Montmorillonite Nanocomposite Hydrogel Based on Poly(acrylicacid-co-acrylamide) : Polymer Carrier for Controlled Release Systems

Zarei, Shahrbanoo

Department of chemistry, Arak Branch, Islamic Azad University, Arak, I.R. IRAN

Rezanejade Bardajee, Ghasem*+

Department of Chemistry, Payame Noor University, PO BOX 19395-3697, Tehran, I.R. IRAN

Sadeghi, Mohamad*+

Department of chemistry, Arak Branch, Islamic Azad University, Arak, I.R. IRAN

ABSTRACT: *In this paper, the synthesis of new montmorillonite nanocomposite hydrogel (MMTNH) based on poly (acrylic acid-co-acrylamide) grafted onto starch, is described. Montmorillonite (MMT) as nanometer base, acrylic acid (AA) and acrylamide (AAm) as monomers, ammonium persulfate (APS) as an initiator, N,N-methylenebisacrylamide (MBA) as a crosslinker and starch as a biocompatible polymer were prepared in aqueous solution and their amounts were optimized to attain the highest water absorbance. The optimized swelling capacity in distilled water was found to be 810 g/g. A mechanism for hydrogel formation was proposed and the structure of the product was confirmed using a set of techniques including FT-IR spectroscopy, thermogravimetric analysis, scanning electron microscopy, transmission electron microscopy, atomic force microscopy, and X-ray powder diffraction. Furthermore, the swelling behaviors of the nanocomposite at different pHs, various salt with different concentrations, the mixture of solvents, were investigated. The methylene blue (MB) dye was used as model drugs to assess the loading and release by MMTNH. The pH response of this MMTNH makes it suitable for acting as a controlled delivery system. The results suggest MMTNH may find applications as promising drug delivery vehicles for drug molecules.*

KEYWORDS: *Nanocomposite hydrogel; Montmorillonite; Starch; Swelling behavior; Release.*

INTRODUCTION

The use of types of biologically active agents, such as dye, fertilizers, drugs, and pesticides, has become an integral part of modern society [1]. Uncontrolled use of these reagents almost inevitably induces harmful effects on the health of humans. To minimize or eliminate these damaging effects necessitates the controlled release

of these active agents. In recent years, attention to the controlled release of biologically active has increased. The controlled release formulation includes an active agent (dye, drug, fertilizer, etc) and a carrier (commonly a polymeric material) to allow the active agent to be released over a while at a controlled rate [1]. It is therefore important to design polymeric matrices, which can readily embed various types and amounts of the active agent, and then to release with response to variations in external environment [2].

Hydrogels are three-dimensional structures, cross-linked networks of hydrophilic polymeric chains [3, 4]. That can be used as a carrier for active substances. Swelling degree from hydrogel in solution dependent on the pH, ionic strength and temperature [5]. Hydrogels have been used in the fields of pharmacy, medicine, food industry, biotechnology, artificial skin, agriculture, etc. Hydrogels have been most widely used for the controlled release of drugs [6-10].

Hydrogel nanocomposites have newly attracted considerable attention. Hydrogel nanocomposites, which include the incorporation of inorganic nanoparticles inside three-dimensional polymeric networks, have been attracted because of their intrinsic advantages over pure hydrogels or inorganic nanoparticles [11-14]. The properties of the nanocomposites can be easily tailored by manipulating the properties of the hydrogel and the composite material [15].

This work aims to study polymeric systems for controlled drug release devices. Methylene blue (MM=319.86 g/mol), a cationic dye, was chosen as a model molecule [16-18] for controlled release from montmorillonite nanocomposite hydrogel (MMTNH). Acrylic acid (AA) as an ionic monomer, acrylamide (AAm) as a neutral monomer, ammonium persulfate (APS) as an initiator, N,N-methylenebisacrylamide (MBA) as a crosslinker, starch as a biocompatible polymer and montmorillonite (MMT) as a nanometer base were preparation. Montmorillonite, are nanocomposite reinforcements [19]. Because of its hydrophilic behavior, MMT has a high swelling capacity. As a result, the incorporation MMT into a hydrogel contributes to increasing water absorption capacity [20]. Also, adding just a small amount of nano montmorillonite to the polymer matrix could improve the mechanical and thermal properties of the polymers and reduce their flammability [21]. Also, molecules MB dyes are readily incorporated into

hydrogels through suitable interactions between functional groups in the hydrogels and the MMT nanoparticle; and led to the selective, sustained, and controlled dyes release from hydrogels. Here, we report the tunable loading of charged MB dye as model drugs into MMTNH, and the release of dyes depending on the pH values. The schematic representation of this release study is shown in Scheme 1.

EXPERIMENTAL SECTION
Materials

Starch (from Merck), ammonium persulfate (APS, from Merck), methylenebisacrylamide (MBA, from Merck), acrylic acid (AA, from Merck), acrylamide (AAm, from Merck), montmorillonite (MMT, from southern clay USA) and methylene blue (MB, from Merck), used without further purification. All other chemicals were also analytical grade. Through experiments, Double Distilled Water (DDW) was used for preparing solutions.

Instrumental analysis

A Shimadzu UV-visible 1650 PC spectrophotometer was used for recording absorption spectra in solution. Fourier Transforms InfraRed (FT-IR) spectra of samples in the form of KBr pellets were recorded using a Jasco 4200 FT-IR spectrophotometer. Thermal properties of samples were evaluated by TA instrument 2050 thermo-gravimetric analyzer at a heating rate of 20 °C/min under nitrogen atmosphere (flow rate 25 mL/min). Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray analysis (EDX) (Hitachi S-5200 SEM), Transmission Electron Microscopy (TEM; Hitachi H-700 CTEM) was taken on a Zeiss TEM at an acceleration voltage of 80 kV. Atomic Force Microscopy (AFM) (Dualscope/Rasterscope C26, DME, Denmark) were used to examine the morphology and dimensions of hydrogel nanocomposites. Formation of nanocomposite hydrogel was analyzed using a Philips X-Ray Diffraction (XRD) equipped. The XRD data were collected on the scale of $2\theta = 5–55°$ scanning speed of 3°/min.

