

Preparation of Sodium Carboxymethylcellulose/Poly(methyl acrylate) IPN Hydrogels and Their Application for Adsorption

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ABSTRACT: Sodium carboxymethylcellulose/poly(methyl acrylate) (NaCMC/PMA) interpenetrating polymer networks (IPNs) were prepared by fractional step in 40 wt % ethanol solution with N,N'-methylenebisacrylamide as a crosslinker. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and differential scanning calorimeter were used to characterize the NaCMC/PMA IPN hydrogels and confirm the IPN structure as well. Simultaneously, adsorption of the obtained IPN hydrogels to methylene blue (MB) was also investigated. It was observed that the adsorption of MB onto the hydrogels was mainly dependent on the initial concentration of MB and the pH of the solution. Adsorption rate of MB was much higher in the first 9 h than that in the following period and saturated adsorption amount of MB was 2370 mg/g at the initial MB concentration of 100 mg/L. Moreover, the adsorption capacity of the IPN hydrogels at the neutral pH condition is much higher than those at acid or alkaline pH conditions. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41101.

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INTRODUCTION

Interpenetrating polymer networks (IPNs) are three-dimensional networks, which can be formed from homogeneous or heterogeneous polymers crosslinked in the presence of one another.¹ An IPN consists of two or more polymers, which is obtained when at least one polymer network is synthesized or crosslinked independently in the immediate presence of the other.² Materials formed from IPNs share characteristic properties of each network^{3,4} and now IPN is recognized as a popular way to change the performance of functional materials, having enhanced physical properties and manipulation of device properties as compared with conventional blends of their components.⁵ IPNs are also applied to prepare the composite hydrogels with pH and/or temperature sensitivities from hydrophilic polymers such as polymethacrylic acid (PMAA) or polyacrylic acid and natural macromolecules such as alginate,^{6,7} guar gum,^{8,9} cellulose,^{10,11} and so on.

Hydrogels are structurally loosely crosslinked network, which have the ability to absorb considerable amounts of water or aqueous fluids to form a stable hydrogel,¹²⁻¹⁴ and the absorbed water is hardly removed under some pressure. Owing to these unique characteristics, hydrogels were introduced into the agriculture, medicine for drug delivery systems and diaper indus-

tries decades ago,^{15,16} and then their applications were extended to the fields where an excellent water-holding property was emphasized.¹⁷ Recently, many researchers focus their attentions on hydrogel to develop new applications such as conducting materials, biomaterials, and flocculants. NaCMC is known to be a derivative of cellulose that is abundant, nontoxic, biodegradable and water soluble, it is a very promising raw material available at low cost for the preparation of various functional polymers. NaCMC is easy to form hydrogels owing to a large number of reactive hydroxyl groups in the polymer chain and it is anionic polyelectrolyte with pH sensitivity for carboxyl groups in the molecule.¹ Therefore, hydrogels based on NaCMC have attracted attentions recently to make them very attractive in various areas, such as controlled release, biochemistry, and adsorbent. However, hydrogels from NaCMC alone always show some performance deficiencies such as low mechanical strength and single responsiveness.^{18,19} To meet application requirements, multifunctional hydrogels are expected to be obtained by modifying, grafting, copolymerizing and blending such as IPNs.

It is known that hydrogels have been widely applied in the removal of metal ions and dyes. The composite hydrogels with natural macromolecules for adsorption of dyes are mostly based on the polyacrylamide,^{20,21} PVA,^{22,23} PMAA,²⁴ and other

hydrophilic polymers, whereas few researches are reported based on hydrophobic polymers as far as we know. To combine the hydrophobic polymers such as poly(methyl acrylate) (PMA) with natural macromolecules, it is common to graft the monomer or polymer to the natural macromolecules to obtain the copolymers.²⁵ Valbhav Jain grafted poly(methyl acrylate) onto wood cellulose fibers to prepare superabsorbent hydrogels^{26–28}; Vijay Kumar Thakur developed a proficient way to rapidly synthesize poly(methyl acrylate)-*graft*-cellulose (PMA-*g*-cellulose) copolymers under microwave conditions.²⁹ Liu kun studied on properties of grafted copolymer of corn starch and MA which showed good plasticity and biodegradability.³⁰ However, it is rarely to find researches about blending hydrophobic polymers with natural macromolecules except for the series researches conducted by Nishioka Noboru.^{31–35} As a highly hydrophobic polymer, PMA is difficult to be applied in aqueous systems. However, it is an elastomeric linear polymer, which can reinforce the physical strength of the materials by adding a little amount. In this work, an IPN hydrogel was prepared with NaCMC and PMA by fractional step method to combine the hydrophobic polymer with natural macromolecules, which not only can broaden the application of PMA in aqueous systems but also increase the physical strength of the hydrogels. Moreover, adsorption ability of the IPN hydrogel to methylene blue (MB) was investigated.

