

Adsorption capacity of poly(N-tert-amylacrylamide-co-Acrylamide/Ionic Liquid) Fe₃O₄ Nanocomposite Hydrogels in Methylene Blue solution

P. Pazhanisamy^{1*}, Indra Sulania², E.Kayalvizhy³, T.Gomathi⁴, B.Uma⁵

¹*Department of Chemistry, Sir Theagaraya College (Affiliated to University of Madras), Chennai-600021, India.*

²*Material Science, Inter-University Acceleration Centre, New Delhi-110067, India.*

³*Department of Chemistry, PSGR Krishnammal College for Women, Coimbatore-641004, India*

⁴*Department of Chemistry, DKM College for Women, Vellore-632115, Tamil Nadu, India.*

⁵*Department of Zoology, Bharathi Women's College. Chennai-600108, India*

E-mail: p_pazhanisamy@yahoo.com

ABSTRACT

Poly (N-tert-amyl acrylamide-co-Acrylamide/AMPS IL) Fe₃O₄ Nano composite Hydrogels were synthesized by free-radical polymerization. About 0.5 g of N-tert-amyl acrylamide, 0.5 g of Acrylamide and 0.5g of AMPSIL monomers were dissolved in 3:1 Methanol/ water medium with MBA crosslinker and APS as initiator maintained at 60°C for 6hr. The synthesized hydrogels washed with the same solvent to remove the unreacted monomers. Fe₃O₄ NPs were intercalated via in situ polymerization. The synthesized Nanocomposite Hydrogels were characterized by FT-IR, SEM, TGA and XRD analysis. SEM analysis showed spherical like Fe₃O₄ NPs are present in the matrix. The Hydrogels are subjected to swelling in the MB dye solution to study the swelling capacity.

KEYWORDS:

Ionic Liquids, Ferrate NPs, Hydrogels, XRD analysis, swelling behavior

INTRODUCTION

Hydrogels are three-dimensional polymeric network in which there are a lot of hydrophilic groups, those swell quickly by imbibing a large amount of water or de-swell in response to changes in their external environment [1]. They have found wide application in bio-medical materials as well as drug control and release. 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 [2]. Hydrogels exhibiting pH sensitive swelling behavior have been usually swollen from ionic network that 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 [3-6].

Fe₃O₄ known as magnetite is one of the oxides of iron which plays a major role in various areas of chemistry, material sciences, physics and medical sciences. Fe₃O₄ crystallizes in mixed oxidation state iron (Fe³⁺ and Fe²⁺) inverse cubic spinel structure. Fe₃O₄ can be used in magnetic resonance imaging, in drug delivery systems, as sorbent for heavy metal, as antibacterial agents and as catalyst. SHI irradiation of polymer materials, poly (N-isopropylacrylamide) offers controlled generation of precise microstructures [7-12]. The aim of this work is to prepare a series of poly(N-tert-amylacrylamide-co-acrylamide/AMPS-IL) Fe₃O₄ Hydrogels, based on NTA, acrylamide and AMPS-IL and to study the swelling behavior of Hydrogels in Methylene Blue dye solution.

EXPERIMENTAL

Preparation of Fe₃O₄ NPs

About 6.1 g of FeCl₃ and 4.2 g of FeSO₄ were in 100 ml of water and 25 ml of 6.5 M sodium hydroxide was added dropwise till a black precipitate is formed. The content was heated at 80 °C for 4 hours and the NPs separated by filtration on Whatman filter paper and it dried at 200 °C [13]



Preparation of Fe₃O₄ nanocomposite hydrogels

Exactly, 0.5 g of NTA and 0.5 acrylamide and 0.1/0.3/ 0.5g of AMPS – IL dissolved in 3:1 methanol / water and the nitrogen is purged for 30 minutes. 0.01g of KPS initiator and 0.01 g of MBA crosslinker (methylene bisacrylamide) were taken in to polymerization tube at 60 °C in temperature water bath. For about 20 hours. The resulting hydrogels are washed with methanol to remove the unreacted monomers. During the polymerization the Fe₃O₄ nanoparticles were added in-situ (during the reaction). The synthesized hydrogels were dried at 50 °C to remove adsorbed water to attain dryness.

Swelling behavior

The swelling capacity was measured by immersing weighed samples of dry nanocomposite hydrogels 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 degree of swelling (Ds) or percentage of swelling (%S) most described as swelling ratio is expressed as increase in weight / gm of dried nanocomposite hydrogel after keeping in contact with dye solution for period of time.