Montmorillonite nanocomposite hydrogel (MMTNH)
a) Synthesis

In general, starch was dissolved in distilled water (25 mL) with a mechanic stirrer (600 rpm) to get a homogenous solution. After homogenizing the mixture,
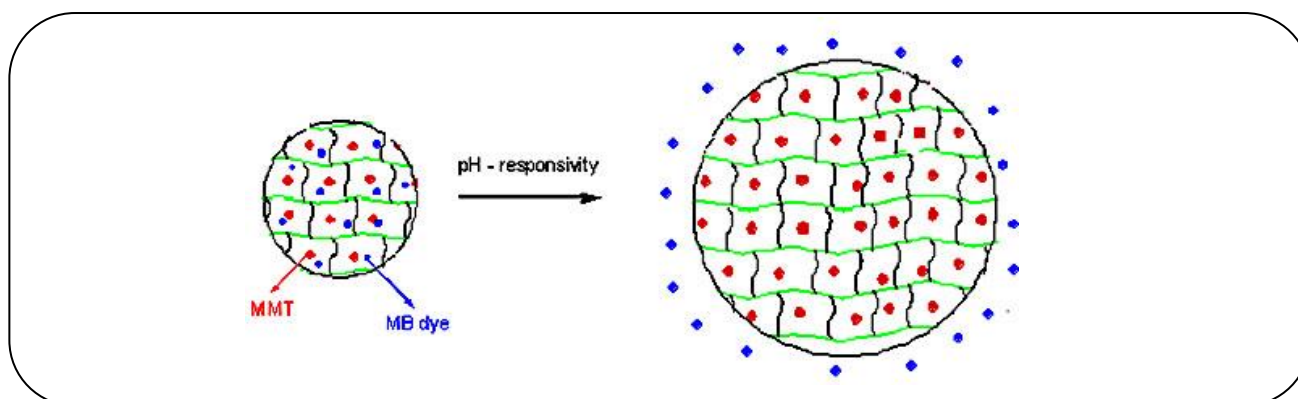
Scheme. 1: Proposed controlled delivery system for pH-sensitive systems.

AA monomer and AAm monomer were added simultaneously. After that MBA crosslinker (dissolved in 10 mL water) and APS (dissolved in 5 mL water) initiator were added to the solution and the reaction mixture was stirred. Then, certain amounts of MMT were added and the reaction mixture was stirred and cooled to room temperature and the obtained hydrogels were dewatered by ethanol and then chopped to small pieces. Finally, NaOH solution was added and the chopped particles were remained in ethanol to completely dewater. The dewatered gel particles were filtered and dried in the vacuum oven at 50 °C for 24 h. After grinding, the powdered hydrogel was stored in the absence of moisture, heat, and light for further experiments.

b) Water absorbency measurements

The degree of swelling was determined by the gravimetric method. 0.1 g of dry powdered sample was placed in bags like a tea bag and was immersed in distilled water (200 mL) for 3 h to reach the swelling equilibrium. Then, the tea bag was hung up for 5 min to remove the excess solution. The Equilibrium Swelling (ES) capacity was measured at the room temperature using the following formula Eq. (1):

$$ES(g/g) = \frac{W_2 - W_1}{W_1} \qquad (1)$$

where W_1 and W_2 are the weights of dry and swollen gels, respectively.

The environmental sensitivity
a) Swelling kinetics

For studying the rate of water absorbency of the hydrogel, a certain amount of sample (0.1 ± 0.01 g)

was immersed in 200 mL distilled water. At consecutive time intervals (1-120 min), the water absorption of the nanocomposite hydrogel was measured according to the earlier mentioned metho (''Water absorption measurement'' section).

b) Effect of pH solution on the swelling

The methods for these examinations are the same as those described in the ''Water absorption measurement'' section. pH dependence of swelling was accomplished by the interaction of a certain quantity of the hydrogel samples (0.1±0.01 g) in solutions (200 mL) with different pHs between 1 and 12. The various solutions were adjusted to the desired pH value by the addition of dilute HCl or NaOH.

c) Effect of salt solution on the swelling

For salt sensitivity measurements, according to the above-mentioned method described for swelling measurements in distilled water (''Water absorption measurement'' section), hydrogel absorbency was evaluated at solutions containing one of NaCl, $CaCl_2$, and $AlCl_3$ salts with different concentrations.

d) Effect of a mixture of solvents on the swelling

The procedures for these experiments are the same as a mentioned method in the prior section (''Water absorption measurement'' section), but instead of distilled water, methanol-water (40:60), 2-propanol–water (40:60), acetone–water (40:60) was used.

Loading and releasing studies

In this study, the release property of MMTNH hydrogel was investigated by using Methyl Blue (MB)

as model drugs. MB dyes were chosen to study the selective release properties of MMTNH. MB dyes are soluble in water and UV-active, making their release from hydrogel convenient to be followed.

Typically, MB was loaded into MMTNH by dispersing 0.1 g of MMTNH with a certain concentration of MB solution during 2 days, until the hydrogels were formed with the entrapped dyes. For loading tracing, the amount of loaded MB was determined at favored times by UV spectroscopy using a calibration curve constructed from a series of MB solutions with known concentrations. After that, the loaded MMTNH was dried in the oven at 40 °C. For the releasing study, the dried gel was dispersed in 50 mL buffer with different pH (pH = 3 -12). At specific intervals, 2.00 mL filtered samples were withdrawn to measure the optical density of release. Finally, the amount of MB releasing was calculated at 663 nm by UV–vis spectrophotometer.

RESULTS AND DISCUSSION
Synthesis mechanistic aspect

Poly (acrylic acid) (PAA) and poly (acrylamide) (PAAm) were simultaneously grafted onto starch as a biocompatible, biodegradable and non-toxic in a homogeneous medium using APS as a radical initiator, MBA as a crosslinking agent and MMT as nanoparticles. A simple scheme for the polymerization process of the entitled system is suggested in Scheme 2. The APS initiator is decomposed under heating to generate sulfate anion-radical. The radical abstracts hydrogen from the starch hydroxyl groups of the polysaccharide substrate to form alkoxy radicals on the substrate. So, this persulfate–saccharide redox system has resulted in active centers on the substrate to radically initiate polymerization of AA and AAm led to a graft copolymer. Since MBA presents in the reaction mixture, a three-dimensional nanocomposite network results at the end of the polymerization reaction. Indicating that the montmorillonite nanocomposite hydrogel networks around nanoparticles were suitable for the loading of absorbing MB dye and subsequently release MB dye.

Spectral characterization

Starch-g-poly (AA-co-AAm) (NH), MMT/starch-g-poly (AA-co-AAm) (MMTNH) were analyzed by FT-IR and the results are shown in Fig. 1.

The IR spectra of NH (Fig. 1b) shows the peaks at 1730 cm^{-1} and 1623 cm^{-1}, which corresponds to the carbonyl group of carboxylic unit and acrylamide unit, respectively. This confirms that both carboxylic and acrylamide have been grafted onto the starch. MMTNH (Fig. 1a) has shown all the mentioned characteristic peaks for NH. Also, the absorption peak at 1026 cm^{-1} and 917 cm^{-1} relating to the Si–O stretching and Al-O stretching of MMT, respectively [22, 23].

In all spectra, the broad bands at 3000-3300 cm^{-1} is also observed due to the stretching vibrations of OH and COOH functional groups.

