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Two-step synthesis of polyacrylamide/polyacrylate interpenetrating network hydrogels and its swelling/deswelling properties

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Abstract A two-step polymerization technique is introduced to synthesize polyacrylamide/polyacrylate interpenetrating network (PAM/PAC IPN) hydrogels. The swelling ratio of the IPN hydrogel increases with the increase of the PAC content in PAM/PAC, and is smaller than the traditional PAM or PAC superabsorbents. A non-Fickian mechanism is observed in the swelling process, and the swelling changes from non-Fickian mechanism to Fickian mechanism with the increase of polyacrylate dosage in the hydrogel. The IPN hydrogel has typical pH-sensitivity and on–off effect. The deswelling properties and methyl orange dye removal are carried out based on the chelation of the carboxylic/carboxylate groups on the hydrogels with multivalent cations in solution. The hydrogel is expected to be used in the removal of heavy metal ions and dyes.

Introduction

Superabsorbent polymers, such as polyacrylamide (PAM) and polyacrylate (PAC), have a typical three-dimensional (3D) network structure with a suitable crosslinking density [1, 2]. Not only can it absorb a large amount of water to form a stable hydrogel but also the absorbed water is hardly removed under pressure. About three decades ago [3], superabsorbent polymers were introduced into the agriculture and diaper industries, and then their applications were extended to other industries where an excellent water holding property was of prime importance. Based on superabsorbent polymers, some kinds of superabsorbent hydrogels have been researched, many biomedical and technological applications such as artificial implants, contact lens, pharmaceutical, biosensors, and metal ions reclamation have been resolved and novel conducting hydrogel have been developed [4].

Environmental pollutants in water, caused by the waste products of industry increase the need of novel hydrogel materials with the purpose of removing and separating toxic heavy metal ions and dyes through adsorption, complexation, and ion exchange mechanism [5]. The hydrogels containing amide, amine, carboxylic acid, and ammonium groups, can bind heavy metal ions and dyes through the polar functional groups, and be used as good absorbents for water purifications [6, 7].

Polyacrylamide (PAM) and polyacrylate (PAC) are typical superabsorbent polymers; however, the mechanical strength of single PAM or PAC is feeblish, which cannot meet the application requirement as a water treater [8, 9]. In this paper, to improve the mechanical strength of single PAM or PAC, a PAM/PAC with interpenetrating network (IPN) hydrogel was synthesized by using a simple two-step polymerization technique. The swelling and deswelling behaviors of PAM/PAC IPN hydrogels are investigated. The applications in metal ions and dye removals are discussed. Owing to the interpenetrating network structure and functional groups, PAM/PAC hydrogel is expected to have good application in heavy metal ions and dye removals.

Experimental

Materials

Acrylic acid (AA) monomer from Sigma Chemicals was distilled under reduced pressure prior to use. Acrylamide

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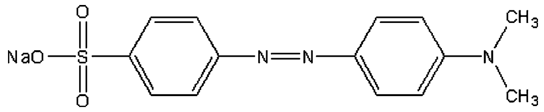

Scheme 1 The structure of MO molecule

(AM) monomer was used as received. Potassium hydroxide was used to neutralize acrylic acid monomer to needed neutralization degree and produce acrylate (AC). Ammonium peroxydisulfate (APS) was a radical initiator for the synthetic reaction of PAM and PAC. *N,N′*-methylene bisacrylamide (NMBA), as a crosslinker for the synthesis of PAM/PAC IPN hydrogel, was purified by recrystallization from 66 wt. % ethanol/water solution. Hydrochloric acid and potassium hydroxide were used for adjusting the pH values of solution medium. Methyl orange (MO, Scheme 1) was used as a drug model. Ca(II), Cu(II), Fe(III) ions from $CaCl_2$, $CuSO_4$, and $FeCl_3$ solutions were used as a medium for the release of absorbed MO. The above materials were all purchased from Shanghai Chemical Reagents Co., China.

Synthesis of PAM/PAC IPN hydrogel

Ten grams of acrylamide (AM) was dissolved in 10 mL of distilled water. Under nitrogen atmosphere and stirring, the AM solution was heated to 80 °C in a water bath for 10 min, and then the initiator (0.03 g, $m_{APS}/m_{AM} = 0.003$) was added. Under stirring, the first polymerization reaction AM carried out for a few minutes until viscosity of the reactant solution becomes 140 mPa s. A 10 mL mixed solution consisting of crosslinker, AA and AC in a desired neutralization degree was poured into the above prepolymerization system, and the same initiator (0.03 g) was added again. Under a nitrogen atmosphere and stirring, the second polymerization reaction was carried out until the viscosity of the reaction system reached 180 mPa s. The system was cooled down to room temperature and polymerized equably. Half of the products were rinsed with distilled water and vacuum dried at 80 °C for more than 12 h to remove any oligomer and impurities. The samples with AC (or AA) dosages of 5, 10, 15, 20, 30 g were designated S1, S2, S3, S4, and S5, respectively.

