

Frontal Polymerization Preparation of Poly(acrylamide-co-acrylic acid)/Activated Carbon Composite Hydrogels for Dye Removal

Shengfang Li,¹ Hongping Huang,¹ Min Tao,² Xianli Liu,² Tao Cheng³

¹School of Chemical and Material Engineering, Hubei Polytechnic University, Huangshi, People's Republic of China

²Hubei Key Laboratory of Mine Environmental Pollution Control and Remediation, Hubei Polytechnic University, Huangshi, People's Republic of China

³School of Civil Engineering, Hubei Polytechnic University, Huangshi, People's Republic of China

Correspondence to: S. Li (E-mail: lishengf_@163.com)

ABSTRACT: A series of poly(acrylic acid-co-acrylamide) (PAA)/activated carbon (AC) composite hydrogels were rapidly prepared via frontal polymerization (FP). It was found that an increase in the concentration of AC caused an increase in the front velocity (V_f) and the highest front temperature (T_{max}). It may be attributed to that AC particles could increase the liquid viscosity of reaction mixture and remain the reaction heat during FP. The Fourier transform infrared and scanning electron microscopy (SEM) confirmed that AC particles had entered the hydrogel network, and many spherical AC particles with an average diameter of 0.5–1 μm had been dispersed homogeneously in the PAA hydrogel matrix. The swelling behavior showed that the equilibrium swelling values of hydrogels increased when the concentration of AC particles increased. Adsorption studies showed that incorporation of AC particles into PAA hydrogel matrix could increase the sites of interaction between the hydrogels and crystal violet molecules and result in an increase of adsorption capacities of hydrogels toward dyes. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3737–3745, 2013

KEYWORDS: frontal polymerization; composite hydrogel; adsorption; dye

Received 6 November 2012; accepted 6 February 2013; published online 4 March 2013

DOI: 10.1002/app.39139

INTRODUCTION

In recently, the wastewater caused by dyes has become a current problem for many counties. The discharges of dyes and their break down products into receiving waters cause toxic effects to aquatic life.^{1–3} Thus, it is very important to remove dyes from industrial effluents before they are mixed up with unpolluted water.^{4–7} A number of methods such as physical–chemical and biological treatment technologies have been used on this purpose. Among all the treatment technologies, adsorption is considered as one of the most promising techniques that have been employed for the removal of dyes from water.⁵ The adsorbents are often inorganic or organic materials such as activated carbon (AC), montmorillonite, zeolites, biomass, modified chitosan, and polymeric hydrogels.^{6–10} Among above adsorbents, AC is widely used as adsorbents owing to its low production costs, extensive surface area, and excellent adsorption properties. However, despite so many advantageous features, the aggregation of powered AC under various experimental conditions and, secondly, pollution after adsorption limited its application as adsorbents in wastewater treatment.¹¹

Frontal polymerization (FP) is a rapid polymerization method to convert monomer into polymer in a localized reaction zone

under the level-to-level regime that spreads over the entire volume, as shown in Figure 1. This method has been successfully explored for synthesis of polymers since it was first discovered by Chechilo and Enikolopyan.^{12–16} As a consequence, many reports concerning hydrogels prepared by FP have exponentially increased. Recently, Feng and coworkers prepared multilayer nanocomposite hydrogels with high mechanical strength by FP.¹⁷ Alzari et al. synthesized stimuli responsive hydrogels via FP from *N*-isopropylacrylamide and *N*-vinylcaprolactam.¹⁸ Chen and coworkers reported a facile strategy for quickly fabricating poly(2-hydroxypropyl acrylate–vinyl versatate) amphiphilic hydrogels toward removal of toxic solvents by FP.¹⁹ Very recently, in our previous research,²⁰ poly(acrylic acid–acrylamide) hydrogels were investigated to be prepared by FP technique and used for cationic dyes removal.

In the present study herein, new poly(acrylic acid-co-acrylamide) (PAA)/AC composite hydrogels were rapidly prepared via FP for removal of dye from aqueous solution. Micro- and nano-scales of AC particles were rapidly embedded into the PAA hydrogels by simple FP technique to avoid aggregation and, secondly, pollution of AC particles after dye adsorption process. It was expected that micro- and nano-scales of AC

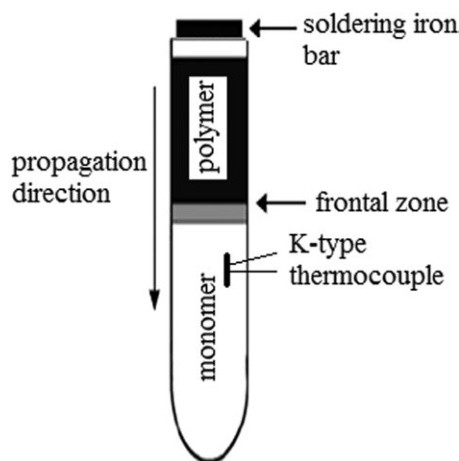


Figure 1. Schematic of propagation front of the PAA/AC composite hydrogels prepared by FP.

particles could enhance the adsorption capacities of hydrogels toward dye. Therefore, the effects of AC particles on the front velocity and the highest front temperature were discussed. The effects of AC particles, pH values of solutions, and other factors on swelling and adsorption properties of PAA/AC composite hydrogels were investigated in detail.

EXPERIMENTAL

Materials

Acrylic acid (AAc) was purchased from Tianjin Chemical Reagent Co. (Tianjin, China) and was distilled before use. Acrylamide (AM), potassium persulfate (KPS), *N,N'*-methylenebisacrylamide (MBA), dimethyl sulfoxide (DMSO), and crystal violet (CV) were purchased from Shanghai Reagent Co. (Shanghai, China). AC was purchased from Chengdu Kelong Chemical Reagent Co. (Chengdu, China). The Brunauer, Emmet and Teller (B.E.T.) surface area and pore volume of AC are $909 \text{ m}^2 \text{ g}^{-1}$ and $0.47 \text{ cm}^3 \text{ g}^{-1}$, respectively. The average diameter of particles is in the range of $0.5\text{--}1 \text{ }\mu\text{m}$. All the reagents were of analytical grade and used as received without any further purification.

