Research Paper Chemistry

Synthesis and Dye Adsorption Studies of Poly (N-tert -butylacrylamide-co-acrylamide/ Maleic acid) Ferrogel

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ABSTRACT

The present study describes the preparation of magnetic field sensitive Ferrogel is a two step process. The first step is the synthesis of the poly(N-tert -butylacrylamide-co-acrylamide/Maleic acid), denoted as poly(NTB -co-AM/MA). In the second step magnetic Fe3O4 particle was formed in the hydrogel via co-precipitation of Fe2+ and Fe3+ ions in alkaline medium at 70°C. Ferrogel adsorbs all type of dyes. Both the concentration of magnetic particles and cross linking density of the ferrogel play an essential role in the adsorption. The adsorption rates for the dye stuffs are slow during first two minutes and it increases after 10 to 15 minutes.

KEYWORDS

Introduction

Ferrogel is defined as two or multi component system consisting of a three dimensional network of polymer chain and filled with water in the space between macro molecules. The ability to absorb aqueous solution without losing its shape and mechanical strength depends on the properties of the polymer, nature and the density of the network and accordingly they can absorb and retain various amount of water. Chains are connected by electrostatic force of hydrogen bond, hydrophobic interaction and such gels are not permanent. They can be converted into polymer by heating [1-4].

Disperse dyes are commonly used in textile products such as colouring polyester, nylon, colouring cellulose acetate. As some disperse dyes have allergenous potential to human skin and even act as a carcinogen there is a possible threat to human health [5]. The EU safety directive 92/59/EEC restricted the usage of forty such hazardous dyes in a stringent manner. Thus the adsorption of these hazardous dyes becomes imperative. The dye adsorption study was carried out using Crystal Violet and Solvent yellow – 2. The United States Food and Drug Administration (USFDA) reported the mutagenic effects of crystal violet in rodents. The higher dosage of crystal violet is linked to bladder cancer in human. The Azo derivative like Solvent yellow- 2 is considered to be carcinogenic and genotoxic [6]. Thus these two dyes are recognised for high human health hazards. Nowadays there are serious concerns for the restricted usage of these dyes all over the world. The present study aimed at the synthesis of N-tert-butylacrylamide based Ferrogel since it serves as an alternative adsorbent for the removal of dyes.

Experimental

The Poly(NTB-co-AM/MA) Ferrogel was prepared by the free radical cross linking copolymerisation of NTB , AM and MA in 3:1 mixture of methanol water. Ammonium per sulphate used as redox initiator system. The N-tert -butylacrylamide - 0.5g, acrylamide – 0.5g, Maleic acid 0.1-0.3 g, ammonium per sulphate 0.05g were dissolved in 20 mL of 3:1 mixture of methanol-water. The solution was purged with Nitrogen for 30 minutes, after the addition of methylenebisacrylamide (MBA)(0.045g) as crosslinker. The reaction was carried out in the polymerization tube and it was immersed in the thermostat for one day at 60°C. Upon completion of the reaction the hydrogel was removed from the polymerization tube and immersed in the large excess of deionised water at room temperature for at least 72 hours. The water was replaced 3-4 times every day to remove the unreacted materials.

After cleaning procedure the swollen gel was transferred in to an aqueous solution containing $FeCl_3.6H_2O$ (0.2M in 20mL) and $FeSO_4.7H_2O$ (0.1M in 20 mL) at room temperature for 10 days. After adsorption procedure, the metal ion loaded hydrogel was treated with the mixture of KOH (0.5M in 50mL) and KNO_3 (2.0M in 50mL) at 70°C for an hour, which resulted in the precipitation of the corresponding oxide Fe_3O_4. The obtained ferrogel was finally neutralised with deionised water by repeated washing. The chemical reaction of magnetite precipitation is considered to be as follows.

$$Fe^{2+} + Fe^{3+} + 8OH^- \xrightarrow{KNO_3} Fe_3O_4 + 4\,H_2O$$

SEM Analysis

The surface morphology of the freeze-dried Ferrogel was studied by scanning electron Microscopy. It was performed using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification. To prepare samples for SEM, the swollen Ferrogel was freeze-dried and then sputter coated with gold.

