Synthesis and Properties of Starch-Graft-Acrylic Acid/Na-Montmorillonite Superabsorbent Nanocomposite Hydrogels

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ABSTRACT: The graft copolymerization of acrylic acid (AA) onto starch was carried out with monomer/starch weight ratio = 1.5. Cerium ammonium nitrate (CAN) and N,N'-methylenebis acrylamide (NMBA) were used as initiator and crosslink agent, respectively. Na-montmorillonite was used as nanoparticles. Starch-*graft*-acrylic acid/Na-MMT (S-g-AA/MMT) nanocomposite hydrogels were characterized by X-ray diffraction (XRD) and FTIR analysis. The effect of Na-MMT content in nanocomposite hydrogels on the swelling behavior was investigated. Increasing the Na-MMT/monomers ratio up to 1% causes an increment in water absorbency, which indicates that Na-MMT can improve the ability of water absorbency but further increase of Na-MMT causes a decrease in water absorbency. In addition, we describe the removal of safranine T from aqueous solutions using S-g-AA/MMT nanocomposite hydrogels. Effects of various parameters such as treatment time, initial dye concentration, and amount of the Na-MMT were investigated. The Freundlich equations were used to fit the equilibrium isotherms. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 16–22, 2008

Key words: starch; nanocomposite hydrogel; basic dye; safranine T; montmorillonite

INTRODUCTION

Starch is an abundant, biodegradable, natural polysaccharide and a low-cost material. Chemical modification of starch via oxidation, hydrolysis, esterification, etherification, grafting have been extensively studied.[1] Grafting of acrylamide,[1–4] acrylonitrile,[2,5,6] methylacrylonitrile,[7] alkyl methacrylates,[8,9] vinyl ketones,[10] 2-(dimethylamino)ethyl methylacrylate,[11] acrylic acid (AA)[12–16] onto starch has been investigated. The chemical grafting of vinyl monomers onto polysaccharides has been the subject of extensive investigation using tetravalent cerium and other initiating systems.[5] Starch graft copolymers are becoming increasingly important because of their potential applications in industry. It has been used as hydrogels, flocculants, ion exchangers, and superabsorbents.[9]

In recent years, the study of organic–inorganic nanocomposites has become a very important field.[17] Many layered, inorganic mineral micropowders such as mica, attapulgite, and kaolinite have been used in the preparation of polymers to achieve lower production costs and higher properties. Montmorillonite (MMT), a layered aluminum silicate with highly exchangeable cations and reactive groups on its surface, also has been widely used to improve the hydrogel properties of polymers.[18] Traditional superabsorbent network from synthetic polymers, such as poly(sodium acrylate) and polyacrylamide, often have some limitations besides poor biodegradability, and these flaws restrict its application widely.[19] Starch-graft copolymers have greater demand in industry due to their low cost and biodegradable properties and thus environmental friendly. Starch-graft copolymers have become the focus for the preparation of inorganic–organic superabsorbent nanocomposite because of the environmental factors. Luo et al. reported the synthesis of starch-grafted poly(acrylamide-*co*-acrylic acid)/MMT with a γ-ray irradiation technique.[20] Li and coworkers investigated the properties of starch-based attapulgite nanocomposite hydrogels.[19,21]

Colored organic effluent is produced in the textile, paper, plastic, leather, food, and mineral processing industries.[22] The main pollution source of textile effluent emerges from the dyeing process. Dyeing and finishing wastes in the textile industry have high color and organic content. Synthetic organic dyes present certain hazards and environmental problems. Effluents discharged from dyeing industries are highly colored with low biochemical oxygen demand (BOD) and high chemical oxygen demand (COD).[23] Disposal of these effluents into water can be toxic to aquatic life.[24] The dyes upset the biological activities in water bodies. They cause a health

problem because they may be mutagenic and carcinogenic[25] and can cause severe damage to human beings such as in the liver and the central nervous system.[23,26] Different techniques, such as membrane separation, flocculation, chemical oxidation, and adsorption, are investigated to treat reactive dyes wastewater. Among them adsorption technology is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes in an effluent.[27] Dyes can be effectively removed by adsorption process. Activated carbon,[23,28] natural clays,[29] modified clays,[30,31] some industrial wastes and by-products[28] have been used as adsorbents for removal of organic compounds from wastewater. In addition, chitin and chitosan,[32,33] starch derivatives,[34–36] carbonized wool waste,[37] agricultural residues such as banana pith,[38–40] maize cob,[40,41] coconut tree sawdust,[40] and bagasse pith,[42–44] have been investigated widely as adsorbents.