Swelling experiments

The dried sample of 10 g was immersed in enough distilled water for 24 h to reach absorption equilibrium. The unadsorbed water was removed by filtering over a 40-mesh stainless steel screen and draining for 5 min. The swelling ratio (SR, $g \cdot g^{-1}$) was measured according to Eq. 1:

$$\text{Swelling ratio (SR)} = \frac{W_2 - W_1}{W_1} \quad (1)$$

where W_1 is mass of dried sample (g) and W_2 is mass of swollen hydrogel (g).

Deswelling experiments

The swollen hydrogel was put in salt solutions with different concentrations. The weight of the deswelled hydrogel was measured at intervals. Each experiment was repeated three times with errors of approximately ± 4.5%. Deswelling ratio (DR, $g \cdot g^{-1}$) of the sample was obtained according to the Eq. 2:

$$\text{Deswelling ratio (DR,\%)} = \frac{W_0 - W_t}{W_0 - W_d} \quad (2)$$

where W_0 and W_t are weights of hydrogels at time 0 and *t*, W_d is weight of the dried sample.

MO absorption and release

The dried sample of 1 g was immerged in 150 mL MO solutions with a concentration of 0.2 M for 24 h to reach absorption equilibrium. The absorbency measurements were performed with a Shimadzu UV-3100 UV–VIS–IR spectrophotometer at $\lambda_{max} = 462.6$ nm, using a glass cell of 15 mm for the color intensity of MO. The regression equation MO solution working curve was $A = 39.17c-0.01348$, $r = 0.9994$. The swollen PAM/PAC IPN hydrogels absorbing MO solution of 20 g were put in 200 mL $CaCl_2$ $CuSO_4$, and $FeCl_3$ solutions, respectively, and the release amounts were calculated by measuring the absorbency of MO solutions at 462.6 nm with the same method.

FTIR spectrum and micromorphology observation

The powdered samples were identified by IR spectroscopy on a Nicolet Impact 410 FTIR spectrophotometer using KBr pellets. The surface of PAM/PAC hydrogel was examined using a scanning electron microscope (Hitachi S-5200, JAPAN). Swollen PAM/PAC hydrogel and deswelled hydrogel were cut into a thin piece, mounted on metal stub, and coated with gold; subsequently, its surface was observed and photographed by a scanning electron microscope (SEM).

Results and discussion

Synthesis

The PAM/PAC IPN hydrogel was synthesized by a two-step polymerization method, which is different from the conventional method for IPN hydrogel. In the first step, AM monomers are initiated and polymerized to produce oligo-acrylamide (OAM). After viscosity of the reactant reached 140 mPa s, the second step was carried out; OAM reacts with AC to form PAM/PAC with IPN structure. The typical process is expressed as:

$$\mathrm{AM} \xrightarrow[\text{Step I}]{\text{initiator}} \mathrm{O-AM} + \mathrm{AC} \xrightarrow[\text{Step II}]{\text{initiator+crosslinker}} \mathrm{PAM/PAC}$$

The OAM is a chainlike oligomer with low molecular weight synthesized in the first step in the absence of the crosslinker. While in the second step, the crosslinker is necessary and used for the formation of PAC network with a 3D structure. Once the PAM with full 3D network is formed and PAC intercalates into the PAM 3D network, the whole system becomes a typical IPN structure. The static polymerization is indispensable for the formation of excellent IPN structure. If the second step reaction is carried out continuously after the viscosity of the system exceeds 180 mPa s at 80 °C, the reaction will be accelerated and a sudden polymerization occurs which is unfavorable for the preparation of an even IPN hydrogel. In addition, the two-step synthesis technique is useful for preparing the IPN hydrogels with high mechanical strength. Using this method, we have synthesized polyacrylamide/polyacrylamide, polyacrylamide/poly(vinyl alcohol) IPN hydrogels [10, 11] with a tensile strength of 2.4 MPa for stress and 3000% for strain, which is the highest record for these hydrogels.

