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Article

Poly (N-tert-amylacrylamide -co- Acrylamide/ Sodium acrylate) Fe_3O_4 Nanocomposite Hydrogels as polymer catalyst for the reduction of Methylene Blue Dye

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Abstract

Fe_3O_4 Nanocomposite Hydrogels were prepared by free radical polymerization using N-tert-amyl acrylamide , Acrylamide and Sodium acrylate monomers at 60°C. Fe_3O_4 NPs was intercalated via in situ method. The synthesized nanocomposite Hydrogels conformed by FT-IR spectroscopy. Surface morphology of the nanocomposite hydrogels indicated the ferrate nanoparticles are intercalated uniformly throughout the polymer matrix. The XRD pattern of the hydrogel showed the presence of nanoparticles in the matrix with certain crystallinity nature. UV-visible absorption studies reveal the catalytic activity of Methylene Blue dye molecules in the aqueous medium by the Nanocomposite hydrogels.

Keywords:

1. 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 [2-8]. 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[9-12].

Fe_3O_4 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. Fe_3O_4 crystallizes in mixed oxidation state iron (Fe^{3+} and Fe^{2+}) inverse cubic spinel structure . Fe_3O_4 can be used in magnetic resonance imaging, in drug delivery systems, as sorbent for heavy metal, as antibacterial agents, as catalyst, as electrochemical biosensors, as shielding material in electromagnetic interference and for energy harvesting . It has been reported that separation between valence band of Fe(4s) and O(2p) in Fe_3O_4 is 4–6 eV (309-206 nm). The aim of this work is to prepare a series of poly(N-tert-amylacrylamide-co-acrylamide/AcNa) Fe_3O_4 Hydrogels, based on NTA ,acrylamide and sodium acrylate and to study the swelling behavior of Hydrogels.Hydrogels were prepared by free-radical crosslinking polymerization of NTA,AM and AcNa in the presence of N,N'-methylenebis acrylamide(MBA) as the cross linker

2. Material and Method

2.1 Materials

Acrylamide (AM, Merck) was crystallized from acetone/ethanol mixture. Acrylic acid was distilled twice by vacuum distillstion at 63 ^{0}C/25 mmHg and stored in a refrigerator. Sodium acrylate was prepared by neutralizing the acrylic acid using sodium hydroxide. The crosslinker N,N'-methylene-bis-acrylamide (MBA) was used as received. Acrylonitrile was first washed with 5% NaOH solution in water to remove the inhibitor and then with 3% Ortho phosphoric acid solution in water to remove basic impurities. Then the Acrylonitrile was washed with double distilled water and dried over anhydrous $CaCl_2$. The acrylonitrile was then distilled in an atmosphere of Nitrogen and reduced pressure. It was then collected in a clean dry amber colored bottle and kept in the refrigerator at 5°C

2.2 Preparation of N-tert-amylacrylamide (NTA)

The monomer N-tert-amylacrylamide(NTA) was prepared by the reaction of t-amyl alcohol with acrylonitrile.N-tert-amylacrylamide was recrystallised in warm benzene.The white crystals have a mp.91^{0}C(Lit.91-92^{0}C)and the yield was 87%[13].

2.3 Synthesis of Fe_3O_4 nanoparticles

A solution was prepared by suspending 16.25 g $FeCl_3.6H_2O$ in 100 mL distilled water. Similarly, another solution was prepared by suspending 6.35 g $FeCl_2.4H_2O$ in 100 mL distilled water. Both solutions were mixed in a glass beaker. Then, NH_4OH was added dropwise to mixture formed by mixing of first two solutions of $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ under continuous stirring at 70 °C till pH 10. The resultant precipitate was filtered, washed, and dried.