Frontal Polymerization Preparation of PAA/AC Composite Hydrogels

Firstly, the appropriate amount of AC particles was sonicated in DMSO and mixed with AAc, AM, MBA, and KPS. Then, the mixture was placed for 5 min and became homogenized black without stratification. Then, it was poured into a glass test tube (10 mL; 12.8 mm diameter). In order to monitor the temperature change, a K-type thermocouple connected to a digital thermometer was immersed into the mixture at about 3 cm from the bottom of the tube. The filled tube was clamped into a holder 1 cm from the top of the tube and kept at ambient temperature. The upper side of the mixture was heated by a soldering iron until the hot propagating front commenced. After the completion of the reaction, the sample was removed from the tube and cut into small pieces and immersed in deionized water over 3 days to dissolve soluble materials. The end composite hydrogel products were dried in vacuum at 50°C to a constant weight and stored for further use. The feed composition for FP samples was listed and designed as FP n in Table I.

Velocity and Temperature Measurements

The front velocities were confirmed by measuring the front position as a function of time. A straight line of the front position versus time indicated an occurrence of a pure free-radical FP. Temperature profiles were determined by measuring the temperature at a fixed point as a function of time, using a K-type thermocouple, and converted to spatial ones using front velocities. After the completion of the reaction, the samples were cooled to room temperature and removed from the tube for further investigation.

Characterization of PAA/AC Composite Hydrogels

Fourier transform infrared (FTIR) spectroscopy was used to confirm the structure of composite hydrogels. The composite hydrogel samples were analyzed on a Bruker EQUINOX FTIR spectrophotometer in the region of $400\text{--}4000 \text{ cm}^{-1}$. Before the measurements, the dried composite hydrogel samples were crushed down (KBr, pellet). Morphology of xerogels was observed by scanning electron microscope (SEM; JSM-5610LV) with an acceleration voltage of 10 kV. The equilibrium swollen gels were frozen by liquid nitrogen for 6 h, then freeze-dried, and fractured. The fractured specimens were covered with gold vapor, and then the morphology of the fractured surface of the dry hydrogel was observed by SEM.

Swelling Studies of PAA/AC Composite Hydrogels

The swelling properties of the as-prepared composite hydrogels were performed by gravimetric analysis. Briefly, the dry composite hydrogel was immersed in the swelling medium at 25°C . At regular time intervals, the gels were removed from the medium; the weight of the swollen composite hydrogel was determined after the removal of the surface water through blotting with filter paper. The measurements were continued until the weight of hydrogels reached a constant value. The swelling ratio was calculated by the following equation:

$$\text{Swelling\%} = [(W_t - W_0)/W_0] \times 100 \quad (1)$$

where W_t is the mass of the swollen hydrogels at t , and W_0 is the initial mass of dry hydrogel. Some parameters (i.e., diffusion characteristics) were calculated using swelling data. All of the experiments were triplicated.

Adsorption Studies of PAA/AC Composite Hydrogels

For the adsorption of hydrogels, the hydrogels were immersed in 50 mL of $10\text{--}40 \text{ mg L}^{-1}$ dye CV solution. Adsorption experiments were carried out at 25°C , in magnetically stirred (160

Table I. Feed Composition in FP

| Samples | AAc/AM (wt/wt) | MBA (wt %) | KPS (wt %) | AC (g mL ⁻¹) |
|---------|-------------------|---------------|---------------|-----------------------------|
| FP0 | 3 : 7 | 1 | 0.1 | 0 |
| FP1 | 3 : 7 | 1 | 0.1 | 0.002 |
| FP2 | 3 : 7 | 1 | 0.1 | 0.005 |
| FP3 | 3 : 7 | 1 | 0.1 | 0.007 |
| FP4 | 3 : 7 | 1.2 | 0.1 | 0.007 |
| FP5 | 7 : 7 | 1 | 0.1 | 0.002 |

rpm) cylindrical glass vessels, in batch conditions. The sample was stirred with dye solution under the experimental conditions described above, and the residual dye concentration was determined by a UV–visible spectrophotometer at λ_{max} (nm) = 598 nm at regular time intervals. The dependence of adsorption capacities on time was determined, and the adsorption kinetics was investigated in detail. All of the experiments were triplicated. The amounts of dye adsorbed on the hydrogel at time t , q_t (mg g^{-1} dried hydrogel), were determined according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where V is the solution volume (L), m is the weight of dried hydrogel (g), and C_0 and C_t are the CV concentrations at initial and indicated time (mg mL^{-1}), respectively. When the adsorption of hydrogels reached equilibration at equilibrium time t , the dye concentration at equilibrium time should be noted as C_e , and the equilibrated amounts of CV adsorbed on the composite hydrogels should be noted as q_e .

RESULTS AND DISCUSSION

FP and the Effect of Concentration of AC Particles

The polymer/activated composite hydrogels were prepared by FP in the presence of AC particles. In order to prevent AC particles from setting down during FP, AC particles were firstly sonicated in DMSO and then mixed with AAc, AM, and initiator to carry out FP experiments. Figure 2 shows a representative time series of visual images illustrating the constant-speed propagation of the polymerization front of the PAA/AC composite hydrogels. Obviously, a clearly interface between the polymeric composite and homogeneous mixture composed of unreacted monomers and AC particles could be seen. The upper white layer was PAA/AC composite, and the lower black layer

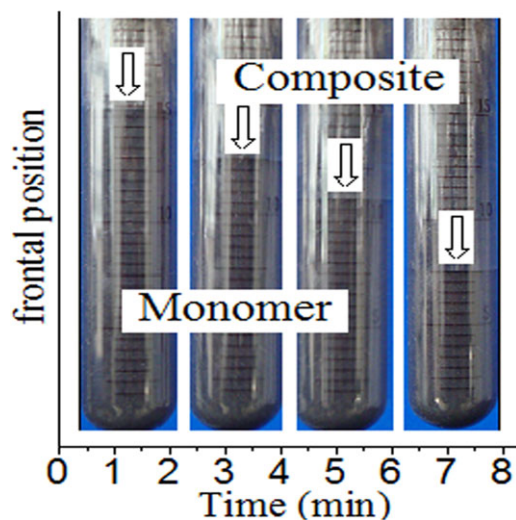


Figure 2. Images acquired in temporal sequence of a self-propagating polymerization front. Initial conditions: KPS = 0.1 wt %, [AAc]/[AM] = 3/7, [AC] = 0.005 g mL^{-1} , MBA = 1 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