EXPERIMENTAL

Materials

NaCMC [molecular weight: 250,000 (DS = 0.9); viscosity: 1500–3100 mPa s] and MB were received from Aladdin. Methyl acrylate (MA) and N,N-Dimethylacetamide (DMAc) were purchased from Tianjin Chemical Factory. N,N'-methylenebisacrylamide (MBA) and Potassium persulfate ($K_2S_2O_8$) were obtained from Sigma-Aldrich. Tetramethylethylenediamine (TMEDA) and ethanol solution were purchased from Shanghai Chongming Industrial Company. All the chemicals were of analytical grade and used as received. Deionized water was used for all the experiments.

Preparation of NaCMC/PMA IPN Hydrogels

NaCMC (0.5 g) was dissolved in 40 wt % ethanol solution by continuously stirring at 80°C till a homogeneous solution was obtained. The solution was degassed by passing nitrogen gas inlet for 30 min. After cooling to ambient temperature, the NaCMC solution was added with 0.5 g of MBA (10% w/w in DMAc) as crosslinking agent and 100 mg of $K_2S_2O_8$ (1% w/w in DMAc) as initiator. The mixed solution was kept for 12 h to complete the crosslinking reaction. The obtained hydrogels were washed for 48 h with frequent replenishment of deionized water to remove any impurities and unreacted species until being transparent, and then freeze-dried for following use.

Freeze-dried NaCMC hydrogel powders (0.5 g) were immersed in 20 mL of 50% (v/v) ethanol solution for 6 h. After that, 1 g MA, 0.8 g MBA, 100 mg KPS, and 80 μ L TMEDA (as an accelerator) were added in sequence and mixed homogeneously. Then the mixture was placed in the oil bath at 80°C and reacted for 12 h. Finally, as-prepared NaCMC/PMA IPN hydrogels were

vacuum-filtrated with a large amount of deionized water and freeze-dried.

Adsorption Experiments

A certain amount of freeze-dried hydrogels were soaked in various concentrations of MB solution (25 mL for effects of pH; 250 mL for initial concentration of MB and adsorption kinetics) for 48 h at 30°C. Adsorption amount of MB can be calculated from the difference between initial and final concentrations using atomic absorption spectrophotometer^{36–38} (Hitachi Z-5000, Japan). The equilibrium adsorption amount of MB was calculated according to the following eq. (1), whereas the adsorption ratio of MB to the initial concentration was calculated according to the following eq. (2):

$$Q_e = (C_0 - C_e)V/W \quad (1)$$

$$R_m = (1 - C_e/C_0) \times 100 \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of MB (mg/L), respectively. V is the volume of the solution (mL) and W is the weight of the dried hydrogels (g).³⁶

CHARACTERIZATIONS

Fourier transform infrared spectroscopy (FTIR) spectral measurements were performed with a Tensor-27 spectrophotometer (Bruker, Germany). Each sample was finely ground with KBr to prepare pellets and spectra were scanned between 400 and 4000 cm^{-1} . Scanning electron microscopy (SEM) micrographs of the freeze-dried hydrogels were recorded by Hitachi S-3700, Japan. Samples were coated with gold on the surface and placed on a copper stub. Differential scanning calorimeter (DSC; Pyris Diamond, Perkin Elmer, Osaka, Japan) was performed on PMA resin and hydrogels. Samples were heated from 0 to 300°C at the heating rate of 10°C min^{-1} in nitrogen atmosphere (flow rate = 25 mL min^{-1}).