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

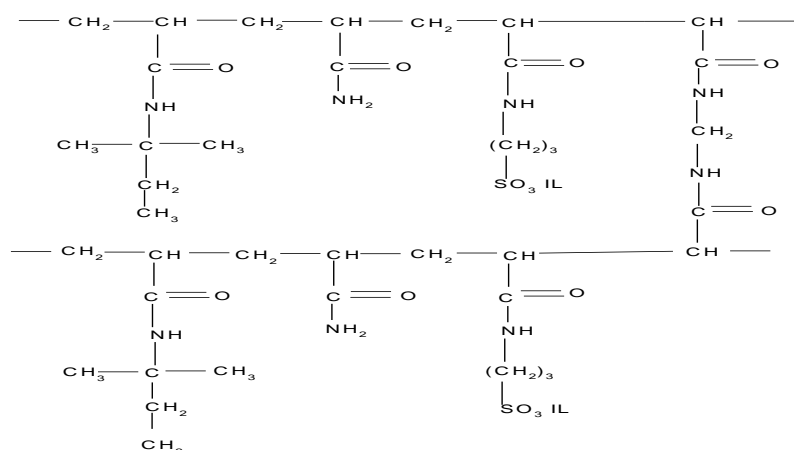
Ds= degree of Swelling

Characterization

The FTIR analysis of the Nanocomposite hydrogel was carried out by FI-IR spectroscopy. Scanning Electron Microscopy of hydrogels were performed using Hitachi, model-JSM-5000 imaging mode at 30KV with varying levels of magnification. The catalytic reduction of MB dye was studied by UV-visible spectrophotometer.

RESULTS AND DISCUSSION

The schematic representation of Hydrogel preparation is shown as scheme.



IL: triethylamine

Scheme. Synthesis of poly (N-tert-amylacrylamide-co-Acrylamide/AMPS IL) Fe₃O₄ Nanocomposite Hydrogels

FT-IR spectral analysis

The FTIR spectrum of the ferrate nanocomposite Hydrogel is shown in Figure 1. The peak absorbed at 3421 cm^{-1} of N-H amide of NTA, AM, and AMPS-IL monomeric units, 2916 cm^{-1} of C-H stretching of CH_2 , 2360 cm^{-1} C-H stretching of CH_3 , 1629 cm^{-1} due to C=O of NTA, AM units, 1122 cm^{-1} for S=O, 617 cm^{-1} due to C-S stretching and 499 cm^{-1} due to Fe-O of ferrate NPs.

SEM with EDAX analysis

SEM image (Fig. 2) showed that the spherical shaped Fe_3O_4 NPs were intercalated in the polymer network and also conformed by the EDAX spectrum.

XRD analysis

The Figure 3. shows the XRD pattern of the Nanocomposite hydrogel, a broad peak indicates the amorphous nature of the hydrogel. The more amorphous the more will be the swelling capacity as showed in the plot (Fig.5). There are three peaks at 2θ values 18, 30 and 42. The Fe_3O_4 peaks are overlapped with the peaks absorbed.

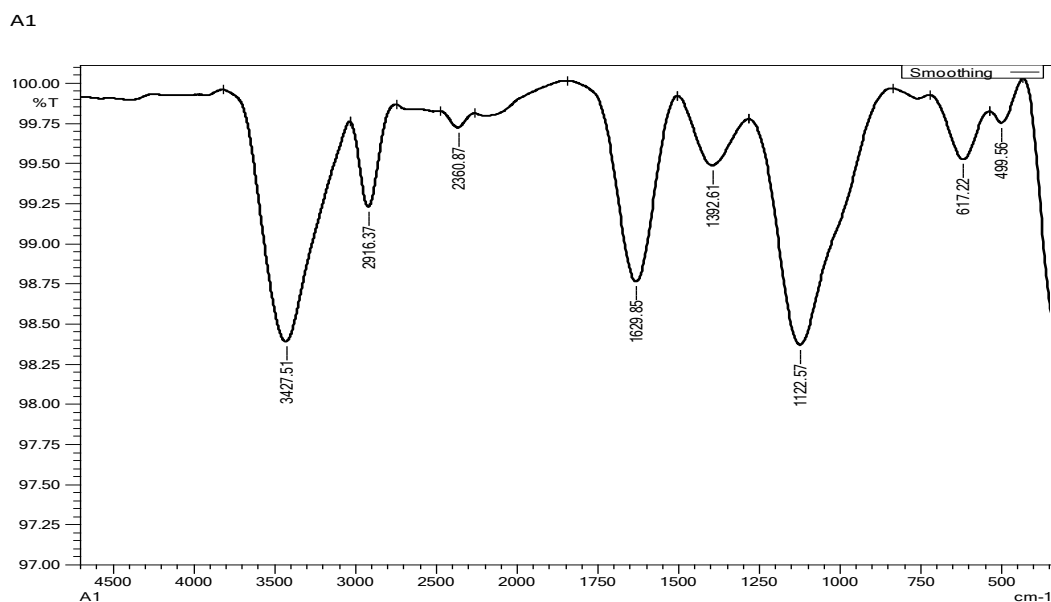


Figure 1. FTIR spectrum of poly(N-tert-amylacrylamide-co-Acrylamide/AMPS IL) Fe_3O_4 Nanocomposite Hydrogels