2.4 Preparation of Poly (N-tert-amylacrylamide–co-acrylamide/Sodium acrylate) Fe_3O_4 Hydrogel

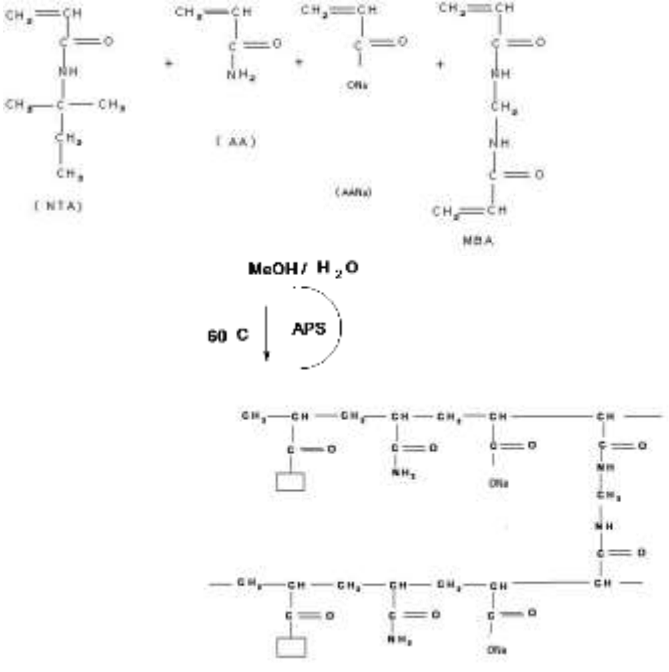
Free-radical crosslinking copolymerization was carried out in methanol /water mixture as the polymerization solvent, at 60^{0}C in the presence of AIBN as initiator and MBA as crosslinker.Aqueous solution containing NTA (0.5g), AM (0.5g),MBA (0.050g), APS (0.050g), AcNa (0.0, 0.1, 0.2, and 0.3g), were prepared in methanol/water mixture. The Fe_3O_4 NPs 50 mg were added during the polymerization by in situ . After bubbling nitrogen for 30 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 resulting Hydrogels were cut into pieces of 3-4mm long. . The extracted Hydrogels were dried in vacuum oven at 50^{0}C to constant weight for further use.

2.5 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.

3. Results and Discussion

The synthesis of hydrogel was shown as scheme



Scheme : Poly (N-tert-amylacrylamide-co-acrylamide / AcNa) Fe_3O_4 Hydrogel

3.1 FT-IR spectroscopy

The synthesized nanocomposite hydrogel was conformed by FT-IR spectroscopy and the characteristic values of functional groups are shown in Table 1.

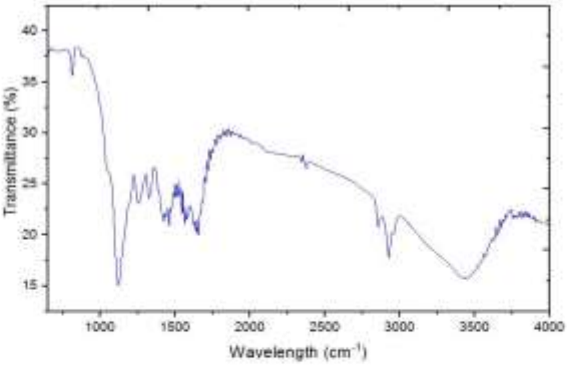
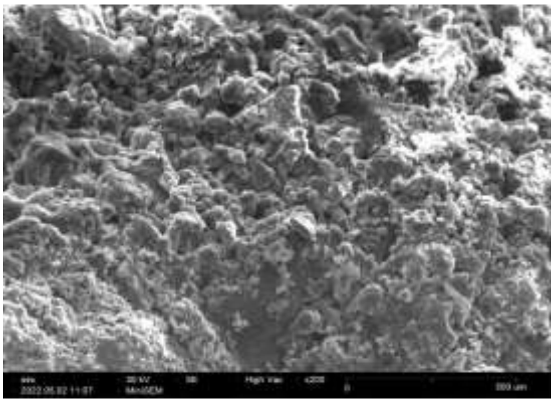