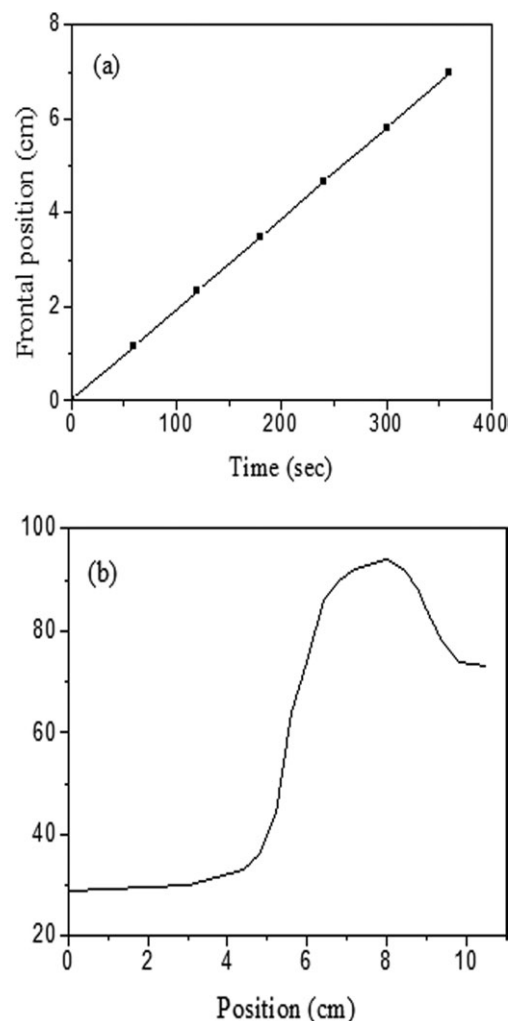


Figure 3. Typical front velocity (a) and temperature (b) profile of PAA/AC composite hydrogel prepared by FP. Initial conditions: KPS = 0.1 wt %, [AAc]/[AM] = 3/7, [AC] = 0.005 g mL^{-1} , MBA = 1 wt %.

was the mixture containing unreacted monomer and AC particles. After FP, it was not observed that AC particles aggregated at the bottom of the tube. This may be due to the rapid polymerization of monomers, which was also one of the advantages of FP. It was also found that the front propagation occurred at a constant velocity with almost no bubbles, which was the same as that of pure monomers (AAc and AM) without AC particles reported previously.²⁰ However, the front velocity of the former was slower than the latter.

One of the key features in pure FP without simultaneous spontaneous polymerization (SP) is a constant front velocity.^{12–16} Figure 3(a) shows the typical profile for the front position versus time; it was found that the experimental data were well fitted by a straight line, meaning that FP propagated at constant velocity and a self-sustaining front was obtained. The typical temperature profile obtained during the FP experiments as shown in Figure 3(b), in less than 2.5 cm, the temperature increased 60°C, and T_{max} was 96°C. Due to the constant temperature value in the region far from the incoming hot front,

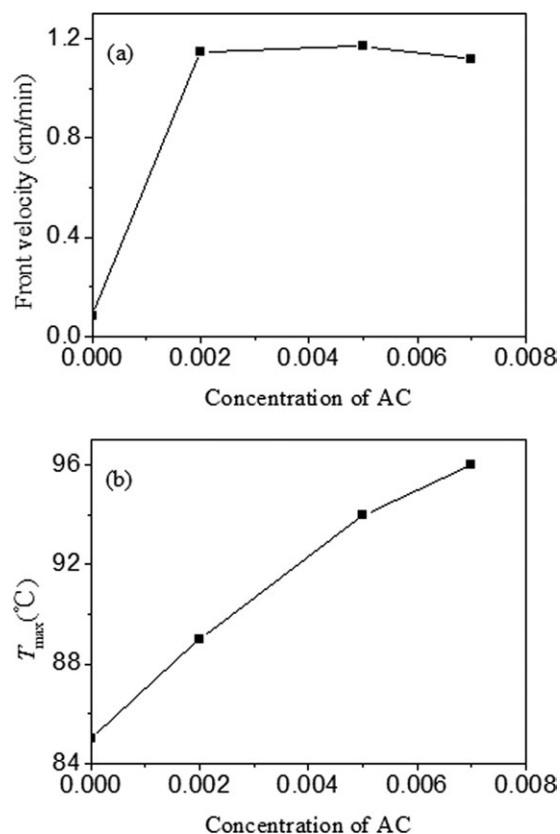


Figure 4. Effect of concentration of AC particles (see FP0, FP1, FP2, and FP3 in Table I) on frontal velocity (a) and front temperature (b).

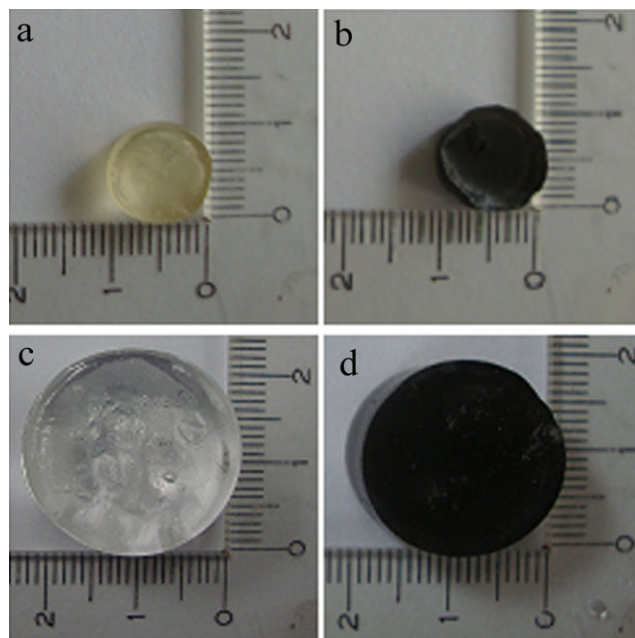


Figure 5. Digital camera images of dry PAA (a), PAA/AC composite (b), water-swollen PAA (c), and PAA/AC composite (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

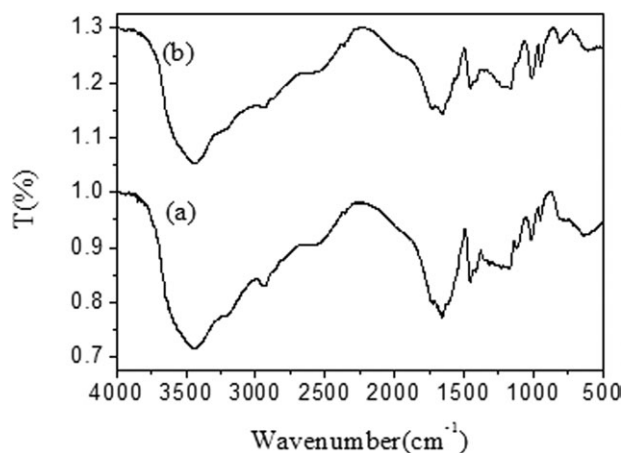


Figure 6. FTIR spectrum of pure PAA (a) and PAA/AC composite (b) hydrogels prepared by FP.