Results and Discussion

The schematic representation of hydrogel preparation is given as follows:

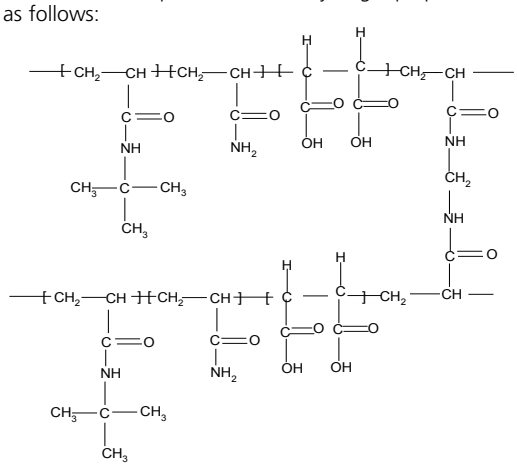

Figure1.Schematic representation of Poly (NTB-co-AM/ MA) Ferrogel

IR Spectral Characterization of Ferrogel

FTIR measurement (Perkin Elmer spectrometer) in the range of 500-2000 cm-1. Before the measurement the originally swollen hydrogel were freeze dried in a dryer for two days for complete removal of water.

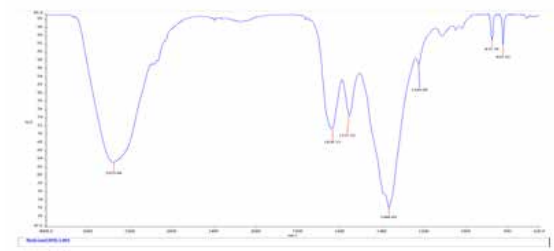

Figure 2. FTIR spectrum of Poly (NTB-co-AM/MA) Ferrogel

The IR analysis of the hydrogel (Fig.2) showed the presence of peaks corresponding to the functional group of monomeric unit present in the copolymeric hydrogel chain. The peaks were observed at ~1227 and ~1336 cm^{-1} [$-C(CH_3)_3$] groups of NTB and at 1636 cm^{-1} amide-I of both NTB and AM) and 1555 cm^{-1} corresponding to $C=ONH_2$ in acrylamide unit. A broad spectrum peak corresponding to NH stretching of acrylamide was observed at 3353 cm^{-1}. There was only new band at 875 cm^{-1} specific for stretching vibration of Fe-O group from magnetic particles which confirmed the presence of magnetic particles inside the hydrogel and is therefore termed as Ferrogel.

SEM analysis

SEM image of Poly (NTB-co-AM/MA) Ferrogel is given in Figure 3.The image indicate the Ferrogel has beads like structure on the surface.

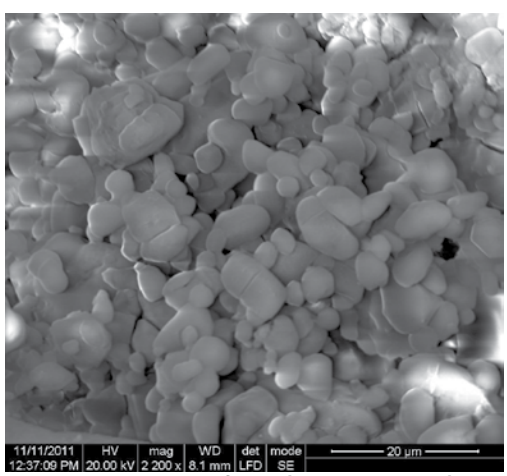

Figure 3.SEM image of Poly (NTB-co-AM/MA) Ferrogel

Dye absorption study

A weighed quantity of nanocomposite ferrogel (0.1g) was immersed separately in each of three dyes such as Crystal violet and Solvent yellow2 having known concentration (1 ppm) The amount of dye absorbed was measured spectrophotometrically (Table1) in both the above dyes at different intervals Fig4-7. The adsorption rate was low during the first few minutes. The absorption rate started an escalation after 10 to 15 minutes. The incorporation of Fe ion was favourable for the absorption of anionic dyes. The removal efficiency was (RE %) was calculated (Fig4.) using the equation 1.

$$RE\% = [(C_0\text{-}C/C_0)] \times 100 \quad \text{----(1)}$$

Where, C_0 and C are the initial and equilibrium concentration of dye solutions respectively.