RESULTS AND DISCUSSION

Formation and Structure of IPN Hydrogel

Figure 1 is the scheme to describe the formation process of the NaCMC/PMA IPN hydrogels. It is considered that initiator KPS could strongly interact with MBA and NaCMC through ionic interactions.³⁶ At the first step of formation, NaCMC molecule chains intertwined with each other and crosslinked by MBA, thus forming a network structure. Then, the polymerization of MA monomers was carried out in NaCMC network, and the chains propagation reaction was proceeded by radical induced. Meanwhile, the PMA chains attached to the NaCMC chains forming an IPN structure. Figure 2 shows the FTIR spectra of PMA resin, NaCMC hydrogels, and NaCMC/PMA IPN hydrogels. Some characteristic peaks in NaCMC hydrogel spectrum [Figure 2(b)] can be ascribed as: 3434 cm^{-1} for O—H stretching vibration, 1112 cm^{-1} for —C—O—C— symmetric stretching vibration, 1527 cm^{-1} attributed to C—N stretching vibration in the amido bond, 1647 cm^{-1} represents C=O stretching vibration in the crosslinking agent MBA. PMA [Figure 2(a)] has a strong stretching absorption bands at 1730 cm^{-1} attributing to C=O stretching vibration in ester group. It is noted that the band also appeared in NaCMC/PMA IPN hydrogel [Figure 2(c)], indicating that PMA entered into the NaCMC networks

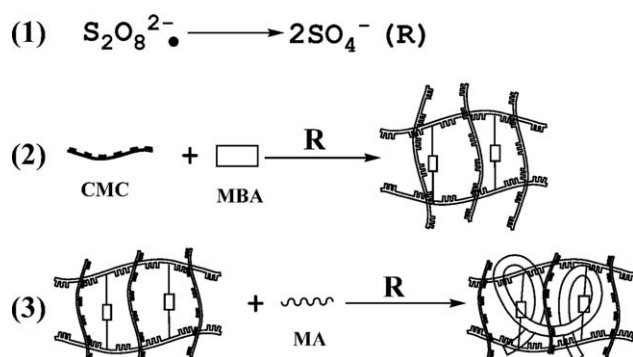


Figure 1. Scheme of the formation process of NaCMC/PMA IPN hydrogels.

successfully. From the spectrum of Figure 2(b,c), the 1527 and 1647 cm^{-1} peak in NaCMC hydrogel shift to 1530 and 1654 cm^{-1} in the NaCMC/PMA IPN hydrogel, respectively. In addition, the bands at 3434 cm^{-1} become broader in NaCMC/PMA IPN hydrogel. There are no new chemical bonds in the IPN hydrogel, which indicates that no chemical reaction between NaCMC and PMA but only PMA chains crossed into the NaCMC networks. All these variations show a convincing evidence of the intermolecular interactions, crosslinking, and good molecular compatibility between NaCMC and PMA.

Network Morphology Analysis

SEM micrographs of NaCMC hydrogel and NaCMC/PMA IPN hydrogels are depicted in Figure 3. It can be clearly observed that the surface of NaCMC hydrogel [Figure 3(a,c)] were held by loose polymeric networks with porous matrix structure; whereas the surface of NaCMC/PMA IPN hydrogels [Figure 3(b,d)] were held by dense and rigid polymeric networks with homogeneous skeleton structure, without showing any obvious macropore. Comparatively, the NaCMC hydrogels present as cotton-style structure while the NaCMC/PMA IPN hydrogels show nest-style structure. This may be due to the shrinking of the matrix at higher extent of crosslinking density, which influ-