In this work, we report the synthesis of superabsorbent composites by graft copolymerization reaction of starch and acrylic acid using N,N′-methylenebisacrylamide (NMBA) as a crosslinker and cerium ammonium nitrate (CAN) as an initiator in the presence of Na-MMT micropowder. The effect of Na-MMT content in nanocomposite hydrogels on the swelling behavior was investigated. In addition, we describe the removal of safranine T from aqueous solutions using starch-*graft*-acrylic acid/Na-MMT (*S*-g-AA/MMT) nanocomposite hydrogels. Effects of various parameters such as treatment time, initial dye concentration, and Na-MMT content were investigated. The Freundlich equations were used to fit the equilibrium isotherms.

EXPERIMENTAL

Materials

Maize starch (food grade) was dried at 110°C and then was stored in vacuum desiccator. Acrylic acid (AA) (Merck, Germany) was purified by vacuum distillation and then was stored in refrigerator. CAN (Merck, Germany) was dried at 110°C and then was stored in vacuum desiccator. Basic dye (Safranine T) was obtained from Merck. The chemical structure of Safranine T is shown in Figure 1. MMT was kindly provided by Kenan Çinku from the Mining Engineering Department of Istanbul University. Rest of the materials was chemically pure grade. All solutions and standards were prepared using distilled water.

Instruments

Spectrophotometric measurements were carried out using Jenway 6105 UV/Vis spectrophotometer.
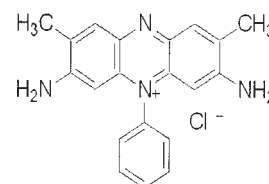

Figure 1 Chemical structure of Safranine T.

X-ray diffraction (XRD) patterns were obtained by using a Rigaku D/Max Ultima + X-ray diffractometer equipped with Cu Kα radiation ($\lambda = 1.5405$).

The infrared spectra of hydrogels were taken with Digilab Excalibur-FTS 3000MX model FTIR spectrophotometer using KBr pellets.

Preparation of graft copolymers

The graft copolymerization of AA onto gelatinized starch was carried out under nitrogen atmosphere in a 500 mL round bottom flask. The gelatinized starch was prepared by constantly stirring a mixture of 4 g of starch and 100 mL distilled water at 90–95°C for 1 h. The slurry was cooled to 35°C and was then treated with CAN (0.005 mol/L) for 15 min to facilitate free radical formation on starch.[12,45] This treatment was followed by the addition of AA (monomer/starch weight ratio = 1.5), Na-MMT (1–10% based on monomer), NMBA as crosslink agent (0.05% based on monomer) and then the total volume of the reaction mixture was made to 120 mL with distilled water. The reactions were maintained at 35°C and 180 min under nitrogen atmosphere. After 180 min, reaction mixture was warmed up to 60°C and neutralized by addition of 10% (weight ratio) NaOH solution until it assumed a brown color. The reactions were maintained at 60°C for about 15–20 min. After cooling the mixture to room temperature, pH was adjusted to 10 with glacial acetic acid. These products were precipitated in excess of cold methanol. The precipitated *S*-g-AA/MMT nanocomposite hydrogels were washed with ethanol and dried under vacuum at 70°C.

Grafting percentage (GP%) was determined by titration method. Nanocomposite hydrogel samples were contacted with 0.1N HCl solution at 2 h. Then these samples were separated with filtration from acid solution and washed with ethanol solution. Dried nanocomposite hydrogel samples were titrated with 0.1N NaOH solution in the presence of phenolphthalein indicator and calculated by the following equation.

$$GP\% = (m_1/m_2)100 \qquad (1)$$

m_1 = amount of grafted AA (g) (calculated from result of titration), m_2 = amount of graft copolymer (g).