there was a horizontal part of the curve, indicating SP was not occurring simultaneously.¹²

In order to investigate the effect of concentration of AC particles on FP, different V_f [Figure 4(a)] and T_{\max} [Figure 4(b)] were obtained with different concentrations of AC particles. As shown in Figure 3 (or see FP0, FP1, FP2, and FP3 in Table I), it can be seen that V_f values increased as the concentration of AC particles increased, ranging from 0.08 to 1.17 cm min⁻¹. The increase in the concentration of AC particles also caused the increase in T_{\max} from 85 to 96°C in agreement with V_f from 0.08 to 1.17 cm min⁻¹. This may be attributed to that AC particles could increase the liquid viscosity of reaction mixture and remain the heat in FP experiments.

In addition, the content of MBA also played an important role in FP experiments. When the content of MBA was raised from 1 to 1.2 wt %, a sudden increment of T_{\max} was observed, with values going from 96 to 102°C. It seemed that high content of

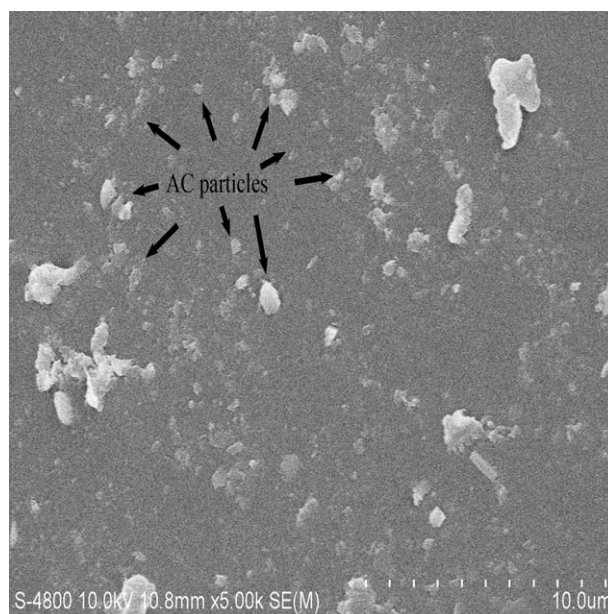
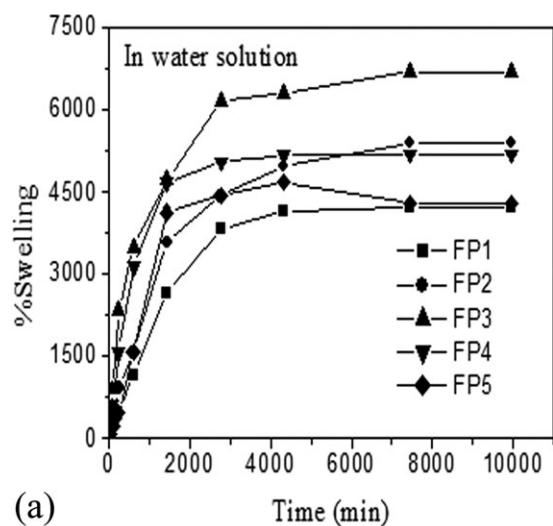
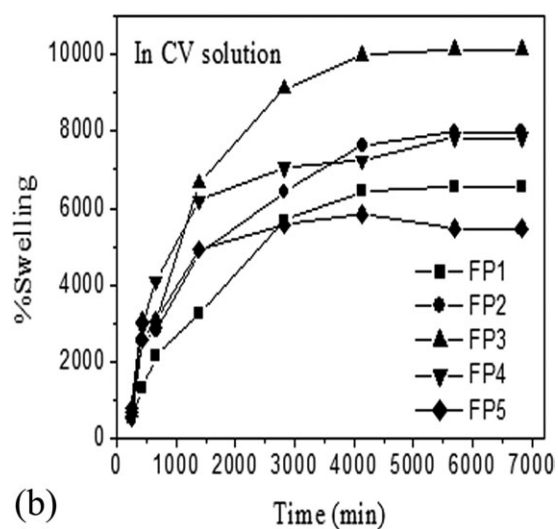


Figure 7. SEM images of FP2 hydrogel.



(a)



(b)

Figure 8. Swelling kinetics of PAA/AC composite hydrogels prepared by FP in water and CV solutions at pH 7.0, respectively.

MBA could increase the cross-linking of monomers, thus increased the liquid viscosity of reaction mixture and remained the reaction heat in the FP experiments. Interestingly, high content of MBA and AC particles could suppress “fingering” phenomenon effectively, and the highly homogeneous compact composite hydrogels could be obtained.¹²

Table II. Variation of the Swelling and Diffusion Parameters of PAA/AC Composite Hydrogels in Water and CV Solutions at pH 7.0

| Samples | In water | | In CV solution | |
|---------|----------|----------|----------------|----------|
| | <i>k</i> | <i>n</i> | <i>k</i> | <i>n</i> |
| FP1 | 0.3832 | 0.4663 | 0.2344 | 0.6056 |
| FP2 | 0.0843 | 0.7750 | 0.1958 | 0.6307 |
| FP3 | 0.3045 | 0.6662 | 0.5714 | 0.5595 |
| FP4 | 1.2533 | 0.6698 | 0.2046 | 0.6881 |
| FP5 | 0.2544 | 0.5381 | 0.2033 | 0.7717 |

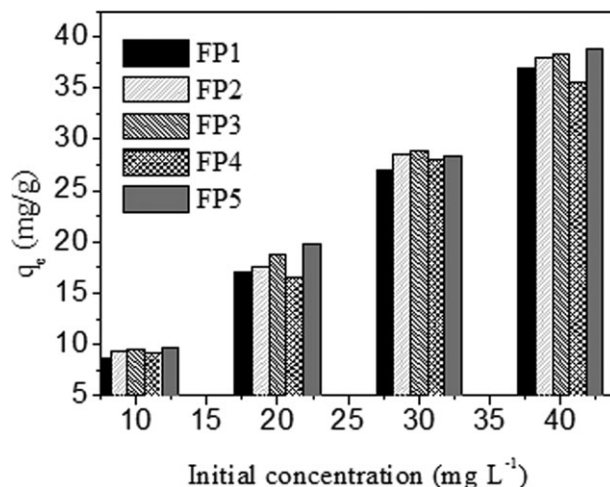


Figure 9. Effect of the initial concentration of dye on CV adsorption of composite hydrogels.