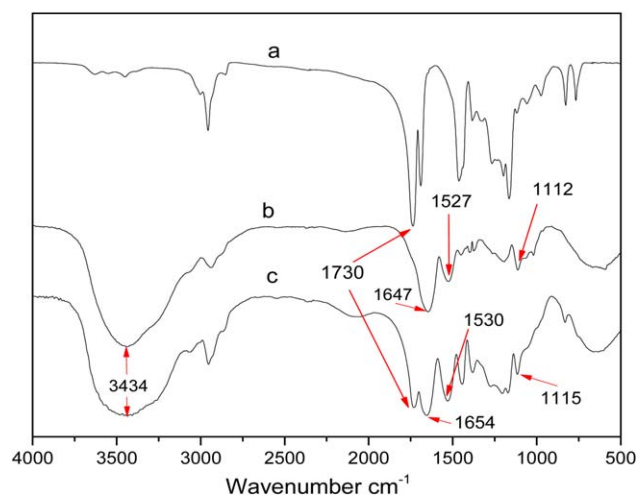


Figure 2. FTIR spectra of PMA (a), NaCMC (b), and hydrogels and NaCMC/PMA IPN hydrogels (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ences rigid matrix structure with almost no porous surface.³⁸ In addition, the IPN hydrogels exhibit better evenness. It implies that incorporating PMA is favorable to improve the surface structure of the IPN hydrogels and the linear PMA macromolecular chains were uniformly dispersed and embedded within NaCMC matrix to form a homogeneous IPN. Moreover, the elasticity modulus of CMC/PMA IPN hydrogel is about 0.3 MPa while CMC hydrogel is hardly to be measured because it was easy to be crushed. The compressive strength of CMC/PMA IPN hydrogel is higher than that of CMC hydrogel owing to a good skeleton interpenetrating structure formed by CMC and PMA.

Thermal Behavior Analysis

DSC curves of NaCMC/PMA IPN hydrogels (a), NaCMC hydrogels (b) and PMA (c) are shown in Figure 4. The PMA resin exhibits a sharp endothermic peak at 53 and 247°C due to polymorphism and corresponding to its melting transition point respectively. However, the characteristic peaks of PMA disappear in the NaCMC/PMA IPN hydrogel due to the endothermic transition of the NaCMC hydrogel polymeric matrix and formation of the rigid IPN matrix structure via chain entanglements. As is shown in Figure 4(a,b), a blunt endothermic peak at 94°C in NaCMC hydrogel shifts to 110°C in NaCMC/PMA IPN hydrogel, which indicates that the introduction of PMA into the NaCMC polymeric network enhance thermal stability of the hydrogel. This may be attributed to the hydrogen-bond interaction between PMA and NaCMC polymeric networks.

Adsorption Properties

Effect of Initial Concentration of MB. To determine the influence of initial concentration of MB on the equilibrium adsorption, the initial concentration of MB varied from 5 to 150 mg/L in 30°C at $\text{pH } 7.0$ solution for 48 h , as illustrated in Figure 5. It shows that the initial concentration of MB solution affected the adsorption capacity of the NaCMC/PMA IPN hydrogel greatly. The adsorption amount increases evidently with the increasing concentration of MB from 5 mg/L to 100 mg/L , thereafter reaches a plateau even for a slight decline, which indicates that MB removal is highly dependent on initial concentration of MB. The maximum adsorption amount is 2370 mg/g when the initial concentration of MB is 100 mg/L , which approaches 1.5 times higher than hydrogels formed by CMC³⁹ or chitosan-g-poly (acrylic acid)⁴⁰ and so on. The larger removal amount of MB at a higher initial concentration of MB is presumably attributed to the active interaction between hydrogel and MB molecules. The findings probably were also due to that an increase in MB concentration could accelerate the diffusion of MB molecules onto the hydrogel as a result of an increase in the driving force of concentration gradient. With the progress of adsorption, the availability of adsorption sites of the hydrogel got diminished⁴⁰ and the adsorption-desorption reached dynamic balance, leading the adsorption amount to be constant or even a slight decline. As is also shown, the adsorption ratio (R_m) decreases with the increase of the initial concentration of MB, which is consistent with the results of the adsorption amount.

Effect of pH. The pH of MB solution is a very important factor for the MB removal, which cannot only change the surface