To illustrate more evidence for the presence of MMT in MMTNH structure and study on their thermal behavior, they were analyzed by TGA/DTG, and the results are presented in Fig. 2. The TGA data of the NH obtained from the optimum condition was compared with the TGA curve of MMTNH synthesized under optimum situations. The TGA curve for NH is completely different than MMTNH. This difference in the thermal behavior of our samples showed that the structure of MMTNH is different from the NH. The DTG curves showed that the maximum decomposition rate occurs at 350 °C and 218 °C of MMTNH and 437 °C and 357 °C of NH.

Fig. 3a shows the Scanning Electron Microscopic (SEM) pictures of the starch and Fig. 3b synthesized MMTNH under optimum situations. From Fig. 3b, clearly indicates the formations of many close-pores with uniformly distributed in MMTNH structure. These pores are mainly responsible for swelling and water absorbency of MMTNH. However, SEM image of starch shows a unique structure without any porous.

The morphology and microstructure of MMTNH was characterized by TEM. TEM image (Fig. 3c) demonstrated that some MMT layers with the dispersion of delaminated sheets can be identified. This finding points out that, montmorillonite with nanometer-size have layer sheets morphology distributed in the matrix of montmorillonite nanocomposite hydrogel synthesized under optimum conditions.

The AFM image to identify its morphology and investigate the structural features of MMTNH is shown in Fig. 3d. As one can see from these graphs, the presence of porous is obvious which is homogeneously dispersed in the matrix of MMTNH. The AFM image supports
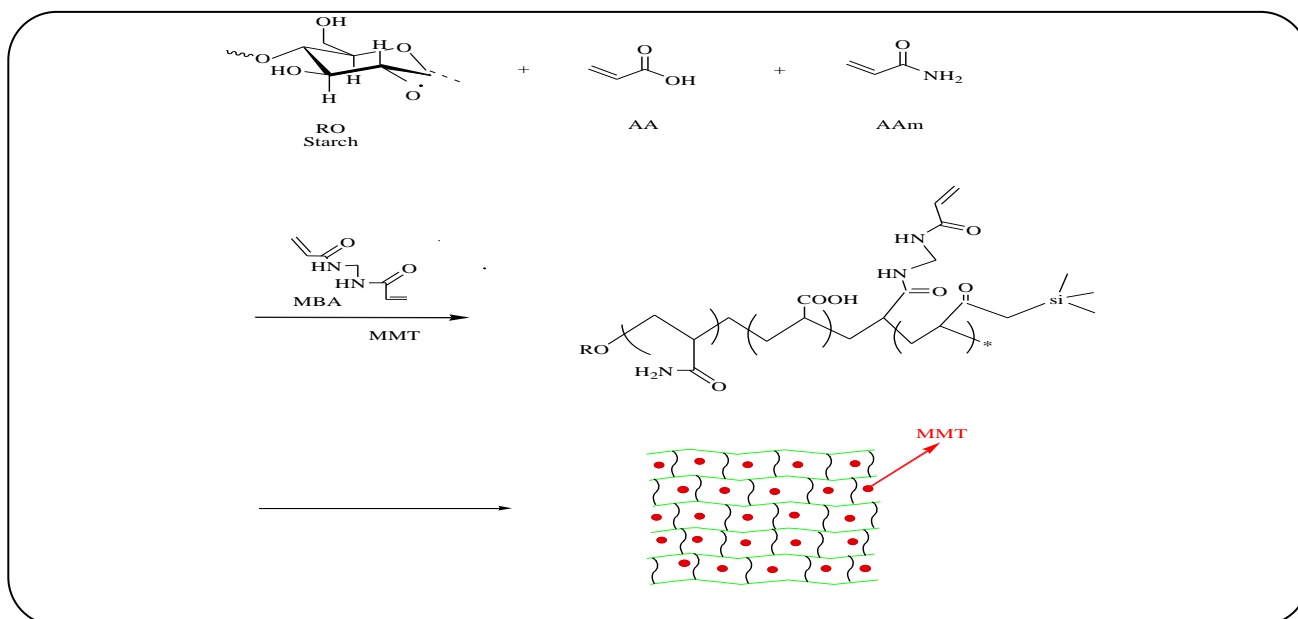
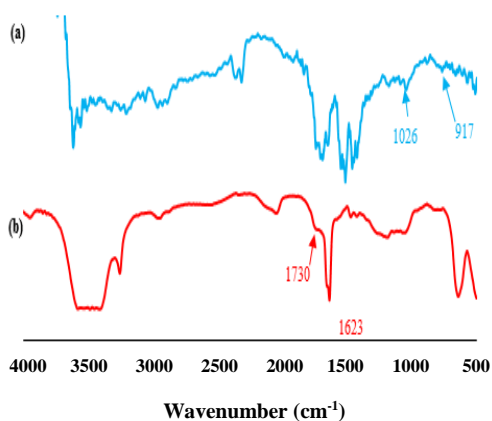*Scheme 2: Proposed mechanism pathway for the synthesis of MMTNH.*
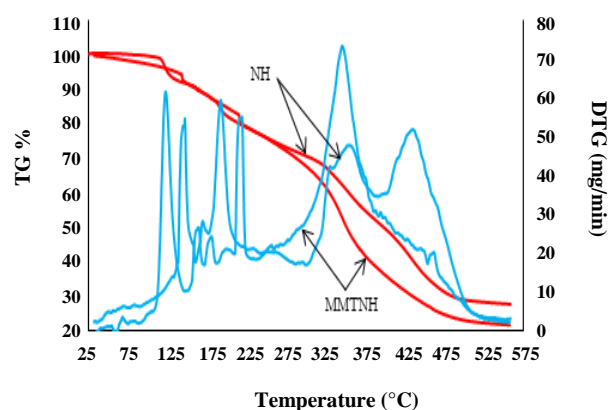

Fig. 1: FTIR spectra of (a) MMTNH and (b) NH.

Fig. 2: TGA and DTG curves of NH and MMTNH.

the morphological conclusions are drawn from SEM image observations

Fig. 3e shows the X-ray diffraction patterns of MMTNH and NH. Note that the diffraction signal is different in the presence and absence of MMT. Diffraction signal of the MMTNH was observed at $2\theta=44.45°$. There was this signal for the MMTNH, but in a way less marked than that of the NH. EDX analyses were carried out to confirm the presence of MMT in the MMTNH sample.

EDX analyses were carried out to corroborate the presence of MMT in the MMTNH sample. An EDX spectrum of the MMTNH is described in Fig. 3f.

The spectrum indicates characteristic peaks of N, O, C and Si elements which support the existence of Si elements (ascribed to MMT) in the MMTNH. This indicates that MMT exists in the MMTNH.