FTIR spectra

Figure 1a shows the FTIR spectra of (a) PAM/PAC IPN, (b) poly(AM-co-AC), and (c) PAM/PAC hybrid. The absorption peak at $\sim$3432 $\mathrm{cm^{-1}}$ belongs to the N–H bending, the absorption peaks at $\sim$2934 $\mathrm{cm^{-1}}$ is attributed to $-CH_2-$ dissymmetrical stretching, $\sim$1677 $\mathrm{cm^{-1}}$ is for the C=O stretching for PAM (AM band I), $\sim$1617 $\mathrm{cm^{-1}}$ is attributed to N–H in-plane bending in $-CONH_2$ group (AM band II). For PAC, $\sim$1117 $\mathrm{cm^{-1}}$ is for C–H bending, $\sim$1576 $\mathrm{cm^{-1}}$ and $\sim$1397 $\mathrm{cm^{-1}}$ are results of C=O bending in carboxylic and carboxylate groups, respectively. Peak at $\sim$1234 $\mathrm{cm^{-1}}$ corresponds to O–H distortion in carboxylic group, $\sim$1180 $\mathrm{cm^{-1}}$ is for C–O stretching vibration, $\sim$1456 $\mathrm{cm^{-1}}$ belongs to $-COO^-$ stretching, and $\sim$1319 $\mathrm{cm^{-1}}$ is attributed to C–C stretching. The absorption peak at $\sim$1576 $\mathrm{cm^{-1}}$ reflecting C=O bending in carboxylic group in PAM/PAC hybrid has moved to $\sim$1561 $\mathrm{cm^{-1}}$ This indicates that the structure of PAM/PAC IPN hydrogel far from the physical blend, chemical interactions have appeared in PAM and PAC networks [12].

From Fig. 1b, it can be seen that the peaks at $\sim$1561 and $\sim$1397 $\mathrm{cm^{-1}}$ responsible for C=O bending have moved to 1544, 1415. Peaks at $\sim$1250 and $\sim$1456 $\mathrm{cm^{-1}}$ attributed to O–H distorting in $-COOH$ and $-COO^-$ stretching have weakened and disappeared in the chelate complex. All of which are the results of chelation of hydrogel and multivalent metal cations.

Swelling behaviors

The influence of AC content in PAM/PAC on swelling rate of the hydrogels is shown in Fig. 2a. It can be seen that they have similar swelling tendency and need more than 8 h to reach swelling equilibrium, and the swelling ratio increases with the increase of AC content in PAM/PAC. This is because the hydrophilicity of $-COOH$ and $-COO^-$ groups is higher than that of $-CONH_2$ group. The introduction of AC improves the hydrophilic ability of PAM/PAC IPN hydrogel, which results in the increase of SR with the increase of the AC content. On the other hand, by comparison of traditional superabsorbents consisting of PAM and PAC [13–15], SR of the PAM/PAC IPN hydrogel is much lower. This is due to the IPN structure of the hydrogels. Using the two-step polymerization technique, PAM network and PAC network entangle each other, and the hydrogen bonds interactions increase. Thus the amount of the effective crosslinking points also increase, which results in a decrease in the network space between PAM and PAC chains, and leads to a decrease in

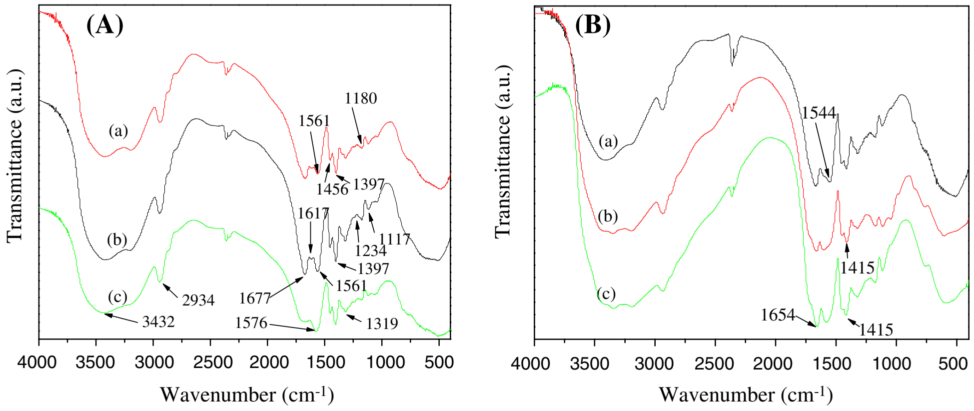

Fig. 1 (**A**) FTIR spectra of (a) PAM/PAC IPN, (b) poly(AM-co-AC), and (c) PAM/PAC hybrid. (**B**) FTIR spectra of PAM/PAC IPN hydrogel deswollen in (a) Ca^{2+}, (b) Cu^{2+} and (c) Fe^{3+}