Characterization of PAA/AC Composite Hydrogels

Figure 5 shows the digital camera images of dry and water-swollen PAA and dry and water-swollen PAA/AC composites, respectively. As shown in Figure 5, the pure PAA hydrogel was white, whereas the PAA/AC composite hydrogel was black. All PAA/AC composite hydrogels like pure PAA hydrogel obtained via FP, were highly homogeneous and had good water adsorption. This high homogeneity of PAA/AC composite hydrogels mainly resulted from the rapid conversion reaction of monomers into polymer via the FP technique, which effectively limited or avoided the occurrence of AC precipitation during FP.

As shown in Figure 6, for both the pure PAA and PAA/AC composite hydrogels, the absorption peaks at 2926 and 1459 cm^{-1} were the stretching and bending vibrations of $-\text{CH}_2-$ groups, respectively. The absorption peak at 3000–4000 cm^{-1} corresponding to the $-\text{NH}_2$ and $-\text{OH}$ groups could be observed in each one. Comparing with FTIR spectra of PAA/AC composite hydrogel and pure PAA hydrogel, it was found that there was an

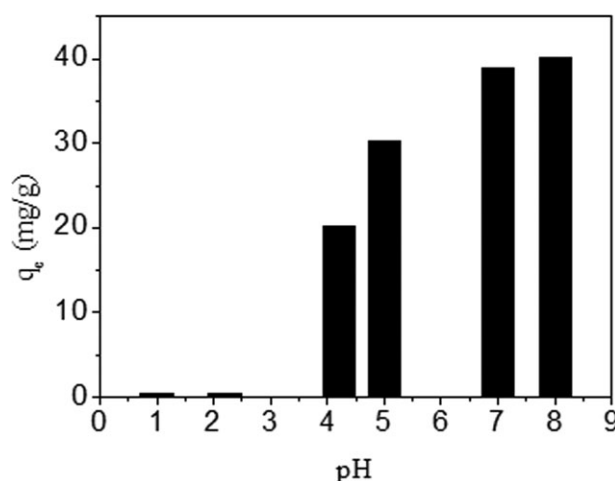


Figure 10. Effect of the pH of solutions on CV adsorption of FP5 composite hydrogel.

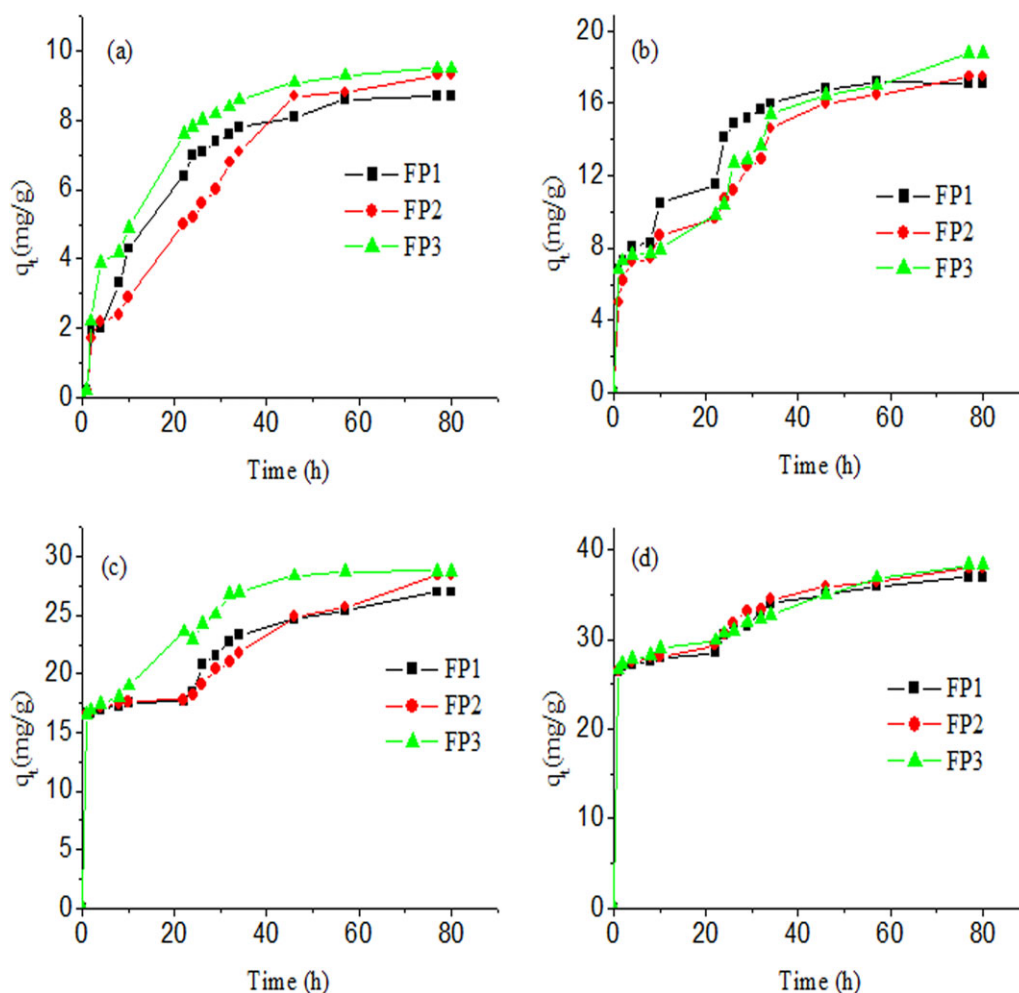


Figure 11. Effect of concentration of AC particles on CV adsorption. (a) CV solution: 10 mg L^{-1} , (b) CV solution: 20 mg L^{-1} , (c) CV solution: 30 mg L^{-1} , and (d) CV solution: 40 mg L^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

obvious decrease in the intensity in region $3000\text{--}4000\text{cm}^{-1}$ and $1500\text{--}1700 \text{ cm}^{-1}$ in PAA/AC composite hydrogel due to the presence of AC. Figure 7 displays the representative SEM micrographs of typical FP2 hydrogel. As shown in Figure 7, it was observed that many spherical AC particles with an average diameter of $0.5\text{--}1 \mu\text{m}$ dispersed homogeneously in the hydrogel matrix. This homogeneous microstructure may be favorable for dye adsorption.

