MB Dye Adsorption Behavior on Poly (N cyclohexylacrylamide-co-Acrylamide/Maleic acid)/ OMMT Nanocomposite Hydrogels

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Abstract

A series of poly (N-cyclohexylacrylamide-co-Acrylamide/Maleic acid) /OMMT nanocomposite hydrogels (NC) were prepared from free-radical copolymerization in water/methanol medium using ammonium persulfate (APS) as a free radical initiator and N,N'-methylene-bis-acryl amide(MBA) as the cross-linker at 60°C. The nanocomposite hydrogels were synthesized via in situ polymerization using organo modified MMT (O-MMT) nano clay. The optimum swelling of nanocomposite superabsorbents was achieved at 0.150g of OMMT nanoclay. The synthesized nanocomposites were characterized by FTIR, SEM, XRD and TGA techniques. Swelling and diffusion parameters in water and dye solution were calculated. The effect of two cationic salt solutions on the swelling was studied. The hydrogel nanocomposites showed up to 99.9% removal efficiency towards methylene blue dye adsorption study.

Keywords: Swelling behavior, Maleic acid, Dye adsorption study, SEM analysis, Nanocomposite hydrogel, Methylene blue.

Introduction

Several industries, such as textile, paper, carpet, prints, cosmetics, leather, paper, and plastic, variety of dyes are used to color their products and discharge wastewater into nearby water bodies. They can be harmful to aquatic life. Coloured waste waters released from dyeing industries contain low biochemical oxygen demand (BOD) and high chemical oxygen demand (COD). The dyes affect the biological activities in water bodies. In addition, some dyes are either toxic or mutagenic and carcinogenic in nature and can cause serious harm in the liver and the central nervous system to people. The pollution created by effluents from various industries becoming a major environmental problem. Nearly, 100,000 types of dye materials are available in the world market [1-6].

Dyes are usually stable to light, heat and very difficult to biodegrade because of their complex aromatic molecular structures. The various physicochemical methods, such

biological treatment, coagulation, flotation, electrochemical techniques, adsorption, and oxidation are commonly used for the dye removal from industrial wastewater. Among them adsorption process generally considered to be an attractive alternative method due to high efficiency, easy handling, inexpensive and readily available. Dyes can be satisfactorily removed by adsorption process. [7]. Methylene blue (MB) is a cationic dye, which is widely used for dyeing cotton, wood and silk and it is toxic and harmful for ecosystem [8].

Recently, crosslinked polymeric hydrogels play a vital role in the wastewater treatment processes. Due to the presence of ionic functional groups, they are able to absorb and trap ionic dyes from industries effluents [9]. When hydrogels are placed in aqueous solutions, they adsorb and hold the dissolved substances. This is the fundamental reason for a few studies proposed as water decontamination agents [10-12]. The use of hydrogels has several limitations and always exhibit poor stability and mechanical properties. Polymer/clay nanocomposite hydrogels have been studied to improve these properties of hydrogels [13–17]. Incorporation of nanoclays reduces costs as well as improves their properties (such as swelling ability, gel strength, mechanical and thermal stability) [18].

In our previous paper [19], we reported Synthesis and Swelling behavior of Poly (N-tert-amylacrylamide-co-Acrylamide/Maleic acid) Hydrogel. The aim of the present study is to synthesize a functional nanocomposite hydrogel consisting of OMMT clay and synthetic polymers to be evaluated as an adsorbent for methylene blue dye. This has been achieved by terpolymerization of NCA, AM and MA in the presence of MBA and clay in methanol/water medium and its effectiveness as an anionic adsorbent for removal of dye has been investigated MB as model cationic dye.

Experimental

Materials

Acrylamide (AM), maleic acid (MA) and initiator ammonium persulphate (APS), crosslinker N, N'-methylene-bis-acrylamide (MBA), OMMT Clay and methylene blue (MB) were received from Aldrich. Acrylamide monomer was recrystallized in acetone/ethanol mixture before use. Acrylonitrile was purified and distilled under reduced pressure. Double distilled water was used throughout the experiments.