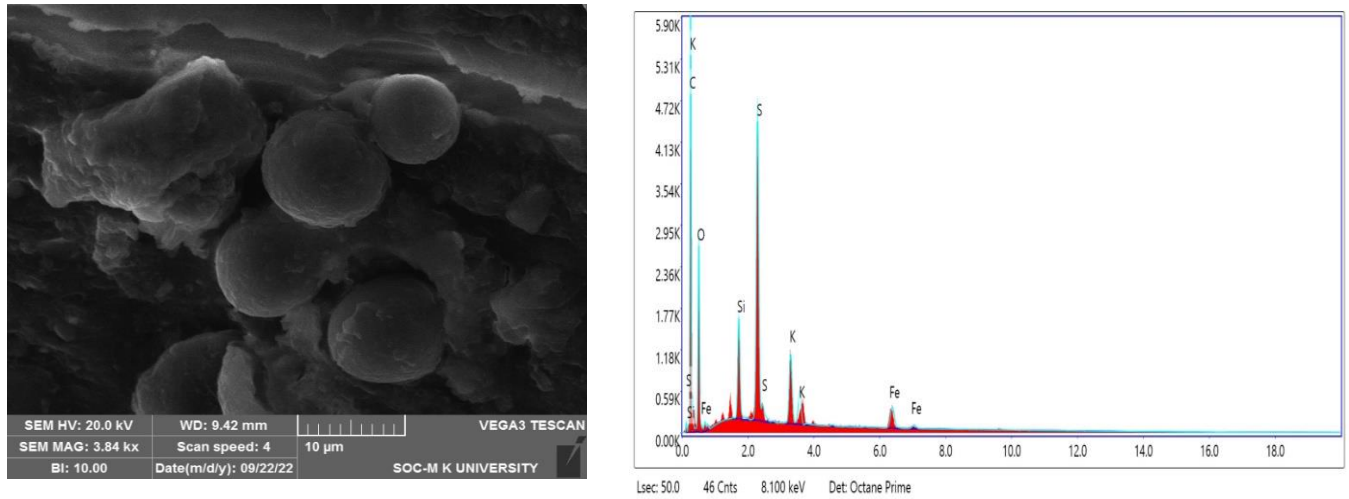


Figure 2. SEM/EDAX of poly (N-tart-amyl acrylamide-co-Acrylamide/AMPS IL) Fe₃O₄ Nano composite Hydrogels

A1 (Coupled TwoTheta/Theta)