Optimizing the parameters affecting swelling capacity

In this study, the crosslinker, initiator, monomers and MMT amounts were important variables affected on the swelling capacity of the hydrogel, were investigated and systematically optimized.

Fig. 4a demonstrates the effect of AA amount on water uptake of the synthesized hydrogels. Different amounts of AA (2-5 mL) was used, where the maximum
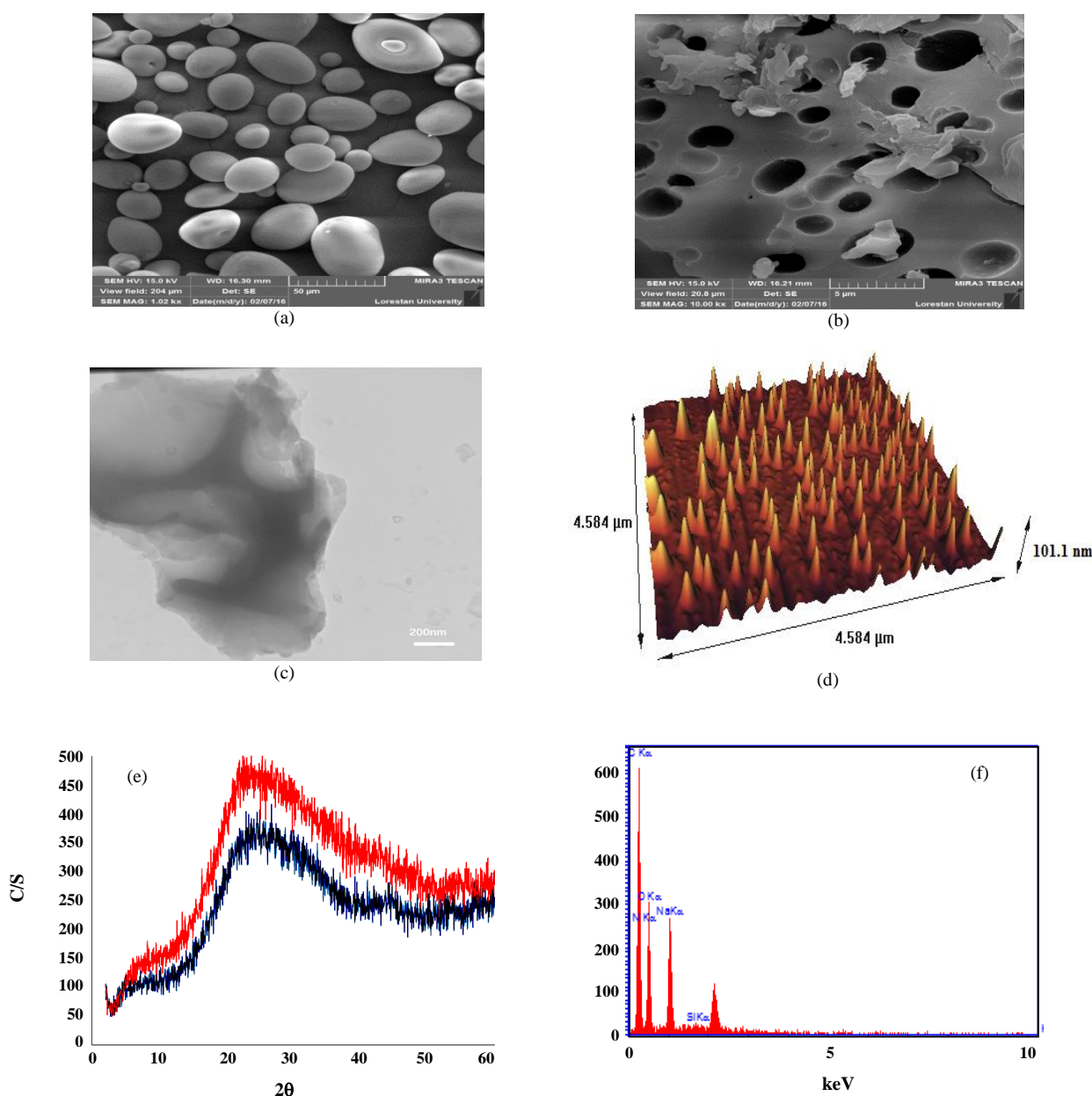
Fig. 3: (a) SEM images of starch, (b) SEM images of MMTNH, (c) TEM image of MMTNH, (d) AFM image of MMTNH, (e) X-ray diffraction patterns of NH and MMTNH and (f) EDX spectrum of MMTNH.

of swelling is achieved at 3 mL of AA amount. By increasing the monomer concentration in the range of 2-5 mL, the swelling capacity is increased initially and then it is decreased. The initial increase in water absorption can be explained by the fact that more AA molecules could be available in the vicinity of the chain starch, which enhances the hydrophilicity of the superabsorbent nanocomposite, and consequently the water absorption is increased. The decreases after the maximum swelling can be attributed to an increase in viscosity of the medium which hinders the movement of free radicals and monomer molecules led to higher graft yield [24].