Synthesis of N-cyclohexylacrylamide Monomer

The monomer N-cyclohexylacrylamide (NCA) was prepared by the Ritter's reaction, as mentioned in the literature [20].

Synthesis of poly (N-cyclohexyl acrylamide -co -acrylamide / maleic acid)/OMMT nanocomposite hydrogel.

The nanocomposite hydrogels were prepared as depicted in our previous work [19]. In situ free radical crosslink copolymerization was employed to synthesize nanocomposite hydrogels. The nanocomposite hydrogels were synthesized by varying the clay content from 0 to 0.200g

,while the other reaction variables kept constant. At first, monomers NCA (0.5g), AM (0.5g), MA (0.200g) and the crosslinker MBA (0.050g) were dissolved in methanol/ water mixture taken in a polymerization tube. To this 0.050g of free radical initiator APS and various amounts of OMMT clay (0, 0.050, 0.100, 0.150 and 0.200g) was added to the reaction mixture. Polymerization reactions were carried out in thermostatic water bath under nitrogen at 60°C for 1day.The gelled mass resulting from the polymerization reaction was then immersed in double distilled water and kept for 2 days by changing water at every 5 h interval in order to remove unreacted monomers. The extracted nanocomposites were dried in vacuum oven at 50°C to constant weight for further use.

Characterization methods

The surface morphology of the freeze-dried nanocomposite was studied by scanning electron Microscopy using Hitach, model-JSM-5000 imaging mode at 30 kV with different levels of magnification. FTIR measurement was carried out by using Nicolet Nexus-670 Spectrometer at room temperature with KBr pellet. The X-ray diffraction studies of the nanocomposite hydrogels were carried out by using a BRUKER D8 Advance diffractometer (Germany), employing rotating Cu anode. The TGA thermograms were recorded on a PerkinElmer-7 at a heating rate of 10°C /min under N₂ protection over a temperature range from ambient temperature to 800°C.

Measurement properties

Swelling studies

Swelling characteristics were measured by immersing weighed samples of dry hydrogel and nanocomposite hydrogels in double distilled water and 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 swollen gel was blotted several times till three consecutive weights are same within limits of experimental error of 1%. All measurements were performed thrice and the reported values are average of at least three individual measurements. The degree of swelling (Ds) most commonly described as swelling ratio was calculated using following Equation (1): [21, 22].

$$Ds(\%) = \frac{(W_t - W_d)}{(W_d)} \times 100 \dots (1)$$

Here, W_t is the weight of the swollen gel at a given time and W_d is the weight of the dry gel. Salt resistant swelling behavior was test by using different concentrations of NaCl and KCl solution at ambient temperature.

Adsorption of Methylene blue

Dye adsorption experiments were carried out at ambient temperature using a batch technique. A weighed quantity of dry nanocomposite hydrogels with different composition were immersed in enough methylene blue solution (25ppm, 20ml) and kept at ambient temperature. The amount of residual dye in aqueous solution was measured spectrophotometrically (λ: 661.6nm) in periodically taken solution samples and again placed in the same vessel so that the liquid volume was kept constant. The removal efficiency (RE %) was calculated using following Equation (2) :

$$RE(\%) = \frac{(C_0 - C)}{C_0} \times 100 \dots \dots \dots (2)$$

Where C_0 and C are the initial and equilibrium concentration of the MB dye solution, respectively [23-24].

Results and Discussion

Characterization of Nanocomposite hydrogel

FTIR Spectroscopy

Fig. 2 shows the FTIR spectrum of poly (NCA-co-AM/MA)/OMMT nanocomposite hydrogel. A broad peak corresponding to NH stretching of NCA was observed around 3301 cm^{-1} . In addition to this, the peaks were also observed at 1651 cm^{-1} corresponding to C=O of NCA and C=O of carboxyl unit and 1571 cm^{-1} corresponding to C=ONH₂ AM unit. The band at 2919 cm^{-1} is due to C-H stretching of polymer backbone, and peaks at 2311 cm^{-1} indicates coupled OH in-plane bending and C-O stretching. A peak at 3541 cm^{-1} is due to -OH group between the two planes of the clay. Si-O-Si symmetric stretching mode was observed at 1116 cm^{-1} . A peak 610 cm^{-1} indicates R-O-Si (R=Al, Mg or Li), which confirms the incorporation of the clay into the polymer matrix. The above FTIR analysis indicates the presence of all monomeric units in the crosslinked hydrogels.