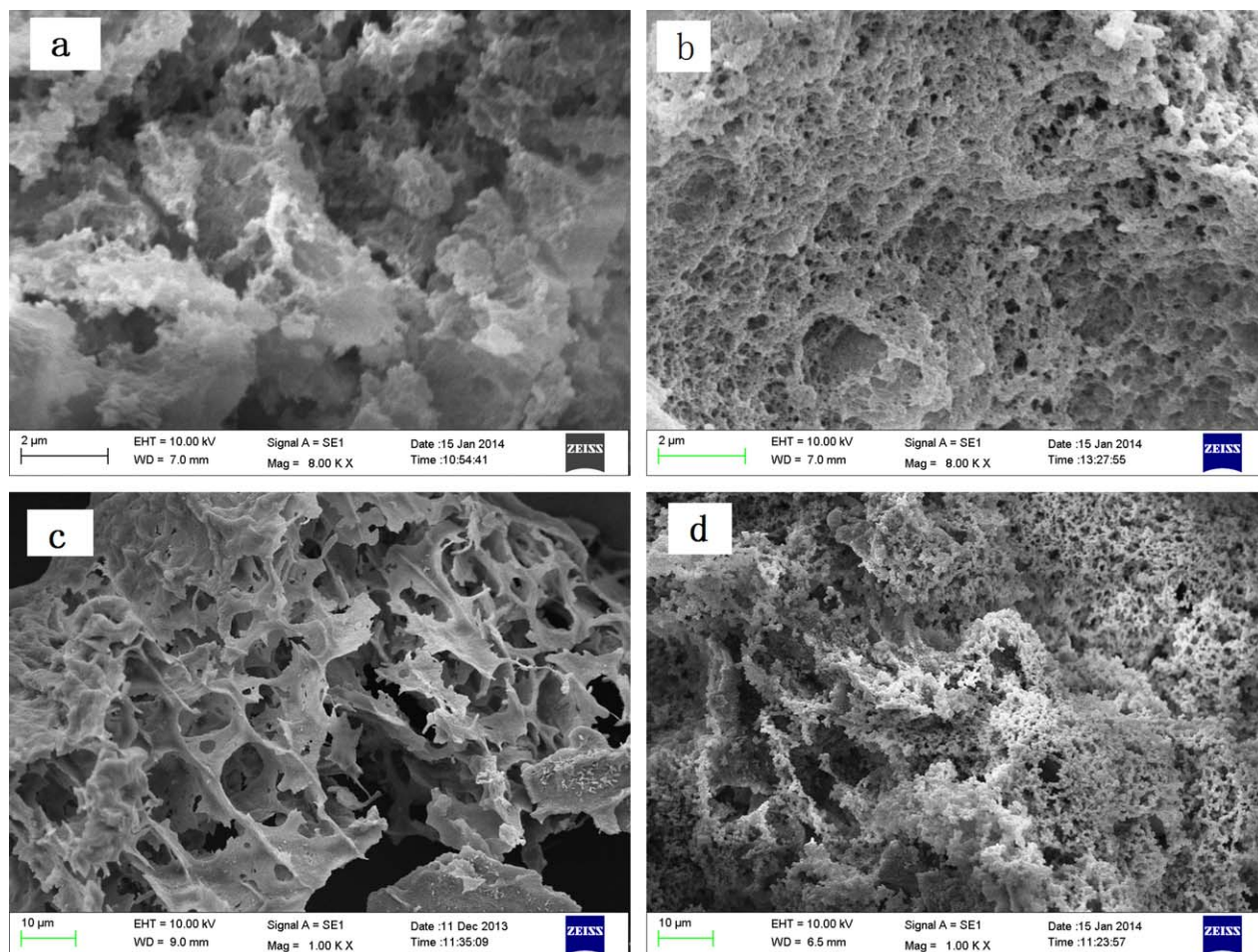


Figure 3. SEM images of NaCMC hydrogels (a and c) and NaCMC/PMA IPN hydrogels (b and d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

charge of the NaCMC/PMA IPN hydrogel, but also can promote or depress the ionization of the hydrogel and MB.⁴⁰ Figure 6(a) shows the effect of pH on MB equilibrium adsorption amount of the NaCMC/PMA IPN hydrogels and Figure 6(b)

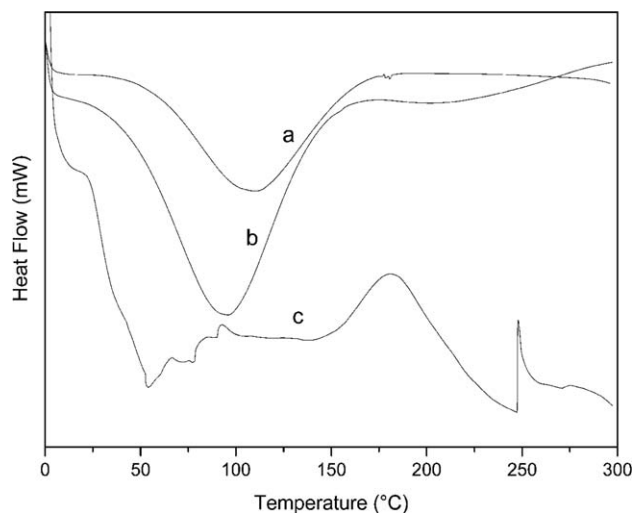


Figure 4. DSC curves of NaCMC/PMA IPN hydrogels (a), NaCMC hydrogels (b), and PMA (c).