Determination of water absorption capacities

S-g-AA/MMT nanocomposite hydrogels were swollen in distilled water and water absorption capacities were determined by tea-bag method. The tea bag was made of 250-mesh nylon screen, contains a known amount of dried hydrogel sample, and was immersed entirely in known amount of water sample and kept there to attain swelling equilibrium for a certain time (Q_t), then hung up for 1 min to drain the excess solution, and weighed. The water uptake was calculated by the following equation.

$$Q_t = (W_{wet} - W_{dry})/W_{dry} \qquad (2)$$

where W_{wet} and W_{dry} is the weight of the swollen and dried hydrogel samples, respectively.

Adsorption studies

Safranine T solutions were prepared by dissolving dye in deionized water to the required concentrations. The S-g-AA/MMT nanocomposite hydrogels (0.05 g) were added into Safranine T solutions (100 mL) (initial concentrations of dye solutions were 500 mg/L). The amount of residual dye in aqueous solution was followed by UV–vis spectrophotometer up to 24 h. In experiments of equilibrium adsorption isotherm, a fixed amount of 0.05 g adsorbents were contacted with 100 mL of aqueous solutions Safranine T with different concentrations (100–500 mg/L). The amount of residual dye in aqueous solution was determined by UV–vis spectrophotometer after 24 h. The equilibrium adsorption capacity, q_e (mg/g), was calculated from the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \qquad (3)$$

where C_o is the initial concentration (mg/L), C_e is the residual concentration at equilibrium (mg/L), V is the volume of solution (L), W is the weight of the copolymer (g).

TABLE I
S-g-AA/MMT Nanocomposite Hydrogels

Symbols	Graft (%)	Na-MMT (%)
S-g-AA/MMT-0	30	0
S-g-AA/MMT-1	28	1
S-g-AA/MMT-3	27	3
S-g-AA/MMT-5	26	5
S-g-AA/MMT-10	26	10

Reaction conditions: AA/starch weight ratio = 1.5; N,N'-methylene-bisacrylamide (NMBA) as crosslink agent (0.05% based on monomer); CAN as initiator (0.005 mol/L).
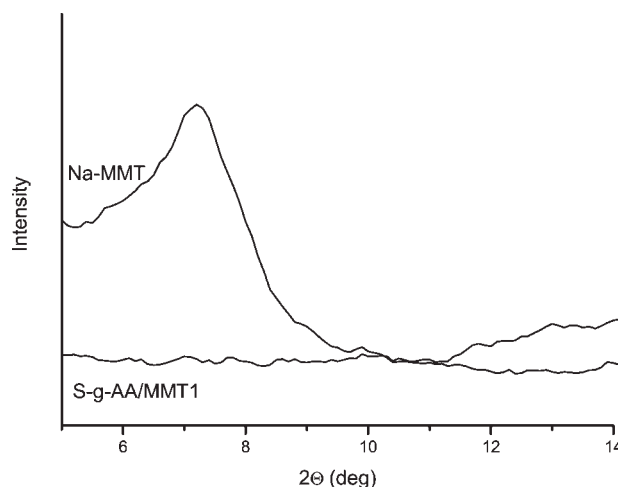
Figure 2 XRD spectra of Na-MMT and S-g-AA/MMT nanocomposite hydrogel.

RESULTS AND DISCUSSION

The graft copolymerization of AA onto starch was carried out with monomer/starch weight ratio = 1.5. CAN and NMBA were used as initiator and crosslink agent, respectively. Na-MMT was used as nanoparticles. The grafting reaction initiated by the CAN is characterized with first producing free radicals on the starch backbone and then adding AA molecules to the starch macro-radicals formed. The structures of the polymers and grafting reaction mechanism were submitted to our previous work.[15] The grafting percentages and amount of the Na-MMT of the S-g-AA/MMT nanocomposite hydrogels are shown in Table I. As shown in Table I, grafting percentage of the S-g-AA/MMT nanocomposite hydrogels decreased (from 30 to 26%) with increase in amount of the Na-MMT (from 1 to 10%). This case is probably due to the physical hindrance; higher the Na-MMT amount higher is the physical hindrance and lower is the grafting percentage.