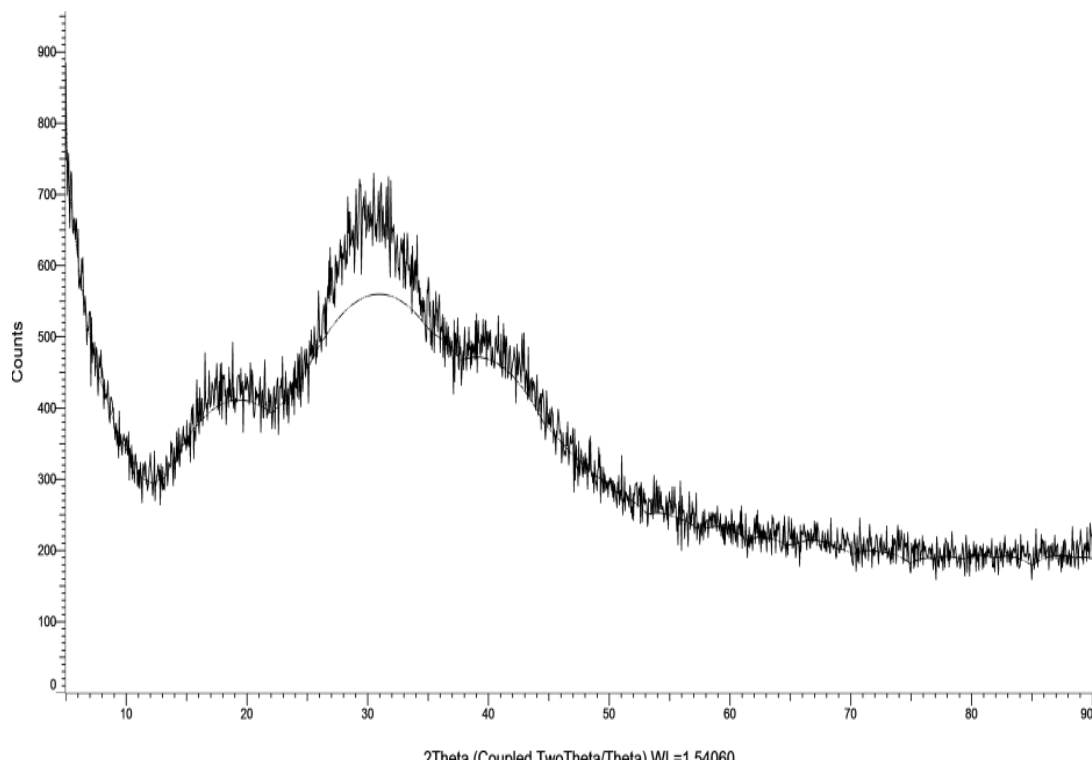


Figure 3. XRD pattern of Nanocomposite Hydrogel

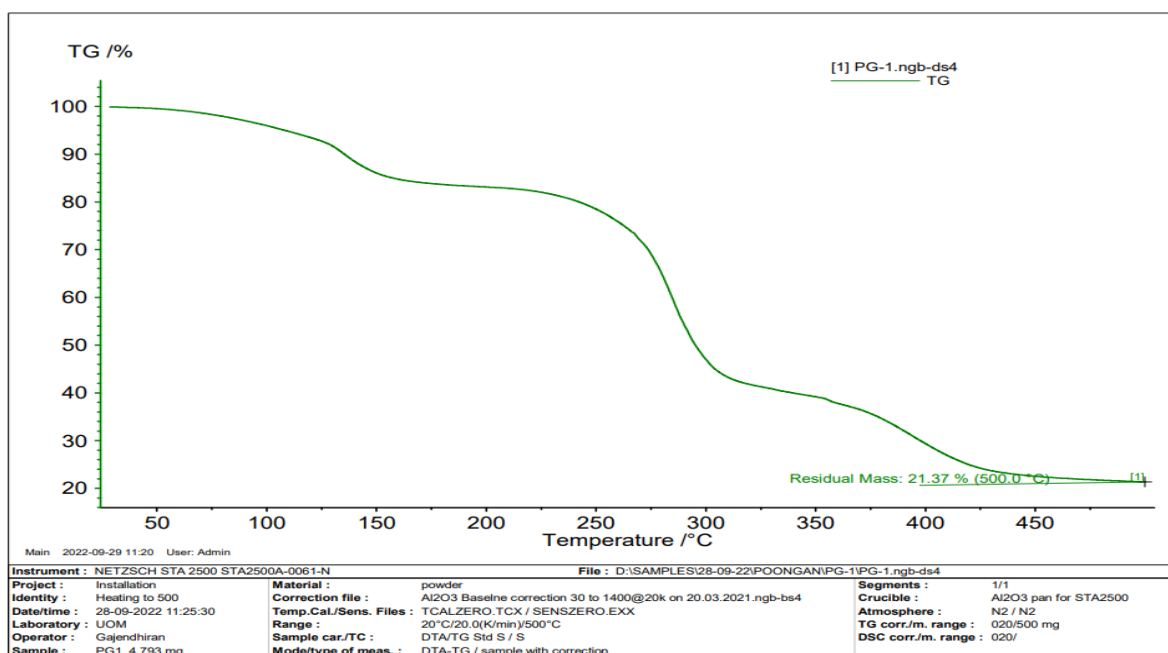


Figure 4.TGA curve of Nanocomposite Hydrogel

Thermogravimetric analysis

The TGA analysis showed initial weight loss (10%) is due to moisture absorbed by the Hydrogel. It undergoes double stage decomposition, the first stage due to scission of amide linkage (38%) and second stage (20%) due to breakdown of polymer network. The residual mass (21%) indicates the charred content of the polymer and Ferrate NPs

Swelling behavior

Swelling capacity of the nanocomposite hydrogel is shown in Figure 5. The degree of swelling increased with increasing amount of AMPS-IL content from 0.1g to 0.5g. The swelling capacity increases with respect to time and reaches the maximum capacity from 200 g to 44500 g(in % with respect to weight of hydrogel). Due to the presence of hydrophilic group the expansion of network develops after 400 mins. Almost 98% of MB dye adsorbed by the hydrogel[12,13].