Figure 1. FT-IR spectrum of Poly (N-tert-amylacrylamide-co-acrylamide/AcNa) Fe_3O_4 Hydrogel

Table 1. Interpretation of IR spectra of Fe_3O_4 Nanocomposite Hydrogel

3489 cm^{-1}	N-H of NTA and N-H stretching of AM
2923 cm^{-1}	Methyl C-H symmetrical stretching
1671 & 1735 cm^{-1}	C=O of NTA and AM
1110 cm^{-1}	C-O stretching
1266 cm^{-1}	C-C stretching
1392 cm^{-1}	COO group of AcNa
1418 cm^{-1}	C-N stretching of amide
719 cm-1	Fe-O stretching of Fe_3O_4

SEM analysis of Poly (N-tert-amylacrylamide-co-acrylamide/AcNa) Fe_3O_4 Hydrogel



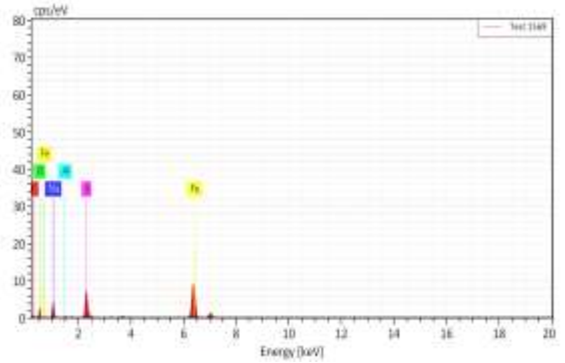


Figure 2. SEM image with EDAX of Ferrate nanocomposite hydrogel

SEM/EDAX micro analysis was employed to determine the constitution of the ferrate nanoparticles dispersed in the hydrogel matrix. The EDAX spectrum, Figure 2 shows well resolved peaks for Iron, Carbon, Oxygen and Sodium which are the elements present in the ferrate nanocomposite hydrogel. The SEM image showed the Fe_3O_4 NPs were intercalated uniformly throughout the polymer matrix.

3.2 XRD Pattern of the Hydrogel

XRD pattern of the hydrogel was shown in Figure 3, the peak at 2ϴ value 20 having broad peak which indicate amorphous in nature . The peaks at 20.5, 30.0, 50.0, 55.5 and 88.2 2ϴ are conforms the presence of Fe_3O_4 NPs in the polymer matrix.

3.3 Catalytic reduction of MB dye

The catalytic reduction of methylene Blue dye molecules in aqueous solution by hydrogel is shown in Figure 4. About 20 mL of 50 ppm MB solution was taken in a beaker and few drops of sodium borohydride along with the 0.1g of nanocomposite hydrogel was added into the beaker. After 30 mins the dye solution are taken out to UV-visible absorption study. The absorption peaks shows the complete degradation of MB dye molecules in aqueous solution as shown in the Figure 5 [14] [5].

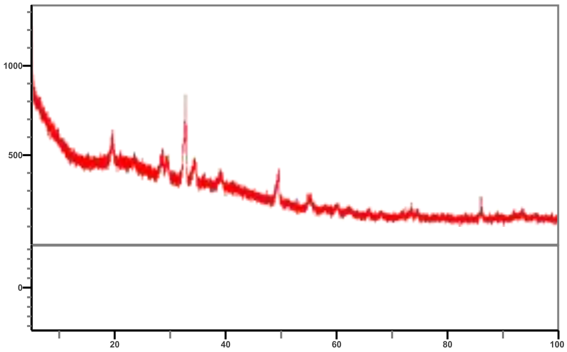


Figure 3. XRD pattern of Poly (N-tert-amylacrylamide-co-acrylamide/AcNa) Fe_3O_4 Hydrogel

