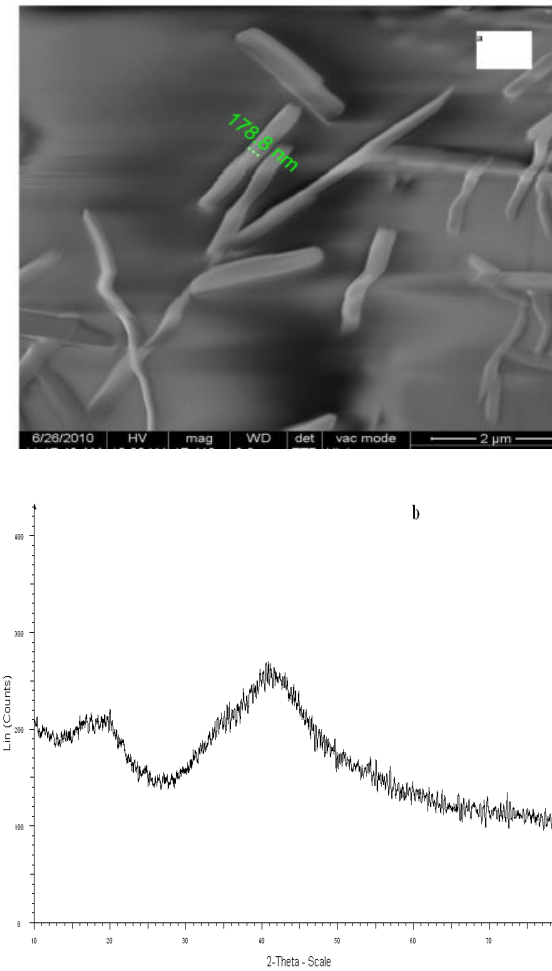

Figure 3.SEM (a)XRD(b) image of Hydrogel containing 0.3g of AMPS Na

Dye adsorption study

The MB dye adsorption studies of all hydrogels are shown in Figure 4. Almost all Hydrogels showed good removal efficiency towards methylene blue dye. When the clay content was 150 mg the RE(%) is reached quickly than the other hydrogels. The dye removal efficiency is reached about 95% from 85 % by varying the content of nano clay in the hydrogel matrix.

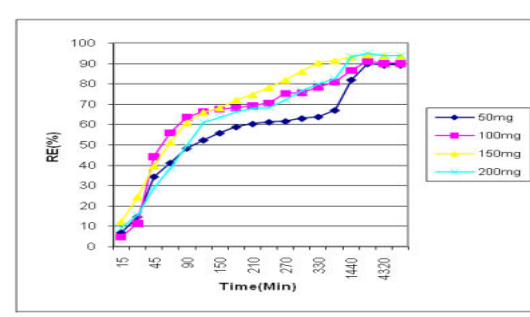

Figure 4.MB dye adsorption of Nanocomposite Hydrogels

Kinetic study (swelling Mechanism)

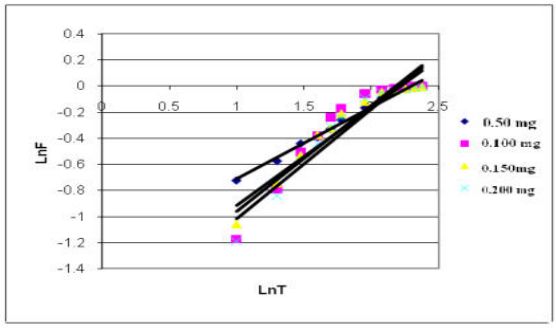

Figure 5. Kinetic study of Nanocomposite Hydrogels

$F_{swp} = Kt^n$ ---------- (3)

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

The Kinetic study of all hydrogels are shown in Figure5. The plots of LnF against LnT gives a straight line whose slope is "n", which is equal to 0.55, 0.81,0.75 and 0.83. These values of " n" is in the range between 0.50< n<1.00 which indicates that the diffusion is non-Fickian. In the diffusion mechanism, diffusion and relaxation are said to be isochronal effective.