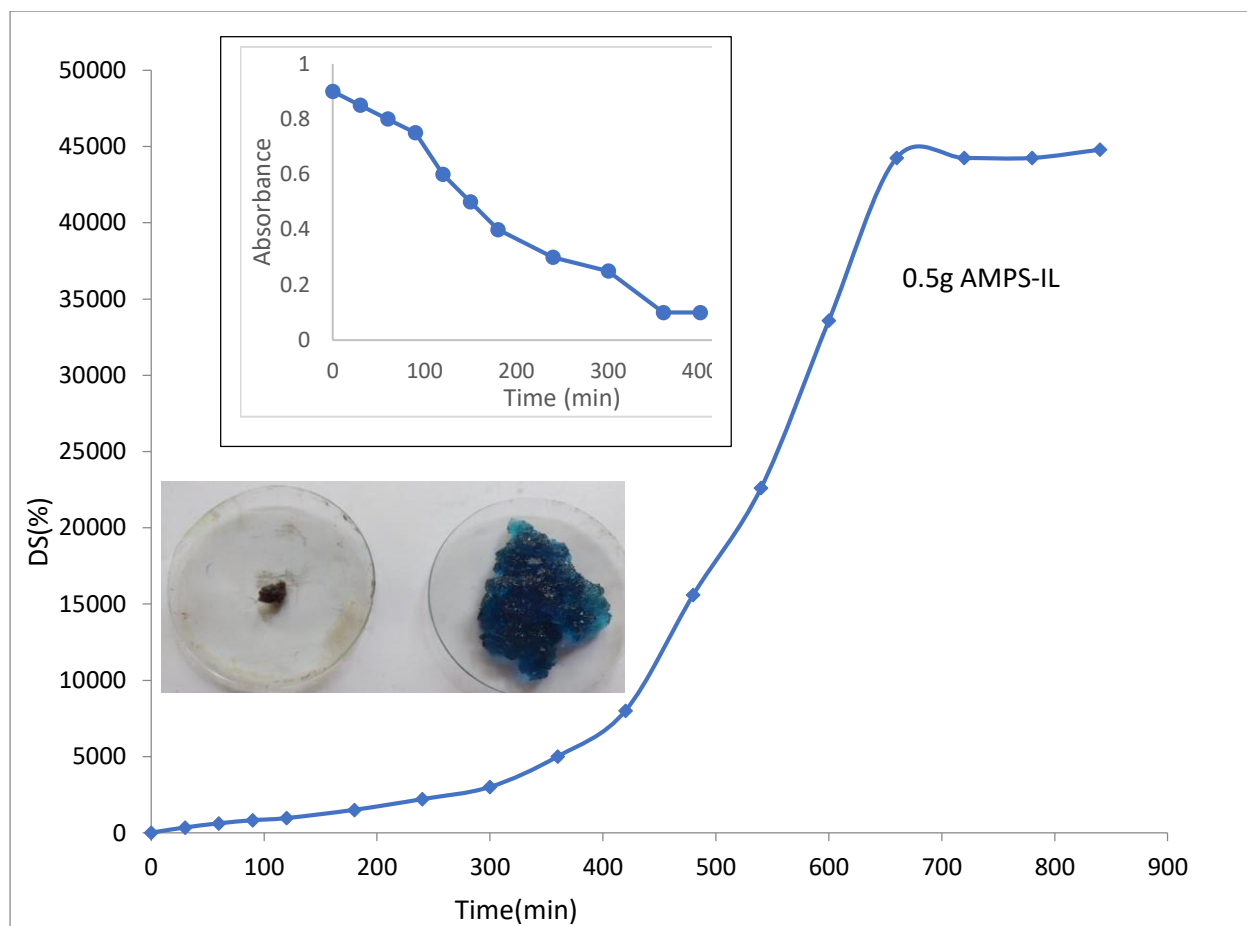


Figure 5. Swelling behavior of Nanocomposite Hydrogels

CONCLUSION

The Fe_3O_4 Nanocomposite Hydrogels were synthesized by free-radical polymerization and the NPs intercalated via in situ polymerization. FTIR analysis confirmed the presence of all functional groups in the polymer network. SEM/EDAX analysis indicates the spherical shaped NPs incorporated uniformly throughout the network. TGA analysis showed double stage decomposition, the first stage due to scission in amide linkage and the second stage due to breakdown of the polymer network. Swelling capacity reveals that the nanocomposite hydrogels removed 98% of MB dye from the solution.

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