shows the adsorption behavior over time at various pH. The equilibrium adsorption amounts of NaCMC/PMA IPN hydrogels at the neutral pH condition is much larger than those at acid or alkaline conditions, which indicates that neutral condition is advantage for MB adsorption onto NaCMC/PMA IPN hydrogels. The results may be attributed to the following

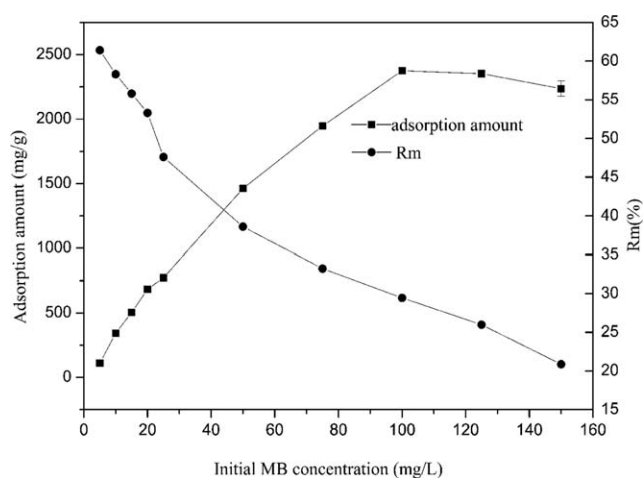


Figure 5. Effect of initial concentration of MB on adsorption.

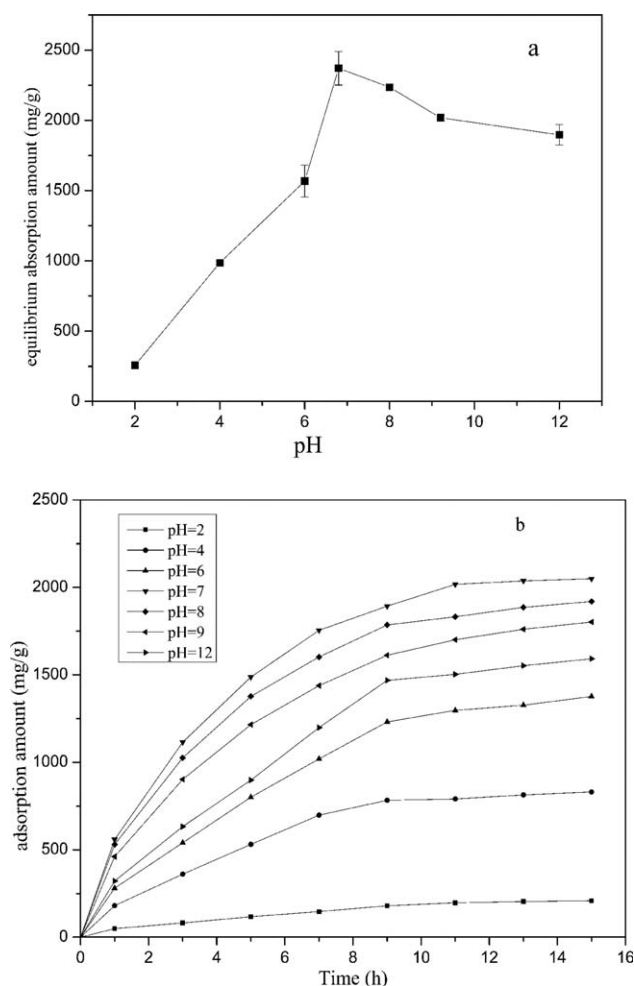


Figure 6. Effect of pH on MB adsorption at 30°C (initial concentration of MB = 100 mg/L).

reasons. At low pH, most of the carboxyl groups of hydrogels exist in the form of $-\text{COOH}$ owing to the pK_a for carboxylic acid is about 4.6, therefore the electrostatic attraction between