Swelling and Diffusion of PAA/AC Composite Hydrogels

To use the PAA/AC composite hydrogels prepared by FP for removal of dye from aqueous solution, the swelling kinetics of these hydrogels in water and CV solutions (pH 7.0) were investigated, respectively. As shown in Figure 8, it can be seen that the swelling behaviors of hydrogels in water and CV solution were similar to each other, and the swelling values of hydrogels in CV solutions were somewhat higher than those in water. The reason was that the CV molecules could interact with the negative charges of PAA/AC composite hydrogel. The interaction increased the swelling values of hydrogels. In addition, in both CV and water solutions, the equilibrium swelling values of PAA/AC composite hydrogels decreased in the following order: $\text{FP3} > \text{FP2} >$

FP1 . In other words, the equilibrium swelling values of PAA/AC composite hydrogels increased when the AC concentration increased from 0.002 to 0.007 g mL^{-1} . In addition, in water solution, the equilibrium swelling values of PAA/AC composite hydrogels decreased in the following order: $\text{FP5} > \text{FP1}$, while, in CV solution, $\text{FP5} > \text{FP1}$. The main reason may be that the content of AAc in FP5 is higher than that in FP1. Higher is the content of AAc, more is the hydrophilicity of hydrogel. Thus, the swelling ratio of FP5 is higher than that of FP1 in water. However, in CV solution, More CV molecules could interact with the negative charges of PAA/AC composite hydrogel. This interaction may prevent water molecules diffusing into the hydrogels. So, the swelling ratio of FP5 is lower than that of FP1 in CV solution.

The swelling curves of the PAA/AC composite hydrogels in Figure 8 were also used to determine the nature of the diffusion of water into hydrogels by the following simple equation:

$$F = M_t/M_\infty = kt^n \quad (3)$$

where M_t and M_∞ are the amounts of equilibrium water uptake at time t and the maximum water uptake, respectively. k is a proportionality constant, and exponent n describes the type of diffusion

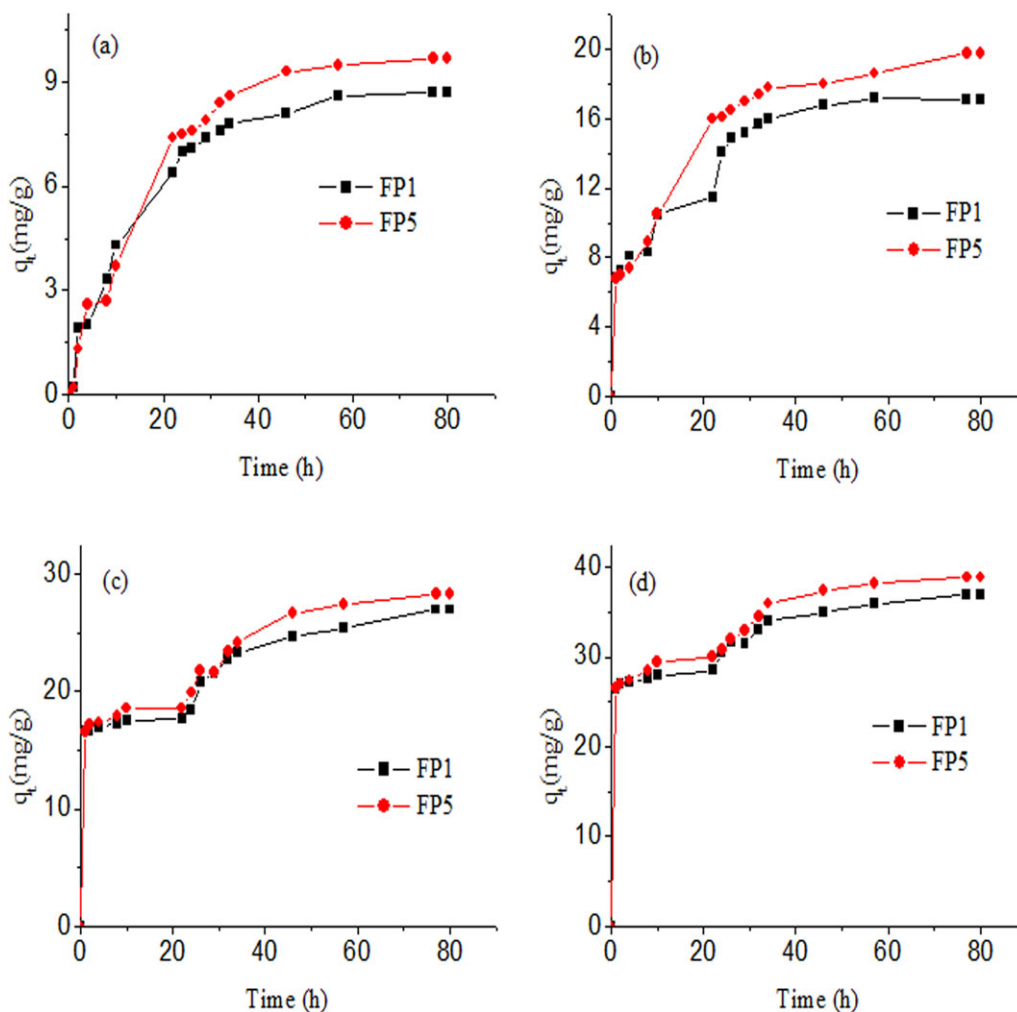


Figure 12. Effect of the ratio of AAc and AM on CV adsorption. (a) CV solution: 10 mg L⁻¹, (b) CV solution: 20 mg L⁻¹, (c) CV solution: 30 mg L⁻¹, and (d) CV solution: 40 mg L⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mechanism.²¹ A plot of $\ln M_t/M_\infty$ vs. $\ln t$ was used to calculate n and k from the slope and intercept. This equation is applicable to the initial stages of swelling and only yields straight lines up to nearly 60% of the maximum amount of absorption water. The exponents n and k were calculated from the slope and intercept of the lines, and the results are given in Table II. From Table II, for FP1, FP2, FP3, FP4, and FP5 hydrogels, the values of n in water were 0.4633, 0.7750, 0.6662, 0.6698, and 0.5381, respectively. Furthermore, the values of n in CV solution were 0.6056, 0.6307, 0.5595, 0.6881, and 0.7717, respectively. It can be found that all values of n were in the range from 0.5 to 1. This indicated that the diffusion of PAA/AC composite hydrogels followed the non-Fickian transport mechanism,²¹ which was also explained as a consequence of the slow relaxation rate of the PAA chains. Different values of n indicated that CV molecules could also interacted with the ionized carboxyl groups on the relaxed PAA chains in different degrees due to the presence of AC particles.