Figure 1. FTIR spectra of Poly (NCA-co-AM/MA)/OMMT nanocomposite hydrogel.

TGA studies

The Fig. 3, the thermogravimetric curve of nanocomposite hydrogel. The TGA thermogram of Poly (NCA-co-AM/MA)/OMMT show three steps degradation. The initial weight losses are

due to the evaporation of free water and inter layered water present in the sample. The first stage and the second stage are attributed to the rupture of the maleic acid main chain and the decomposition of crosslinker respectively. The final stage is due to the main chain scission in the polymer back bone. There is a step after 680°C that can be related to degradation of OMMT clay. The residual weight percentage indicates the content of nanoclay. We can conclude that nanocomposite is stable up to 680°C [25-27].

Figure 2. TGA curves of Poly (NCA-co-AM/MA)/OMMT nanocomposite hydrogel

XRD Studies

The X-ray diffraction patterns of Poly (NCA-co-AM/MA)/OMMT and OMMT clay are shown in Fig. 4a and 4b. A typical diffraction pattern of OMMT, with a strong peak corresponding to a basal spacing of 4.47 nm ($2\theta=19.812^\circ$) was recorded. This meant that the clay has a regular crystal structure. The wide peak shows that the size of the clay is very small, which conforms more amorphous and less crystalline. It showed that the more the amorphous in the matrix more will be the swelling. It was clear that the regular crystal structure of clay was partly destroyed and the clay platelets were intercalated and dispersed in the nanocomposite hydrogel matrix [23,24,28].

Figure 3. XRD diffractograms of (a) Poly (NCA-co-AM/MA)/OMMT and (b) OMMT

SEM Analysis

The SEM micrographs of Clay-150 nanocomposite and clay-free hydrogel are presented in Fig. 5. From the micrographs, it was found that the hydrogels without clay shows a relatively tight surface (Fig. 5b), while the nanocomposite hydrogel (Fig. 5a) contain coarse and undulant surface. The clay was dispersed uniformly in the polymer network and several areas show fine structure. It means that clay has good collaboration with Poly (NCA-co-AM/MA) and improves the network of it which may be favorable for MB dye adsorption [29].

Figure 4. SEM image of Clay-150 nanocomposite (a) and clay-free hydrogel (b)

Swelling behavior

Equilibrium swelling ratio curves of clay-free hydrogel and nanocomposite hydrogels in water and methylene blue dye solution are shown in Fig.6a and 6b and the values are tabulated in Table 2. Results show that swelling ratio increased by added OMMT clay to poly(NCA-co-AM/MA). The swelling curves are similar in shape but differ in size and position. Incorporation of 0.150g clay showed high equilibrium swelling than other. The swelling rate was slow during the first few minutes; it indicates that the initial swelling is due primarily to the water penetrating into the polymeric gel through capillary and diffusion. Then the penetrated water is absorbed by hydrophilic groups such as MA and AM through formation of hydrogen bonds. The swelling is driven by repulsion of hydrophilic groups inside the network and osmotic pressure difference between the gels and the external solution. The swelling rate is gradually increases until the equilibrium swelling is reached [21, 22]. The clay content of 0.150g gives the maximum swelling at ambient temperature. Above 0.150g of OMMT, the water absorbency decreases gradually. The decrease may be attributed to the fact that a greater amount of clay result in the generation of more crosslink points, which increases the crosslinking density of the hydrogel composite and reduces the absorbency of the composites [24, 30].