The effect of AAm monomer amount on water absorption of the MMTNH was investigated by varying the AAm amount from 0.25 to 1.25 g. The maximum absorption was obtained when the AAm monomer amount was 0.75 g. As shown in Fig. 4b, a similar trend was observed with effect AA [25].
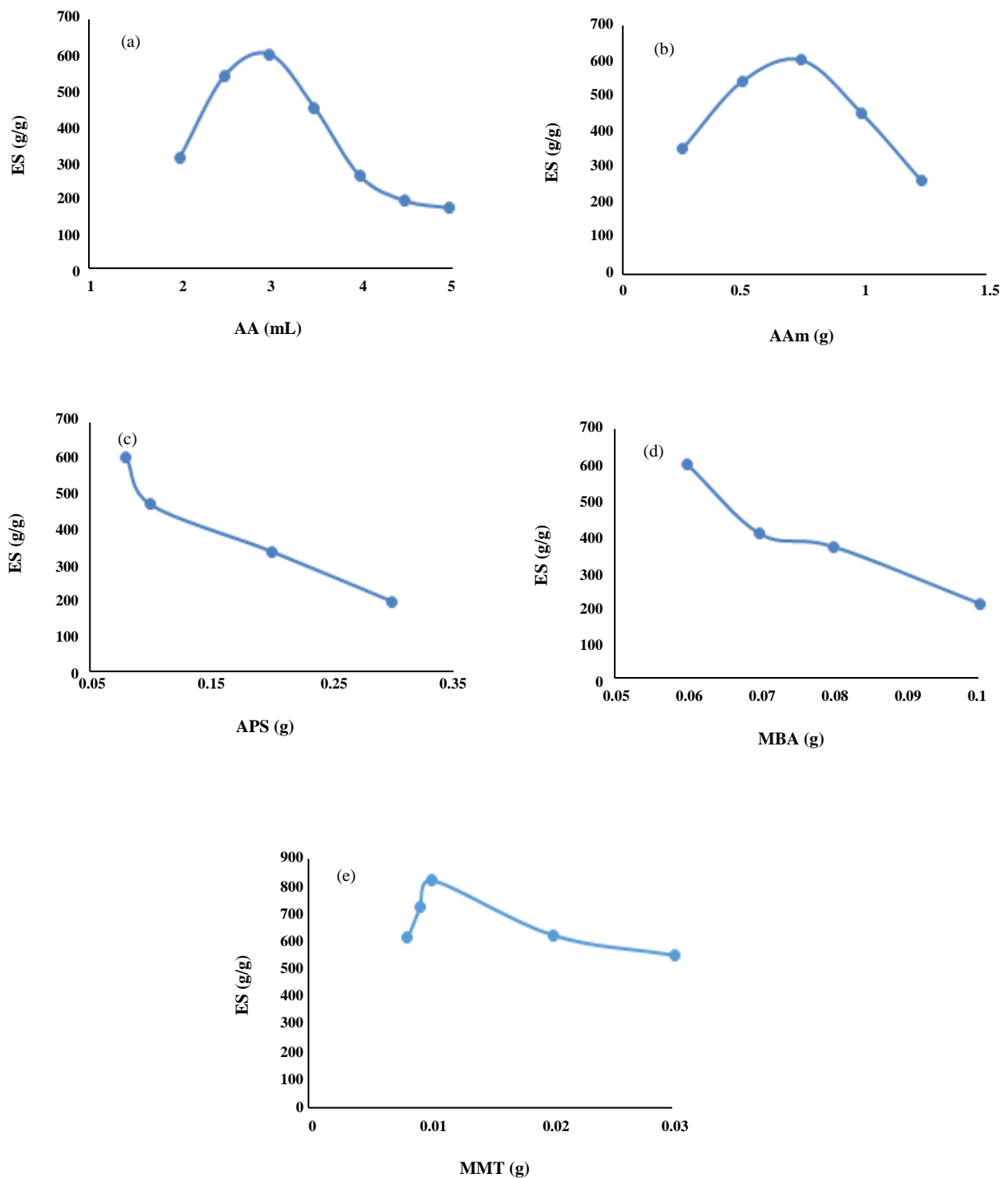
Fig. 4: Fig. 4: Effect of the (a) AA monomer amount (reaction conditions: starch weight: 0.75 g, AAm: 0.75 g, APS: 0.08 g, and MBA: 0.06 g), (b) AAm monomer amount (reaction conditions: starch weight: 0.75 g, AA: 3 mL, APS: 0.08 g, and MBA: 0.06 g), (c) APS initiator amount (reaction conditions: starch weight: 0.75 g, AA: 3 mL, AAm: 0.75 g, and MBA: 0.06 g), (d) MBA crosslinker amount (reaction conditions: starch weight: 0.75 g, AA: 3 mL, AAm: 0.75 g, and APS: 0.08 g), and (e) MMT nanometer base amount (reaction conditions: starch weight: 0.75 g, AA: 3 mL, AAm: 0.75 g, APS: 0.08 g, and MBA: 0.06 g) on equilibrium swelling capacity of the superabsorbent montmorillonite nanocomposite.

Initiator amount is an important swelling-control element. In the next step, the water absorbency was checked as a function of the initiator amount (0.08–0.3 g), whereas the other factors were kept the same (Fig. 4c). Maximum swelling has been obtained at 0.08 g of APS. The decrease in swelling capacity with an increment in initiator, the amount may be ascribed to an increment in the terminating stage reaction by bimolecular collisions, chain termination, and an increment in the cross-link density in turn [26].

It is evident that MBA amount is an important factor influencing water absorbency of the nanocomposite hydrogels and plays a significant role in the formation of the chemically crosslinked network, but its content should be optimized for maximum water absorbency. Fig. 4d shows the influence of the MBA amount from 0.06 to 0.1 g on water absorption of the synthesized MMTNH. It is well known that a higher concentration of MBA increases the extent of crosslinking of the polymeric chains and decreases the free spaces between them; consequently results in a rigid structure that cannot be expanded to hold a large quantity of water.[27].

The influence of MMT amount on water absorbency of the MMTNH was shown in Fig. 4e. Water absorbency in distilled water was increased from 600 g/g in NH to 820 g/g in MMTNH. Maximum swelling has been obtained at 0.01 g of MMT. The -OH of MMT participated in the formation of the MMTNH, which may improve the polymeric network, and increase the water absorbency. Also, MMT has amounted to a lot of cations (dispersed in the polymeric network), that enhances the hydrophilicity nanocomposite. The further decrease in swelling capacity with further increment in MMT amount may be ascribed to, the interaction among MMT, AAm, AA and starch polysaccharide or reduce the free spaces for water in the polymeric network [22].

Environmental sensitivity
Swelling kinetics

Fig. 5 represents the swelling capacities behavior of all the nanocomposite hydrogel samples with different particle sizes in water. The swelling kinetics for the MMTNH is influenced by the size of powder particles. Particles with lower sizes, a higher swelling of water uptake were observed. Initially, the rate of water uptake sharply increases and then begins to level off. The data may be well fitted with a Voigt-based Eq (2) [28]:
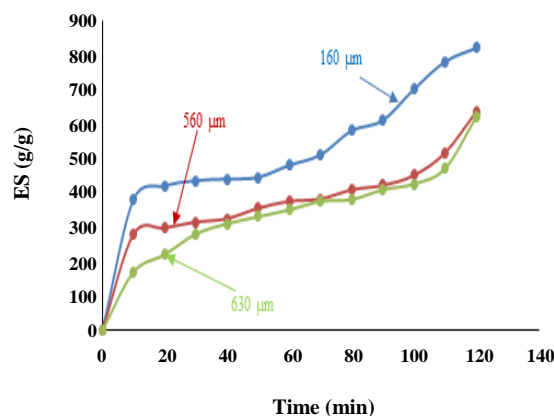

Fig. 5: The swelling kinetics for MMTNH with different particle sizes in distilled water.

$$S_t = S_e \left(1 - e^{-\frac{1}{\tau}} \right) \qquad (2)$$

Where S_t (g/g) is swelling at time t, S_e (g/g) is equilibrium swelling; t (min) is time for swelling S_t, and τ (min) the rate parameter. To calculate the rate parameter using this formula (with a little rearrangement), one can obtain a plot of $\ln(1 - S_t/S_e)$ versus time (t). The slope of the fitted straight line (slope= $-1/\tau$) gives the rate parameter. Since the τ value is a measure of swelling rate (i.e., the lower the τ value, the higher the rate of swelling), it can be used for the evaluation of the rate of water absorbency of hydrogels. The results are summarized in Table 1.