X-ray diffraction and FTIR analysis

Figure 2 illustrates the XRD of Na-MMT and S-g-AA/MMT nanocomposite hydrogel. There is intense diffraction for Na-MMT, while no diffraction peak appears for S-g-AA/MMT nanocomposite hydrogel sample, suggesting that clay sheets are exfoliated and uniformly dispersed in organic network. The FTIR spectra of Na-MMT and S-g-AA/MMT nanocomposite hydrogel are shown in Figure 3. The peaks at 1042, 925, 520, and 466 cm^{-1} are attributed to characteristic peaks of MMT that appeared in spectra of S-g-AA/MMT nanocomposite hydrogel.
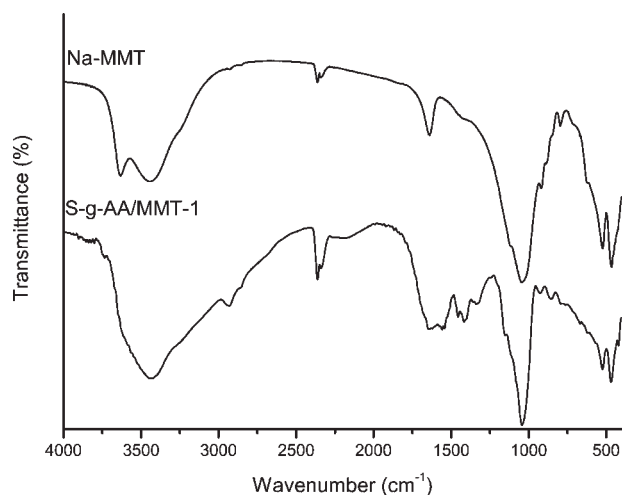
Figure 3 FTIR spectra of Na-MMT and *S*-g-AA/MMT nanocomposite hydrogel.

Effect of Na-MMT content on water absorbency of nanocomposite hydrogels

Figure 4 shows the influence of the content of Na-MMT on the water absorbency of nanocomposite hydrogels. Increasing the Na-MMT/monomers ratio up to 1% causes an increment in water absorbency, which indicates that Na-MMT can improve the ability of water absorbency but further increase of Na-MMT causes a decrease in water absorbency. When the concentration of the clay is too high, the neighboring clay–clay interparticle distance will be too small, and thus make the size of the polymeric networks too small to absorb a large amount of water.[20]

Water absorption speed of nanocomposite hydrogels

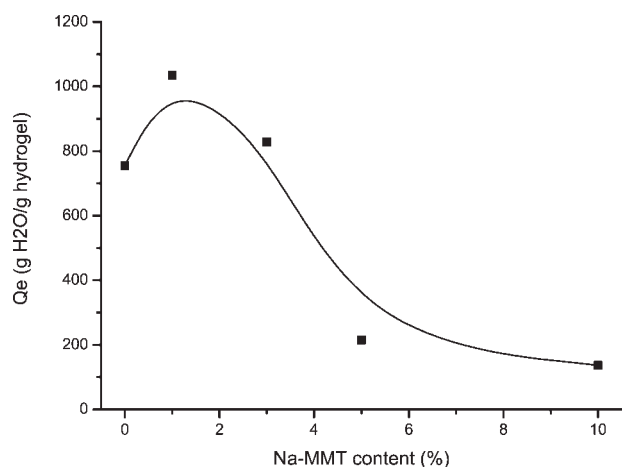Figure 5(a,b) show the water absorption speed of *S*-g-AA/MMT nanocomposite hydrogels. In the first