Figure 5. Dynamic swelling kinetic of nanocomposite hydrogels containing different clay content (a) water and (b) MB dye solution

Table 1 Swelling parameters of nanocomposite hydrogels in water and MB dye solution

Samples	Equilibrium swelling ratio (SR %)	
	Water	Dye
NC-0	769.6	170.9
NC-50	988.4	245.6
NC-100	1100	326.8
NC-150	1513.7	483.7
NC-200	1193.5	396.9

Effect of ionic strength

Salt resistant swelling of nanocomposite hydrogels have been studied by using different concentrations (0.5, 1, 1.5, 2, and 2.5%) of NaCl and KCl are shown in Fig.7. It was found that D_s (%) decreases with increase in salt concentration. Maximum swelling has been found at 0.5% concentration in all the salt solutions. In water, the composites has maximum osmotic pressure, hence the maximum swelling. But when the composite was placed in NaCl and KCl solutions, the osmotic pressure is lower due to Na^+ , K^+ and Cl^- ions. This phenomenon was observed in the swelling of ionic hydrogels and attributed to a charge screening effect of the additional cations causing a non-perfect anion-anion electrostatic repulsion. This led to a decrease in osmotic pressure difference between the composite network and the external solution [31, 32].

Figure 6. Water absorbency of superabsorbent nanocomposite hydrogel in NaCl and KCl aqueous solutions.

Adsorption of Methylene blue

To study the adsorption, a weighed quantity of dry hybrid hydrogel and nanocomposite hydrogels with different composition were placed in aqueous solution of methylene blue for 1 day. After one day all nanocomposites showed dark color compared with the original composites. Also, the color of MB solution became colorless compared with the original solution. Fig. 8 shows the removal efficiency (RE) of methylene blue by clay-free hydrogel and nanocomposite hydrogels. When we use of clay-free hydrogel (NC-0), maximum adsorption is about 47.9%. Removal effect of MB increased when the 0.150g of OMMT clay was added to poly (NCA-co-AM/MA) up to 99.9 %. The cationic dye may have interacted with the OMMT clay by different modes: 1. The cations on clay may exchange with MB cations from solution. 2. The adsorption is on through porous of clay without any ion-exchange. 3. The dye adsorbed on the surface of porous materials [24,33].

Figure 7. Effect of addition of OMMT content on efficiency of MB removal.

Diffusion studies

The diffusion of water through polymer network is associated with the physical-chemical properties of the nanocomposite hydrogels. The plot of $\ln F - \ln t$ and $t^{1/2} - F$ curves for NC-0 and NC-150 in MB dye solution and in water are given in Fig. 9. The number which is used to determine the type of diffusion (n) was found to be over 0.50. Hence, the diffusion of water and monovalent cationic dyes into nanocomposite hydrogels was taken to be of a non-Fickian character. In Non-Fickian the diffusion and relaxation rate are comparable. The values of ' n ' are listed in Table -2.

Figure 8. Plots of $\ln F$ Vs $\ln t$ and F Vs $t^{1/2}$ curves of clay-free hydrogel and nanocomposite hydrogel in MB and in distilled water.

Table -2 Diffusion parameter of NC-0 and NC-150 nanocomposite hydrogels

samples	n	Mechanism
NC-0/Water	0.82	Non-Fickian
NC-0/Dye	0.65	Non-Fickian
NC-150/Water	0.833	Non-Fickian
NC-150/Dye	0.56	Non-Fickian

Conclusions

we have synthesized poly (NCA-co-AM/MA)/OMMT nanocomposite hydrogel with various clay content. The SEM shows that OMMT clay was uniformly dispersed in polymer matrix and XRD clearly shows that the regular crystal structure of clay was partly destroyed and the clay platelets were intercalated. TGA data showed that OMMT didn't leave from the structure of hydrogels during swelling and adsorption experiments. FTIR confirmed the presence of silane linkage. The incorporation of nanoclay helps the material to improve swelling as well as adsorption of methylene blue dye from aqueous solution. Diffusion of water and the aqueous solution of dye within hydrogel were found to be of non-Fickian character. It was found that the salt effect decreases the swelling capacity of the hydrogel to some extent. Nanocomposites can be easily regenerated with methanol. This characteristic of the possibility for reusing the reactive polymer several times makes it economically suitable for use. Our synthesized

nanocomposite hydrogels may be considered as good candidate for environmental application to retain more water and dye.

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