Effect of pH solution on the swelling

The equilibrium swelling of MMTNH hydrogels was measured in solutions with pHs that ranged from 1 to 12 at 25 °C (Fig. 6).

Maximum swelling (850 g/g) was obtained at pH 8. In the pH region from 1 to 3, most of carboxylate groups are in the form of –COOH and the low swelling values of hydrogels can be attributed to the presence of nonionic hydrophilic COOH and –OH groups in the hydrogel network. The swelling ratio increased rapidly as the pH of solutions was increased from 4 to 8. The carboxylate groups become ionized which can lead to high repulsion between ionic groups and consequently higher swelling degree. The growing concentration of OH⁻ outside the hydrogel in the water at pH region from 9 to 12, can decrease

Table 1: Rate parameters (τ) of the MMTNH with various particle sizes.

Particle sizes	τ
160 μm	16.13
560 μm	17.24
630 μm	31.25
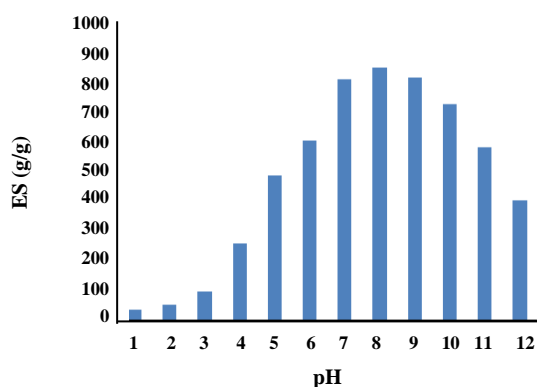
Fig. 6: Swelling dependency of MMTNH on pH.
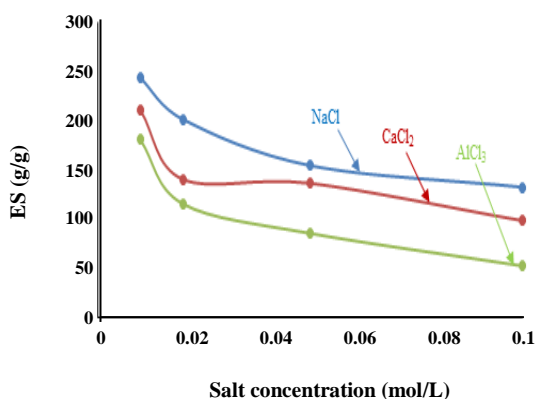
Fig. 7: Equilibrium swelling capacity of MMTNH in different chloride salt solutions in various concentrations.

the osmotic pressure that causes the shrinkage of the hydrogel networks and consequently lower swelling degree [29].

Effect of salt solution on the swelling

In these experiments, the swelling capacity was measured in various salt solutions. The swelling decrease is strongly dependent on the ''type'' and ''concentration'' of salt added to the swelling medium.

The effect of cation type (cations with different radius and charge) on swelling behavior is shown in Fig. 7. With increasing the charge of cation, the degree of crosslinking is increased and swelling is consequently decreased. A decrease in swelling capacity of the hydrogel is attributed to the osmotic pressure difference between the hydrogels and the aqueous phase [30].

There is a well-known relationship between swelling and salt solution concentration that is stated in Eq (3) [31]:

$$\text{Swelling} = K\left[\text{Salt}\right]^{-n} \qquad (3)$$

Where *K* and *n*, are constants for an individual superabsorbent. The *K* value is swelling at a high concentration of salt and the value of n is a measure of the dependence of swelling on salt concentration. The value of n is a measure of salt sensitivity. The K and n values obtained from Fig. 7 are given in Table 2.

Swelling measurements in a mixture of solvents

In the present study, the swelling changes of the optimized composite was examined in mixtures of water and hydrophilic solvents systems. The swelling loss in these mixtures can be explained by the change of the solubility parameter of the solvent−water mixture. Anionic groups are easily solvated by water molecules. However, it is widely restricted in organic solvent−water systems because the organic solvent molecules cannot solvate the anionic groups. As a consequence, the swelling capacities are considerably decreased.

By adding organic solvents to water, the absorption decreased gradually and the swelling behavior of hydrogel in a mixture of water and organic solvents is almost the same. According to the Hildebrand Eq (4), this phenomenon can be attributed to the change of the solubility parameter of the solvent-water mixture [32].

$$\frac{\Delta H_m}{V\Phi_1\Phi_2} = \left(\delta_1 - \delta_2\right)^2 \qquad (4)$$

In Eq (4), ΔH_m is the enthalpy change on mixing of a polymer and a solvent, Φ_1 and Φ_2 are the volume fractions for the solvent and the polymer, V is the whole volume of the solution, and δ_1 and δ_2 are the solubility parameters for the solvent and the polymer, respectively. This equation indicates that to dissolve a polymer in a solvent, the δ values must be close to each other.

Table 2: Parameters (n) and (K) from Voigt Eq for swelling MMTNH in different salt solutions.

Salt	n	K
NaCl	0.091	2.47
CaCl$_2$	0.1	2.39
AlCl$_3$	0.17	2.42

Table 3: Comparison between swelling capacity and parameter (δ) of MMTNH in a mixture of solvents.

Solvent	Water	Methanol-water (40:60)	2-Propanol-water (40:60)	Aceton-water (40:60)
$\delta(or\delta_{mix})$	23.4	19.84	18.64	18
ES (g/g)	810.10	560.10	570.40	584.25

As a consequence, to predict the solubility of a polymer, δ values should be calculated. As the swelling capacity of the synthesized hydrogel in water is maximum, the δ value of water (23.4 (cal/cm^3)$^{1/2}$) can be regarded as its solubility parameter. The solubility parameter for solvent-water mixtures (δ_{mix}) can be calculated using Eq (5) [33]:

$$\delta_{mix} = \delta_1 \Phi_1 + \delta_2 \Phi_2 \qquad (5)$$

Where Φ_1 and Φ_2 are the volume fraction, and δ_1 and δ_2 are the solubility parameters of the two solvents. According to these Eqs. (4 and 5), with increasing of δ_{mix} values toward 23.4, the hydrogel can be highly swollen as in pure water. In other words, the swelling capacity of the hydrogel in the solvent water mixture will be close to that in pure water if δ_{mix} is close to water [34]. The results are summarized in Table 3.

Release studies

To determine the application of MMTNH in release systems, release behavior in different pH were investigated. The release profile from MMTNH hydrogels was studied solutions with different pHs between 3 to 12 by using MB dye (model drug) and shown in Fig. 8. As shown in Fig. 8, the dye released from MMTNH was dependent on the pH solution. The release increases with the increase of pH until pH=8 and then decreases with further raising. Montmorillonite nanocomposite hydrogel due to having carboxylate groups in structure is sensitive to environments with different pH. This behavior of release from MMTNH is justified by the behavior of swelling hydrogel ("Effect of pH solution on the swelling" section). As a result, this type of release can be attributed to the dominant role of the diffusion mechanism for release.