Figure 4 The effect of the content of Na-MMT on the water absorbency of nanocomposite hydrogels.
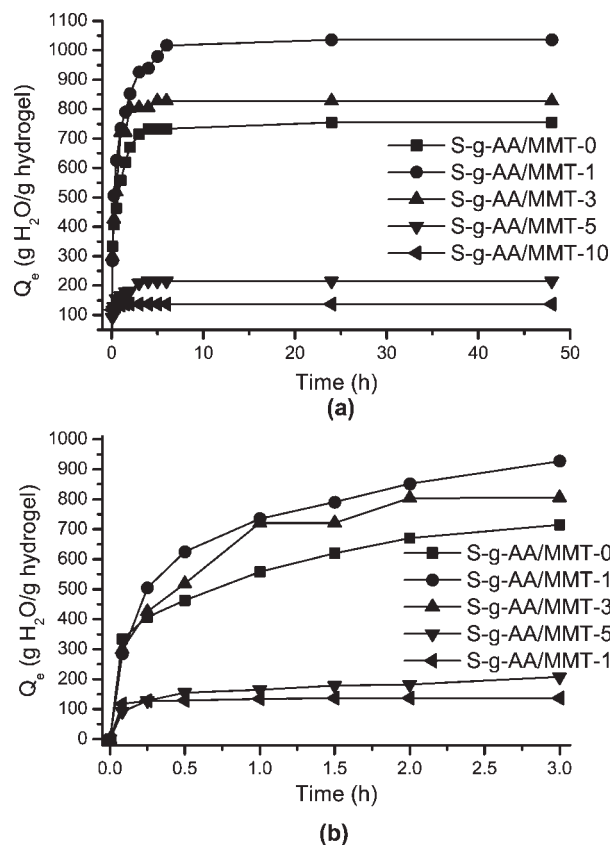

Figure 5 The effect of treatment time on the absorption of the hydrogels. (a) Overall swelling data of *S*-g-AA/MMT nanocomposite hydrogels. (b) The swelling data of the first 3 h.

3 h the nanocomposite hydrogels *S*-g-AA/MMT-1 and *S*-g-AA/MMT-3 absorbs 927 and 806 g H_2O respectively, while the pure hydrogel absorbs 715 g H_2O/ g hydrogel. This case shows that Na-MMT also causes an increase in water absorbency speed like water absorbency capacity. In case of *S*-g-AA/MMT-5 and 10 nanocomposite hydrogels the overall swelling is finished in the first 3 and 1 h, respectively. Because of decreasing neighbor clay–clay interparticle distance the swelling process is completed faster than the other hydrogels; first, water is absorbed by polymeric networks rapidly, but because of the restriction of the swelling process is completed in a few hours.

Dye adsorption studies

Adsorption properties of *S*-g-AA/MMT nanocomposite hydrogels were evaluated by depending on different adsorption conditions such as different initial dye concentration and treatment time. The concentrations of the dyes were determined using UV–vis spectrophotometer at wavelength 530 nm.

Figure 6 illustrates the effect of adsorption time on the adsorption efficiency. The adsorption capacities
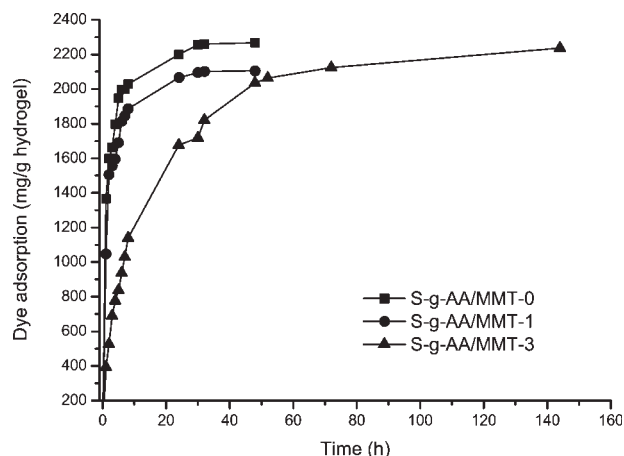
Figure 6 The effect of the treatment time on the adsorption of basic dye from aqueous solutions by *S*-g-AA/MMT nanocomposite hydrogels.

TABLE II
Freundlich Constants of Adsorption Isotherms for Safranine-T onto Nanocomposite Hydrogels

Nanocomposite hydrogels	Freundlich constants		
	K_f	n	R^2
S-g-AA/MMT-0	59	1.008	0.9915
S-g-AA/MMT-1	85	1.276	0.9995
S-g-AA/MMT-3	179	1.700	0.9683

of nanocomposite hydrogels for Safranine T increase with the increase of the adsorption time.