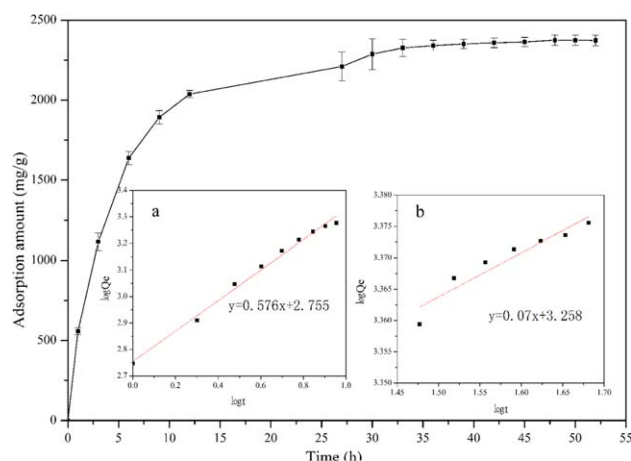


Figure 7. Adsorption kinetics curves of MB (initial concentration of MB = 100 mg/L, 30°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

carboxyl and the MB molecules disappeared which reduced the adsorption amount of MB. At high alkaline pH, more hydroxyls and carboxylate radical occurred, whereas the ion strength in the solution also increased substantially and strong ionic atmosphere was around carboxylate radical as a shield against the attraction between the hydrogel and MB. At neutral pH, both factors are beneficial to adsorption, which may enhance electrostatic attraction and the adsorption capacity for MB of hydrogel. Moreover, the adsorption amount increases nearly linearly with the elongation of adsorption of time at pH 2.0 and 12.0 in the first 9 h while not showing at pH 7.0. It maybe mainly related to physical adsorption of pores in NaCMC/PMA IPN hydrogels at pH 2.0 and 12.0, while there are both chemical and physical adsorptions at pH 7.0.

Adsorption Kinetics Model. To investigate the adsorption kinetics behavior of NaCMC/PMA IPN hydrogels, the adsorption data were simulated using Bangharm equation [eq. (3)]:

$$\log Q_e = \log m + k \log t \quad (3)$$

where Q_e (mg/g) is MB adsorption amount of dry hydrogel, k is adsorption rate constant, and m is physical property parameter. Figure 7 shows adsorption amount versus adsorption time till reaching saturation adsorption. Figure 7(a,b) reflect adsorption amount via adsorption time at various time interval from the beginning to 9 h and 30 h to 48 h, respectively. The results confirm that the adsorption kinetics model of NaCMC/PMA IPN hydrogels to MB obey Bangharm equation. The adsorption amount of the NaCMC/PMA IPN hydrogels to MB increases rapidly with time going on, and reaches the maximum adsorption amount at 48 h. After that, there is no further adsorption with prolonged time, so the equilibrium time is 48 h in this work for the adsorption of MB onto as-prepared NaCMC/PMA IPN hydrogels. Furthermore, the adsorption rate in the first 9 h is higher than that from 30 to 48 h, which indicates the adsorption process mainly conducted within the first 9 h.

CONCLUSION

In this work, novel IPN hydrogel from NaCMC and PMA was prepared via fractional step method in ethanol solution to provide control of their properties and to expand the hydrogels' applicability. Structure, surface morphology, thermal stability, and adsorption behavior to MB of NaCMC/PMA IPN hydrogels were investigated. NaCMC/PMA IPN hydrogels exhibit dense and rigid polymeric network with homogeneous skeleton structure and uniform holes. The compressive strength of CMC/PMA IPN hydrogel is higher than that of CMC hydrogel. Moreover, NaCMC/PMA IPN hydrogels show a higher thermal stability than NaCMC hydrogels. The maximum adsorption amount of the IPN hydrogel to MB reaches 2370 mg/g in this work and the adsorption amount is influenced with initial concentration of MB, adsorption time and pH. The saturated adsorption occurs when the initial concentration of MB is 100 mg/L, the adsorption process mainly precedes within the first 9 h and lasts for 48 h. Furthermore, excessive acid or alkaline conditions impede the adsorption behavior, which is determined by the electrostatic attraction between carboxyl groups of the hydrogel and MB. Based on the results of this work, NaCMC/PMA IPN

hydrogel is a superabsorbent for cationic dyes, which is suitable for adsorption application in neutral medium.

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