Acknowledgment

The author Dr.P.Pazhanisamy thank the UGC, New Delhi, for financial support (MRP-2008, F.No.34-337/2008)

REFERENCES

[1] Kasgoz, H.; Ozgumus, S.; Orbay, M., Modified polyacrylamide hydrogels and their application in removal of heavy metal ions . Polymer, 2003, 44, 1785. | [2] Liu, D.; Shiu, M.; Chen, C.; Yang, Y.; Ho, H. , Release characteristics of lidocaine from local implant of polyanionic and polycationic hydrogels . J. Control Release, 2007, 118, 333. | | [3] Bajpai, A. K.; Giri, A., Synthesis of porous poly(acrylamide) hydrogels using calcium carbonate and its application for slow release of potassium nitrate . Reactive and Functional Polymers, 2002, 53, 125. | [4]Li, P.; Kim, N.; Heo, S. B.; Lee, J. H., Novel PAAm/Laponite clay nanocomposite hydrogels with improved cationic dye adsorption behavior. Composites Part-B, 2008, 39, 756. | [5] Solpan, D.; Duran, S.; Torun, M., Removal of cationic dyes by poly(acrylamide-co-acrylic acid) hydrogels in aqueous solutions. Radiat. Phys. Chem. 2008, 77, 447. | [6] Buchholz, F. In Modern Superabsorbent Polymer Technology, F. L. Buchholz, T. Graham, Wiley-VCH: Network, 1998. | | [7] Yi, J. Z.; Zhang, L. M. , Removal of methylene blue dye from wastewater by Adsorption onto semi-inpenetrating polymer network Hydrogels composed of acrylamide and acrylic acid Copolymer and polyvinyl alcohol. Biores. Technol. 2008, 99, 2182. | [8] Kabiri, K.; Zohuriaan-mehr, M. J. , Superabsorbent hydrogel composites. Polym. Adv. Technol. 2003, 14, 438. | [9] Haraguchi, K.; Takehisa, T ., Nanocomposite Hydrogels: A Unique Organic–Inorganic Network Structure with Extraordinary Mechanical, Optical, and Swelling/De-swelling Properties. Adv. Mater. 2002, 14, 1120. | [10] Lee, W.; Yang, L ., Superabsorbent polymeric materials. XII. Effect of montmorillonite on water absorbency for poly(sodium acrylate) and montmorillonite nanocomposite superabsorbents . J. Appl. Polym. Sci. 2004, 92, 3422. | [11] Luo, W.; Zhang, W.; Chen, P.; Fang, Y ., Synthesis and properties of starch grafted poly[acrylamide-co-(acrylic acid)]/montmorillonite nanosuperabsorbent via γ-ray irradiation technique, J. Appl. Polym. Sci. 2005, 96, 1341. | [12] Lee, W.; Chen, Y. , Preparation of reactive mineral powders used for poly(sodium acrylate) composite superabsorbents . J. Appl. Polym. Sci. 2005, 97, 855. | [13] Wan, T.; Wang, X.; Yuan, Y.; He, W. , Preparation of a kaolinite–poly(acrylic acid acrylamide) water superabsorbent by photopolymerization .J. Appl. Polym. Sci. 2006, 102, 2875. | [14] Wu, J.; Wei, Y.; Lin, S. , Study on starch-graft-acrylamide/mineral powder superabsorbent composite. Polymer, 2003, 44, 6513. | [15] Lin, J.; Wu, J.; Yang, Z.; Pu, M. , Synthesis and Properties of Poly(acrylic acid)/Mica Superabsorbent Nanocomposite. Macromol. Rapid Commun. 2001, 22, 422. | [16] Wu, J.; Lin, J.; Zhou, M., Synthesis and properties of starch-graft-polyacrylamide/clay superabsorbent composite. Macromol. Rapid Commun. 2000, 21, 1032. | [17] Tao, W.; Xiaoqing, W.; Yi, Y.; Wenqiong, H. , Preparation of bentonite–poly[(acrylic acid)-acrylamide] water superabsorbent by photopolymerization. Polym. Int. 2006, 55, 1413. |