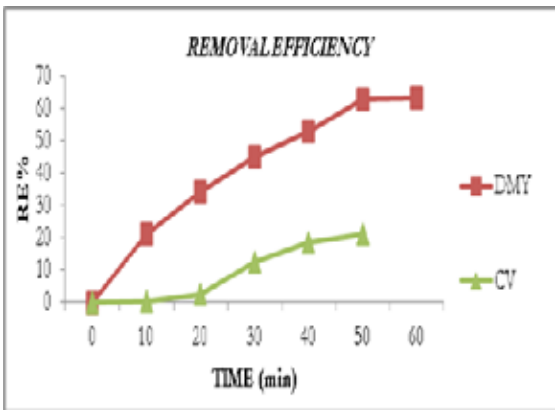

Figure 4. Removal Efficiency of Dyes

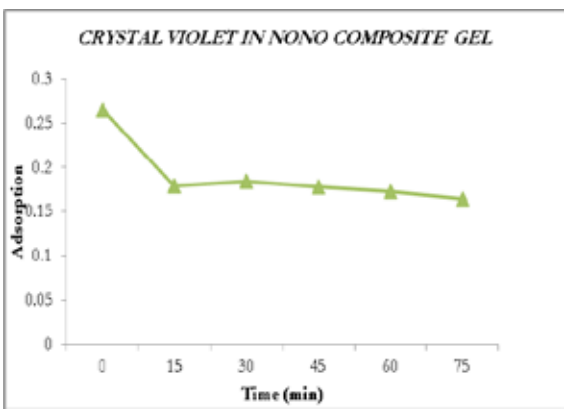

Figure 5. Crystal Violet in Ferrogel

Table 1. Absorption (%)of dyes

Dye	Optical Density		Absorption %
	Initial	Final	
Crystal Violet	0.5785	0.4546	21
Solvent yellow2	0.1935	0.0770	70

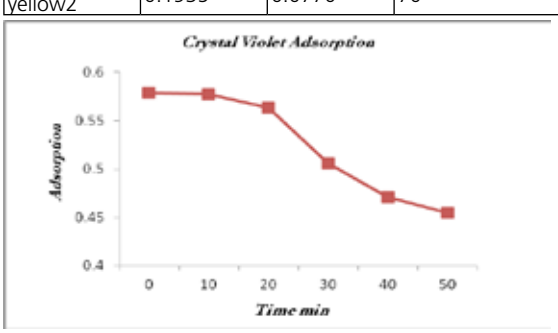

Figure 6. Adsorption of Crystal Violet

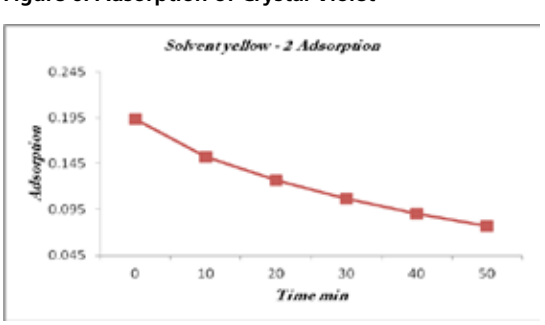

Figure 7. Adsorption of Solvent yellow-2

Conclusion

The process of preparation of poly (N-tert -butylacrylamide-co-acrylamide/) was standardised. The presence of magnetic particles was confirmed by Fe-O stretching frequency through FTIR. The swelling rate is higher in first 60 minutes and then it gradually declines. The adsorption rates for the dye stuffs are slow during first two minutes and it increases after 10 to 15 minutes. The incorporation of Fe ion is favourable for the adsorption of anionic dyes more. From this study it may be concluded that the removal efficiency of dyes from various textile industries effluent by adsorption on ferrogel has been found to be very useful for controlling water pollution due to hazardous dyes. It is clear that the adsorption of dyes is influenced by amount of adsorbent (Ferrogel) and contact time. The removal of dyes is increased with increasing contact time about 70% of Solvent yellow 2. With this environment friendly adsorbent considerable dyes removal can be achieved. So it can be used as substitute for other adsorbent. With the experimental data it is possible to design to optimize an economical treatment process for dyes removal from the industrial effluent.

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