Compared with pure hydrogel, the hydrogel nanocomposites *S*-g-AA/MMT-1 and 3 have greater degree of swelling at equilibrium and enhanced swelling rate as indicated in Figures 4 and 5. In case of adsorption of basic dye, the pure and nanocomposite hydrogels adsorbs almost same amounts of dye in 48 h. But while pure and *S*-g-AA/MMT-1 hydrogels reach their adsorption equilibrium in 24 h, *S*-g-AA/MMT-3 hydrogel continues to adsorb dye and reaches 2063, 2124, and 2237 mg/g hydrogel in 52, 72, and 144 h, respectively. This case shows that *S*-g-AA/MMT-3 nanocomposite hydrogel is more compatible for ''long-time'' processes because its high dye adsorption capacity for long time. In swelling processes, *S*-g-AA/MMT-1 and 3 hydrogels protected their mechanical properties while the pure hydrogel dispersed and lost its physical form (Fig. 7). Thus in ''short time'' processes the nanocomposite hydrogels seems to be more suitable because of their enhanced mechanical properties.

In experiments of equilibrium adsorption isotherm, a fixed amount of 0.05 g adsorbents were

contacted with 100 mL of aqueous solutions Safranine T with different concentrations (100–500 mg/L).

As given above, the equilibrium adsorption capacity, q_e (mg/g), was calculated by eq. (3).

The experimental data (q_e and C_e) were used in Freundlich equation to fit the equilibrium isotherms. The Freundlich equation[46] is the earliest known relationship describing the adsorption equation. Freundlich isotherms were obtained by different initial dye concentrations (100–500 mg/L) and 0.05 g *S*-g-AA/MMT nanocomposite hydrogel dose for a constant time of 48 h. The adsorption isotherms data were correlated with the Freundlich equations and the Freundlich constants K_f (mg/g) and n (intensity of adsorption) were calculated from the following equations:

$$q_e = K_f \times C_e^{1/n} \tag{4}$$

$$\log q_e = \log K_f + 1/n \log C_e \tag{5}$$

where q_e is the amount of dye adsorbed (mg/g) onto *S*-g-AA/MMT nanocomposite hydrogels. The parameters of Freundlich isotherm, K_f and n as well as the correlation coefficients R^2 are given in Table II. Linear plots of log q_e versus log C_e for the different initial dye concentrations illustrated that the adsorption follows the Freundlich isotherm (Fig. 8). Such conclusion can be drawn from data R^2 that the adsorption isotherm of Safranine T onto *S*-g-AA/ MMT nanocomposite hydrogels is very well represented by Freundlich isotherm. The R^2 values were 0.9915, 0.9995, and 0.9683 for *S*-g-AA/MMT-0, *S*-g-AA/MMT-1, and *S*-g-AA/MMT-3, respectively. As it is known, the magnitude of the exponent n gives an indication of the favorability and K_f the capacity of the adsorbent/adsorbate system. The n values between 1 and 10 indicate beneficial adsorption.[46] For all hydrogels the n values are ≥ 1 this case indicates Freundlich isotherm is favorable for these systems. Since the higher K_f value is the higher adsorption capacity is, and K_f values are 59, 85, and 179 for *S*-g-AA/MMT-0, 1 and 3 respectively, the *S*-g-AA/ MMT-3 nanocomposite hydrogel is the most favorable hydrogel for removal of Safranine-T from aqueous solutions.
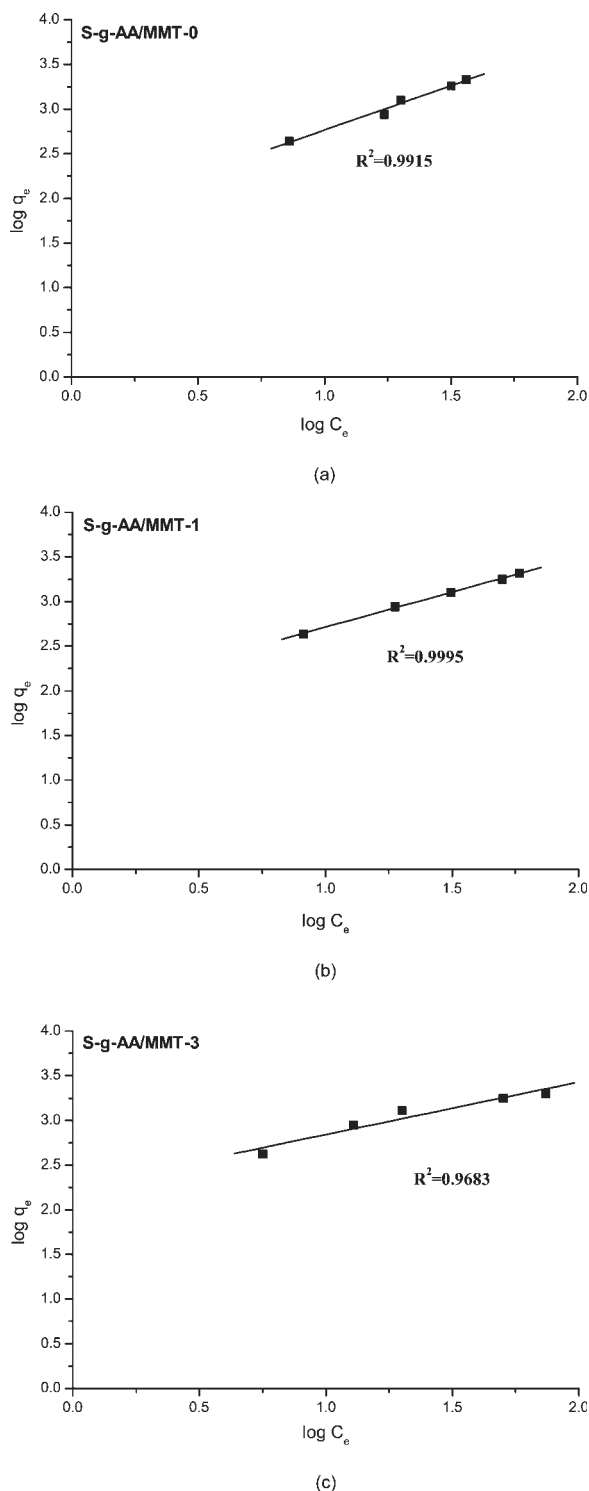