Effect of the Initial Concentration of Dye on CV Adsorption

In order to further investigate the adsorption capacities of PAA/AC composite hydrogels in CV solution, all PAA/AC composite

hydrogels were placed in different concentrations of CV solutions ($C_0 = 10, 20, 30,$ and 40 g L^{-1} , respectively) at pH 7, and the equilibrated adsorption amount is determined in Figure 9. It is clearly seen that, for all PAA/AC composite hydrogels, the equilibrated amounts of CV adsorbed on the composite hydrogels increased with an increase of initial CV concentration. This is attributed to the fact that the increase in the driving force of the concentration gradient with higher initial CV makes more CV molecules penetrate into the inner of composite hydrogels and interact with the PAA chains.²⁰

Effect of pH of Dye on CV Adsorption

As stated above, since FP5 composite hydrogel exhibited the highest increment of equilibrated adsorption amount and high adsorption capacity; therefore, FP5 composite hydrogel was selected as a typical example to study the effect of pH. Namely, FP5 composite hydrogel was placed in CV solutions with different pH values, and the adsorption experiments were investigated with pH values between 2.2 and 8.0. As shown in Figure 10, a dramatic increase in CV adsorption was observed when pH increased from 2.2 to 4.2 and reached a plateau when

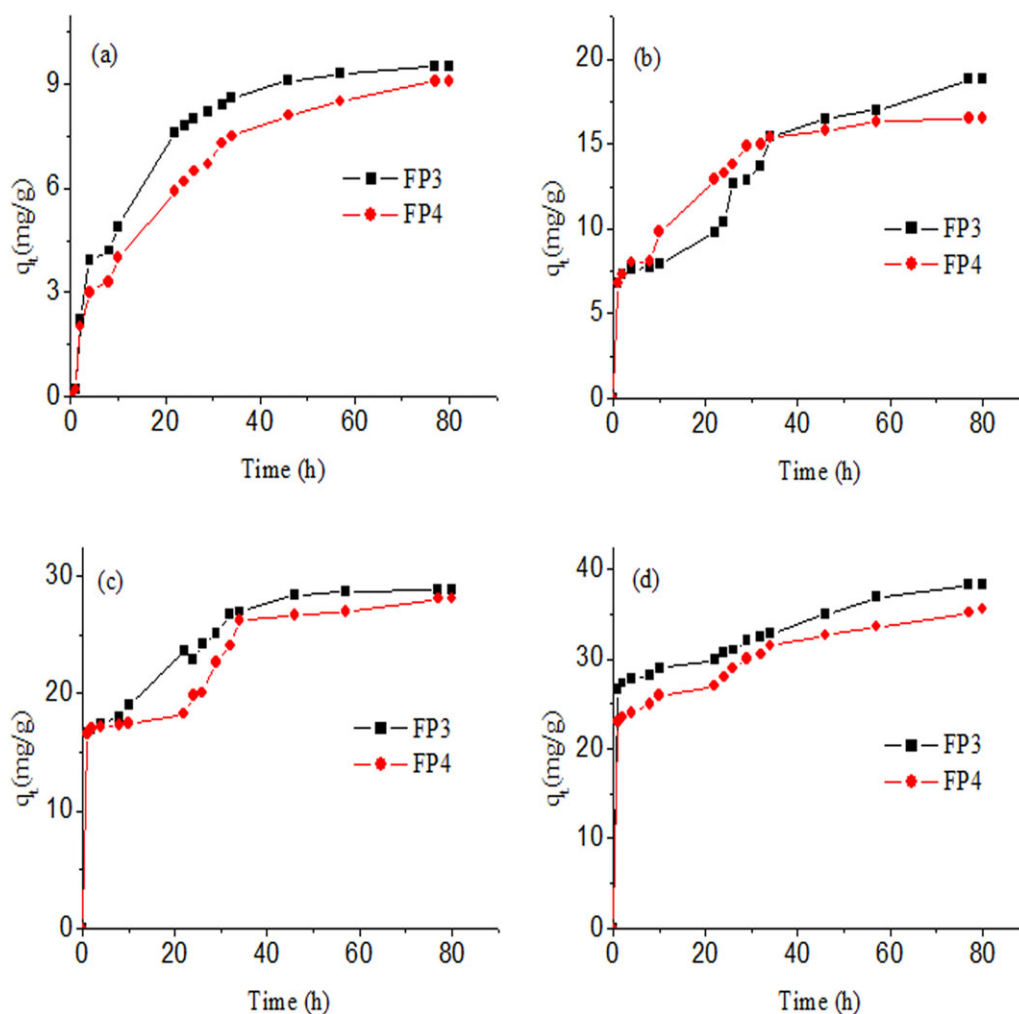


Figure 13. Effect of the content of BMA on CV adsorption. (a) CV solution: 10 mg L^{-1} , (b) CV solution: 20 mg L^{-1} , (c) CV solution: 30 mg L^{-1} , and (d) CV solution: 40 mg L^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pH increased to 8. This may be attributed to the ionization behavior of carboxylic groups (the pK_a of poly(acrylic acid) is ~ 4.28).²² At acidic pHs, the hydrogel was in a shrinkage status because of the existence of hydrogen bonding between the carboxylic and amide groups of the polymer chains in the composite hydrogel. CV molecules are not easy to diffuse into the composite hydrogel. Thus, the adsorption capacity of the composite hydrogel was very low at acidic pHs. While, at basic pHs, the carboxylic groups of composite hydrogel are mostly ionized and the composite hydrogel was in an expansion status due to electrostatic repulsion forces among the ionized carboxylic groups. CV molecules are easy to diffuse into the composite hydrogel and interacted with the CV molecules, which resulted in increasing sites of interaction between CV and composite hydrogel.