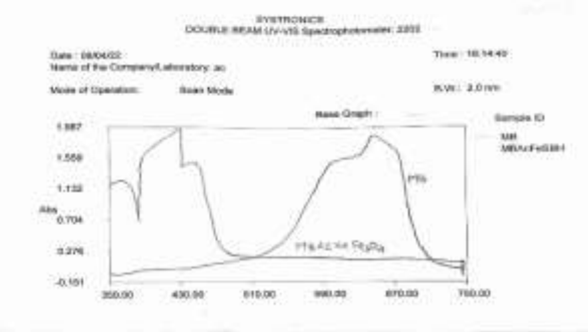


Figure 4. UV-visible absorption spectrum of Nanocomposite Hydrogel

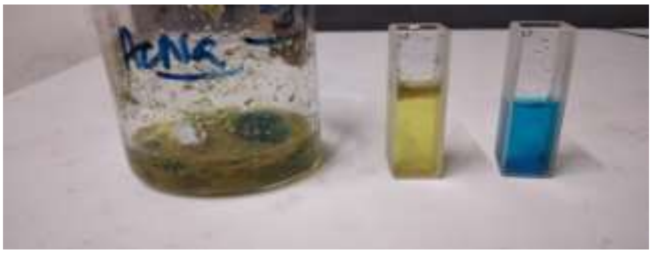


Figure 5. Complete degradation of MB dye by Fe_3O_4 Nanocomposite Hydrogel

4. Conclusions

Poly(N-tert-amylacrylamide-co-acrylamide/AcNa) Fe_3O_4 Hydrogel was synthesized by Free-radical polymerization. The synthesized hydrogels were characterized by FT-IR spectroscopy, SEM analysis, XRD analysis . The SEM /EDAX analysis showed the uniform distribution of nanoparticles in the polymer matrix. XRD pattern shows the amorphous nature of the hydrogel. The complete degradation of MB dye using nanocomposite hydrogel was conformed by UV-visible absorption study..

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References

[1] Bell C.L., Peppas N.A., Biomedical membranes from hydrogels and interpolymer complexes, Adv. Polym. Sci. ,1995, 122, 125–175.
[2] Frank S., Lauterbur P. C Nature,1993, 363, 334–336.
[3] Peppas N. A., Colombo P, Journal of Controlled Release,1997,45, 35–40.
[4] Tanaka T , Phase transitions of gels in'Polyelectrolyte gels: Properties, preparation and applications' (eds.: Harland R. S., Prud'homme R. K.) American Chemical Society, Washington,1992, 480, 1–21.
[5] Suzuki A., Ishii T., Maruyama Y, Journal of Applied Physics,1996, 80, 131– 136.
[6] Khare A. R., Peppas N. K. Biomaterials,1995, 16,559–567.
[7] Zhong X., Wang Y-X., Wang S-CChemical Engineering Science,1996, 51,3235–3239.
[8] Peppas N. A., Huang Y, PharmaceuticalResearch,2002, 19, 578–587.
[9] Brannon-Peppas L., Peppas N. A, ChemicalEngineering Science,1991, 46, 715–722 .
[10] Peppas N. A., Bures P., Leobandung W.,Ichikawa H European Journal of Pharmaceutics and Biopharmaceutics,2000, 50, 27–46.
[11] Brundha B.A and Pazhanisamy P*International Journal of PharmTech/ChemTech Research,2010,2(4), 2192-2197.
[12] Anbarasan S, Brundha B.A andPazhanisamy P*,RasayanJournalofChemistry,2010(3),571-575.
[13] Pazhanisamy P and Reddy B.S.R.,eXPRESS Polymer Letters, 2007,1(11), 740– 747
[14] Ni C and X-X. Zhu , Eur . Polym. J.,2004, 40, 1075-1080.
[15] Youdao Ling , and Mangeng Lu., e-Polymers ,2008, 40, 1-14