To analyze the release mechanism, a simple semi-empirical equation, presented by *Peppas*, had been adopted (Eq. (6)) [35].

$$\log\left(\frac{M_t}{M_\infty}\right) = \log K + n \log t \qquad (6)$$

Where (M_t/M_∞) = fractional solute release; M_t = mass of solute released at time "t"; M_∞ = mass of solute released at equilibrium; t = time; K = rate constant characteristic of the system and n = transport exponent indicating the release mechanism. The values of K and n are found by fitting the data to the above expression. For matrices with n around 0.45, diffusion is the controlling mechanism for drug release which is simply called Fickian type of diffusion. However, for 0.45 < n < 0.89 an anomalous diffusion behavior is followed that is called non-Fickian type of diffusion and finally for n > 0.89, drug release shows a Case II (relaxation) transport, which indicates a mechanism controlled by polymer relaxation and erosion, involving a relaxing boundary (dry glassy/hydrated rubbery polymer interface) moving into the matrix at an increasing rate. Eq (6) was applied to various stages of diffusion behavior and plots of log (M_t/M_∞) against log t yielded straight lines from which the exponent n and K were calculated from the slope and intercept of the lines.

Fig. 9 shows log (M_t/M_∞) vs. log t curves for MB release from the MMTNH in phosphate buffer with pH=8. As can be seen, n value is 0.92 for MMTNH, a slow controlled mechanism was concluded for MMTNH releasing.
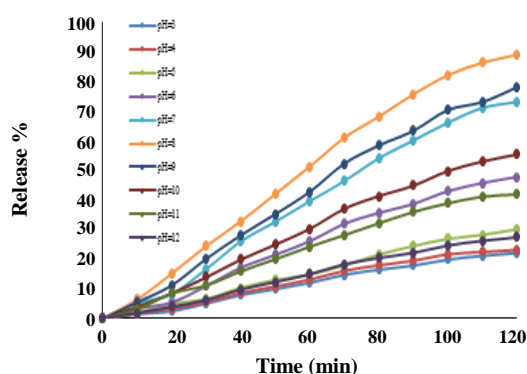
Fig. 8: Effect of pH on MB dye release from MMTNH at 25 °C.

Fig. 9: MB releasing mechanism of MMTNH in buffer with pH=8.

CONCLUSIONS

In the present work, a convenient method for the preparation of a new superabsorbent montmorillonite nanocomposite hydrogel based on poly (acrylic acid-co-acrylamide) grafted onto starch is described.

The optimum conditions for obtaining maximum water absorbency established in the present study are as follows: 0.75 g starch, AA 3 mL, 0.75 g AAm, 0.08 g APS and 0.06 g MBA in the presence of 0.01 g MMT. The product formed was saponified with NaOH and then precipitated more than ethanol. The composite formation was confirmed by Fourier Transform Infrared (FT-IR) spectroscopy and TGA analysis. Studying the surface morphology of hydrogel nanocomposite using SEM showed a highly porous structure for the hydrogel. The dried and finely powdered product showed the maximum water absorbency of 810 g/g. The swelling behavior in different media including pH, salt solution and a mixture of solvents was investigated and a normal behavior was observed. The MMTNH has higher swelling ability and pH-responsivity. We studied the possibility of using a hydrogel as a carrier for controlled drug release. The MB was chosen to model drug compounds that have similar sizes and molecular structures. The response of the prepared nanocomposite against MB dye release at different pHs made this nanocomposite hydrogel suitable for the release in the alkaline environment. To find the origin of different pH-dependent release of MB from MMTNH, the curves for log (M_t/M_∞) vs. log t show a controlled release by polymer relaxation for MMTNH.
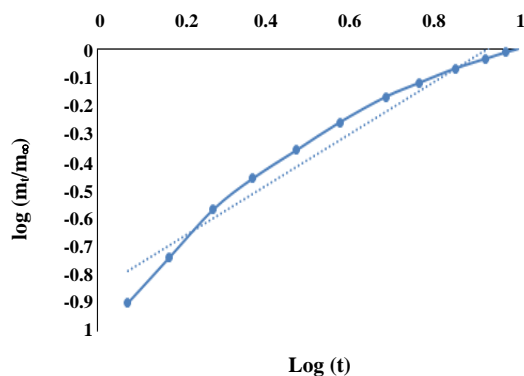
REFERENCES

[1] Fan L-t., Singh S.K., Controlled Release: A Quantitative Treatment, Vol 13, "Springer Science & Business Media" (2012).

[2] Serizawa T., Matsukuma D., Akashi M., Loading and Release of Charged Dyes Using Ultrathin Hydrogels, *Langmuir.,* **21**(17): 7739-7742 (2005).

[3] Van der Linden H.J., Herber S., Olthuis W., Bergveld P., Stimulus-Sensitive Hydrogels and Their Applications in Chemical (micro) Analysis, *Analyst.,* **128**(4): 325-331(2003).

[4] Bennett S.L., Melanson D.A., Torchiana D.F., Wiseman D.M., Sawhney A.S., Next-Generation HydroGel Films as Tissue Sealants and Adhesion Barriers, *Journal of Cardiac Surgery,* **18** (6): 494-499 (2003)

[5] Gupta P., Vermani K., Garg S., Hydrogels: from Controlled Release to pH-Responsive Drug Delivery, *Drug Discovery Today.,* **7**(10): 569-579 (2002).

[6] Qiu Y., Park K., Environment-Sensitive Hydrogels for Drug Delivery, *Advanced Drug Delivery Reviews.,* **53**(3): 321-339 (2001).

[7]   Guilherme M.R., Reis A.V., Takahashi S.H., Rubira A.F., Feitosa J.P., Muniz E.C., Synthesis of a Novel Superabsorbent Hydrogel by Copolymerization of Acrylamide and Cashew Gum Modified with Hlycidyl Methacrylate, *Carbohydrate Polymers.*, **61**(4): 464-471 (2005).

[8] Bardajee G.R., Mizani F., Hosseini S.S., pH Sensitive Release of Doxorubicin Anticancer Drug from Gold Nanocomposite Hydrogel Based on Poly (Acrylic Acid) Grafted onto Salep Biopolymer, *Journal of Polymer Research.*, **24**(3): 24-48 (2017).

[9] Young C-D., Wu J-R., Tsou T-L., Fabrication and Characteristics of polyHEMA Artificial Skin with Improved Tensile Properties, *Journal of Membrane Science.*, **146**(1): 83-93 (1998).