Effect of Concentration of AC Particles on CV Adsorption

Figure 11 shows the effect of concentration of AC particles on the adsorption kinetics of hydrogels in different concentrations of CV solutions at pH 7. For all composite hydrogels, the adsorption amount of CV increased to a maximum (the equi-

brated adsorption amount) gradually with the increase of time in different initial concentrations of dye (i.e., $C_0 = 10, 20, 30,$ and 40 mg L^{-1} , respectively). Comparing FP1, FP2, and FP3, the equilibrated adsorption amount (q_e) of PAA/AC composite hydrogels decreased in the following order (i.e., $C_0 = 40 \text{ g L}^{-1}$): FP3 ($q_e = 38.3 \text{ mg g}^{-1}$) > FP2 ($q_e = 38 \text{ mg g}^{-1}$) > FP1 ($q_e = 37.0 \text{ mg g}^{-1}$). That is to say, the CV adsorption capacities of the composite hydrogels increased with the increase in the concentration of AC particles. This may be explained that more AC particles increased the sites of interaction between the hydrogels and CV molecules.

Effect of the Ratio of AAc and AM and the Content of MBA on CV Adsorption

Figures 12 and 13 also show the effect of the ratio of AAc and AM and the content of MBA on the adsorption kinetics of hydrogels in different initial concentrations of CV solutions (i.e., $C_0 = 10, 20, 30,$ and 40 mg L^{-1} , respectively). Compared with FP1, the equilibrated adsorption amount of FP5 ($q_e = 38.9 \text{ mg g}^{-1}$) was much higher than that of FP1 ($q_e = 37.0 \text{ mg g}^{-1}$) when the initial concentration of CV solutions was 40 mg L^{-1} .

This meant that higher content of AAc in the composition led to higher adsorption capacity. This increase originated from the fact that there were more poly(acrylic acid) units in PAA/AC composite hydrogels. Therefore, on one hand, more ionized carboxylic groups increased the electrostatic repulsion forces, and the composite hydrogels were in highly swelling status in this case. So, it is very easy that the CV molecules diffuse into the inner of composite hydrogels and interact with hydrogel through electrostatic interaction. On the other hand, more ionized carboxylic groups also enhanced the electrostatic interaction sites between the hydrogels and CV molecules. On the contrary, comparing with FP3 ($q_e = 38.3 \text{ mg g}^{-1}$) and FP4 ($q_e = 35.6 \text{ mg g}^{-1}$), it is apparent that an increase in the degree of cross-linking led to a decrease of adsorption capacity.

CONCLUSIONS

In this work, highly homogeneous PAA/AC composite hydrogels were rapidly prepared by FP in the presence of micro- and nano-scales of AC particles. The front velocity and front temperature provided direct evidence that only pure FP occurred. The rapid conversion reaction of monomer into polymeric hydrogels via the FP could effectively avoid the precipitation of AC particles. The increase in the concentration of AC particles caused the increase in front velocity (V_f) and the highest front temperature (T_{max}). The incorporation of AC particles into the hydrogel matrix may enhance the swelling and adsorption properties of hydrogels in CV solutions. Adsorption experiment results showed that the PAA/AC composite hydrogels prepared by FP had higher adsorption capacities than that of pure PAA hydrogels.

ACKNOWLEDGMENTS

The authors are grateful to the science research project of Hubei Provincial Department of Education (D20123001 and Q20114401) and Hubei Key Laboratory of Mine Environmental Pollution Control and Remediation, Hubei Polytechnic University (Grant No. 2012101) for the financial support on this work.

REFERENCES

- Beydilli, M. I.; Pavlostathis, S. G.; Tincher, W. C. *Water. Sci. Technol.* **1998**, *38*, 225.
- Şolpan, D.; Torun, M.; Güven, O. *J. Appl. Polym. Sci.* **2008**, *108*, 3787.
- Karcher, S.; Kornmuller, A.; Jekel, M. *Water. Res.* **2002**, *36*, 4717.
- Üzümlü, O. B.; Kundakci, S.; Durukan, H. B.; Karadağ, E. *J. Appl. Polym. Sci.* **2007**, *105*, 2646.
- Li, S.; Liu, X.; Zou, T.; Xiao, W. *Clean—Soil Air Water* **2010**, *38*, 378.
- Li, S.; Liu, X.; Huang, W.; Li, W.; Xia, X.; Yan, S.; Yu, J. *Polym. Adv. Technol.* **2011**, *22*, 2439.
- Singh, T.; Singhal, R. *J. Appl. Polym. Sci.* **2012**, *125*, 1267.
- Singh, V.; Sharma, A. K.; Sanghi, R. *J. Hazard. Mater.* **2009**, *166*, 327.
- Dögan, M.; Alkan, M. *Chemosphere* **2003**, *50*, 517.
- Mostafa, K. M.; Samarkandy, A. R.; El-Sanabary, A. A. *J. Appl. Polym. Sci.* **2010**, *118*, 2728.
- Karadağ, E.; Üzümlü, O. B.; Saraydın, D. *Eur. Polym. J.* **2002**, *38*, 2133.
- Pojman, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6284.
- Frulloni, E.; Salinas, M. M.; Torre, L.; Mariani, A.; Kenny, M. *J. Appl. Polym. Sci.* **2005**, *96*, 1756.
- Chekanov, Y.; Pojman, J. A. *J. Appl. Polym. Sci.* **2000**, *78*, 2398.
- Zhou, J.; Tang, W. Q.; Wang, C. F.; Chen, L.; Chen, Q.; Chen, S. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 3736.
- Sanna, R.; Sanna, D.; Alzari, V.; Nuvoli, D.; Scognamiglio, S.; Piccinini, M.; Lazzari, M.; Gioffredi, E.; Malucelli, G.; Mariani, A. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 4110.
- Qin, X.; Zhao, F.; Liu, Y.; Feng, S. *Eur. Polym. J.* **2011**, *47*, 1903.
- Alzari, V.; Monticelli, O.; Nuvoli, D.; Kenny, J.; Mariani, A. *Biomacromolecules* **2009**, *10*, 2672.
- Yu, C.; Zhou, J.; Wang, C. L.; Chen, S. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 2000.
- Li, S.; Zhang, H.; Feng, J.; Xu, R.; Liu, X. *Desalination*, **2011**, *280*, 95.
- Ritger, P. L.; Peppas, N. A. *J. Control. Rel.* **2005**, *102*, 37.
- Li, S.; Li, H.; Yang, Y.; Yang, X.; Xu, H. A. *J. Appl. Polym. Sci.* **2007**, *106*, 3792.