Figure 7 The appearance of the hydrogels after adsorption of basic dye. (a) *S*-g-AA/MMT-1, (b) *S*-g-AA/MMT-0.

Figure 8 Freundlich isotherm for the adsorption of basic dyes (a) S-g-AA/MMT-0, (b) S-g-AA/MMT-1, and (c) S-g-AA/MMT-3.

CONCLUSIONS

The graft copolymerization of AA onto starch was carried out with monomer/starch weight ratio = 1.5. CAN and NMBA were used as initiator and cross-link agent, respectively. Na-MMT was used as nano-particules. S-g-AA/MMT nanocomposite hydrogels were characterized by XRD and FTIR analysis. The effect of Na-MMT content in nanocomposite hydrogels on the swelling behavior was investigated. In addition, we describe the removal of safranine T from aqueous solutions using S-g-AA/MMT nanocomposite hydrogels. The following conclusions can be drawn:

- Increasing the Na-MMT/monomers ratio up to 1% causes an increment in water absorbency, which indicates that Na-MMT can improve the ability of water absorbency but further increase of Na-MMT content causes a decrease in water absorbency.
- In case of adsorption of basic dye, the pure and nanocomposite hydrogels adsorbs almost same amounts of dye in 48 h. But while pure and S-g-AA/MMT-1 hydrogels reach their adsorption equilibrium in 24 h, S-g-AA/MMT-3 hydrogel continues to adsorb dye and reaches 2063, 2124, and 2237 mg/g hydrogel in 52, 72, and 144 h, respectively.
- S-g-AA/MMT-1 and 3 hydrogels protected their mechanical properties while the pure hydrogel dispersed and lost its physical form. Thus in ''short-time'' processes the nanocomposite hydrogels seems to be more suitable because of their enhanced mechanical properties.
- The adsorption isotherms data were correlated with the Freundlich equations. Linear plots of $\log q_e$ versus $\log C_e$ for the different initial dye concentrations illustrated that the adsorption follows the Freundlich isotherm. The R^2 values were 0.9915, 0.9995, and 0.9683 for S-g-AA/MMT-0, S-g-AA/MMT-1, and S-g-AA/MMT-3, respectively.

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