[10] Abusafieh A., Siegler S., Kalidindi SR., Development of Self-Anchoring Bone Implants. I. Processing and Material Characterization, *Journal of Biomedical Materials Research.*, **38**(4): 314-327 (1997).

[11] Mahdavinia G.R., Marandi G.B., Pourjavadi A., Kiani G., Semi-IPN Carrageenan-Based Nanocomposite Hydrogels: Synthesis and Swelling Behavior, *Journal of Applied Polymer Science.*, **118**(5): 2989-2997 (2010).

[12] Zhou C., Wu Q., A novel Polyacrylamide Nanocomposite Hydrogel Reinforced with Natural Chitosan Nanofibers, *Colloids and Surfaces B: Biointerfaces.*, **84**(1): 155-162 (2011).

[13] Zhang Y-T., Zhi T-T., Zhang L., Huang H., Chen H-L., Immobilization of Carbonic Anhydrase by Embedding and Covalent Coupling into Nanocomposite Hydrogel Containing Hydrotalcite, *Polymer.*, **50**(24): 5693-5700 (2009).

[14] Wang Y., Chen D., Preparation and Characterization of a Novel Stimuli-Responsive Nanocomposite Hydrogel with Improved Mechanical Properties, *Journal of Colloid and Interface Science.*, **372**(1): 245-251 (2012).

[15] Satarkar N.S., Hilt J.Z., Hydrogel Nanocomposites as Remote-Controlled Biomaterials, *Acta Biomaterialia.*, **4**(1): 11-16 (2008).

[16] Li P, Dou X-Q., Tang Y-T., Zhu S., Gu J., Feng C-L., Zhang D., Gelator-Polysaccharide Hybrid Hydrogel for Selective and Controllable Dye Release, *Journal of Colloid and Interface Science.*, **387**(1): 115-122 (2012).

[17] Lira L.M., de Torresi S.I.C., Conducting Polymer–Hydrogel Composites for Electrochemical Release Devices: Synthesis and Characterization of Semi-Interpenetrating Polyaniline–Polyacrylamide Networks, *Electrochemistry Communications.*, **7**(7): 717-723 (2005).

[18] Nagai Y., Unsworth LD., Koutsopoulos S., Zhang S., Slow Release of Molecules in Self-Assembling Peptide Nanofiber Scaffold, *Journal of Controlled Release.*, **115**(1): 18-25 (2006).

[19] Bao Y., Ma J., Li N., Synthesis and Swelling Behaviors of Sodium Carboxymethyl Cellulose-g-poly (AA-co-AM-co-AMPS)/MMT Superabsorbent Hydrogel, *Carbohydrate Polymers.*, **84**(1): 76-82 (2011).

[20] Pavlidoua S., Papaspyrides C.D., A Review on Polymer–Layered Silicate Nanocomposites, *Prog. Polym. Sci.*, **33**(12): 1119-1198 (2008).

[21] Mojtaba S., Narmin B.A., Mohammad S.H., Fateme Z., Mostafa Y., Synthesis and Properties of Plasticized Sulfur-Montmorillonite Nanocomposites by Melt-Blending, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **36**(6): 1-9 (2017).

[22] Luo W., Zhang W.A., Chen P., Fang Ye., Synthesis and Properties of Starch Grafted Poly [acrylamide-co-(acrylic acid)]/montmorillonite Nanosuperabsorbent via γ-Ray Irradiation Technique, *Journal of Applied Polymer Science.*, **96**(4): 1341-1346 (2005).

[23] Mohammad K., Ali N., Montmorillonite Nanoparticles in Removal of Textile Dyes from Aqueous Solutions: Study of Kinetics and Thermodynamics, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **36**(6): 127-137 (2017).

[24] Pourjavadi A., Harzandi A., Hosseinzadeh H., Modified Carrageenan 3. Synthesis of a Novel Polysaccharide-Based Superabsorbent Hydrogel via Graft Copolymerization of Acrylic Acid onto Kappa-Carrageenan in Air, *European Polymer Journal.*, **40**(7): 1363-1370 (2004).

[25] Pourjavadi A., Jahromi PE., Seidi F., Salimi H., Synthesis and Swelling Behavior of Acrylatedstarch-g-Poly (Acrylic Acid) and Acrylatedstarch-g-Poly (Acrylamide) Hydrogels, *Carbohydrate Polymers* **79**(4): 933-940 (2010)

[26] Chen J., Zhao Y., Relationship between Water Absorbency and Reaction Conditions in Aqueous Solution Polymerization of Polyacrylate Superabsorbents, *Journal of Applied Polymer Science.,* **75**(6): 808-814 (2000).

[27] Kabiri K., Zohuriaan-Mehr M., Superabsorbent Hydrogel Composites, *Polymers for Advanced Technologies.,* **14**(6): 438-444 (2003).

[28] Omidian H., Hashemi S., Sammes P., Meldrum I., A Model for the Swelling of Superabsorbent Polymers, *Polymer.,* **39**\(26): 6697-6704 (1998).

[29] Elvira C., Mano J., San Roman J., Reis R., Starch-Based Biodegradable Hydrogels with Potential Biomedical Applications as Drug Delivery Systems, *Biomaterials.,* **23**(9): 1955-1966 (2002).

[30] Pass G., Phillips G., Wedlock D., Interaction of Univalent and Divalent Cations with Carrageenans in Aqueous Solution, *Macromolecules.,* **10**(1): 197-201 (1977).

[31] Rosiak JM., Yoshii F., Hydrogels and Their Medical Applications, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms.,* **151**(1): 56-64 (1999).

[32] Jianqi F., Lixia G., Swelling/Deswelling Behavior of Thermally Induced PVA/PAA Hydrogel Fiber in Aqueous Salt Solutions, *Journal of Polymer Materials,* **19**(1): 103-112 (2002).

[33] Pourjavadi A., Bardajee G.R., Soleyman R., Synthesis and Swelling behavior of a New Superabsorbent Hydrogel Network Based on Polyacrylamide Grafted onto Salep, *Journal of Applied Polymer Science.*, *112*(5): 2625-2633 (2009).

[34] Zohuriaan-Mehr M., Motazedi Z., Kabiri K., Ershad-Langroudi A., Allahdadi I., Gum Arabic–Acrylic Superabsorbing Hydrogel Hybrids: Studies on Swelling Rate and Environmental Responsiveness, *Journal of Applied Polymer Science.,* **102**(6): 5667-5674 (2006).

[35] Bardajee G.R., Pourjavadi A., Ghavami S., Soleyman R., Jafarpour F., UV-Prepared Salep-Based Nanoporous Hydrogel for Controlled Release of Tetracycline Hydrochloride in Colon, *J. Photo. Biol.*, **102**(3): 232-240 (2011).