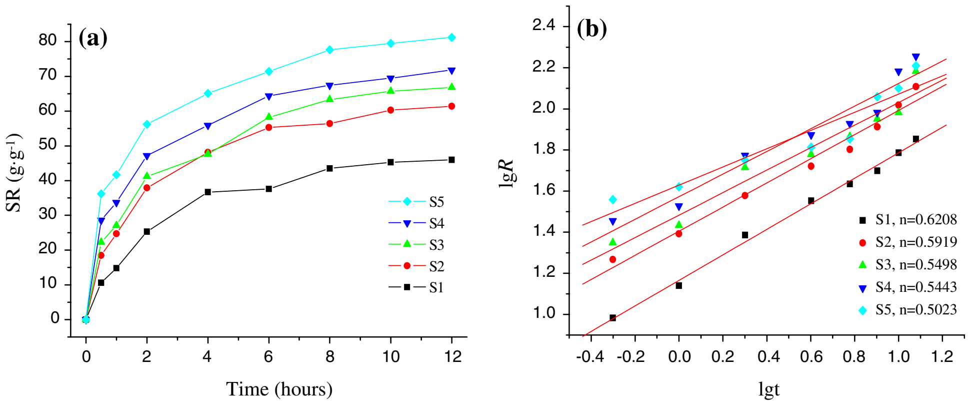

Fig. 2 (**a**) Swelling rate of PAM/PAC IPN hydrogels in distilled water. (**b**) lg$R$ as a function of lg$t$

SR. The effects of the IPN are similar to that of crosslinker to a certain extent [2].

Figure 2a is a typical diagram of swelling process of the PAM/PAC IPN hydrogels in distilled water. The swelling ratio is fast at the beginning and then becomes slower until the hydrogels reach their maximum SRs. The same method as that of Firestone and Siegel to study the kinetics in theory is used here [16]. R value is used to describe the swelling kinetics from Eq. 3:

$$R = \frac{W_t}{W_0} - 1 \quad (3)$$

where W_t is the weight of swollen hydrogel at time t and W_0 is the weight of the dry hydrogel.

The data of the process are fit to a rate equation:

$$R = kt^n \quad (4)$$

where k is the swelling rate front factor and n is the kinetic exponent. Equation 4 is a phenomenological law in which n is related to the type of sorption mechanisms of hydrogels. For Fickian kinetics in which the rate of penetrating diffusion is rate-limiting, n equals 0.5. If a non-Fickian process occurs during the swelling, n will have a value between 0.5 and 1. To get the value of n, $\log_{10}R$ (lg$R$) is plotted versus $\log_{10}t$ (lg$t$) and the slope is the value of n. Linear fitting results values of n are shown in Fig. 2b. It can be seen that n is larger than 0.5. Namely, the swelling process is a typical non-Fickian. With the increase of AC dosage from S1 to S5, the exponent n decrease. For instance, the exponent n is 0.6208 for S1 and 0.5023 for S5, the swelling process is closer to be Fickian diffusion. The swelling process depending on water diffusion and group ionization describes the above phenomenon. If the water diffusion rate is slower than the ionization rate, the swelling is diffusion rate-limiting and shows Fickian kinetics. Contrarily, it is ionization rate-limiting and shows non-Fickian kinetics. With the increase of AC dosage, the more –COOH or –COOK groups are ionized, the swelling gradually changes from ionization rate-limiting to diffusion rate-limiting, and shows non-Fickian to Fickian kinetics.

pH sensitivity

Figure 3a indicates the pH-dependent SRs of the obtained PAM/PAC IPN hydrogels. The pH-sensitivity of the hydrogels was measured in buffer solutions of pH from 2 to 11 at room temperature. It is found that increasing pH leads to swelling of the PAM/PAC IPN hydrogels like other PAC based hydrogels. The sensitivity is related to pH-dependent ionization of carboxylic acid (–COOH) side groups of acrylic acid monomers. As the solution becomes less acidic, the ionization of the carboxylic acid groups occurs, resulting in electrostatic repulsion between the carboxylate (–COO$^-$) groups and the expanding of the space network, which cause larger SR of the hydrogels [17].

Furthermore, as seen clearly from Fig. 3a, with the increase of PAM component in the hydrogel, the SR sensitivity depended on pH is weakened. Especially at pH 4.5, the curves are crossed. This is because the acrylamide group (–CONH$_2$) on the PAM segments has a weaker hydrophilicity than –COOH or –COO$^-$ groups on PAC segments, and cannot ionize in aqueous solution [18]. Consequently, with the increase of PAM content, the SR of the hydrogel decreases and the sensiticisity dependent on pH weakens. When the pH value of the medium solution is 4.5, which is the pKa value of pure PAC, the most sensitivity pH value of ionization for the –COOH group to –COO$^-$ group, the curves are crossed.

Owing to the different swelling behaviors of the PAM/PAC IPN hydrogels in acidic and alkaline solutions, we investigated the reversible swelling–deswelling behavior of the hydrogels in buffer solutions of pH 3 and 9 (Fig. 3b). At pH = 3, the hydrogels shrink rapidly due to the protonation of carboxylic acid groups and production of hydrogen bonds, which similarly increase crosslinkage of the hydrogels. The network space diminishes and the hydrophilic capability reduces. The result is diffusion of superfluous water and shrinkage of hydrogels. Once the hydrogels are immersed at pH 9, the hydrogels swell under the drive of electrostatic repulsions and osmotic pressure.

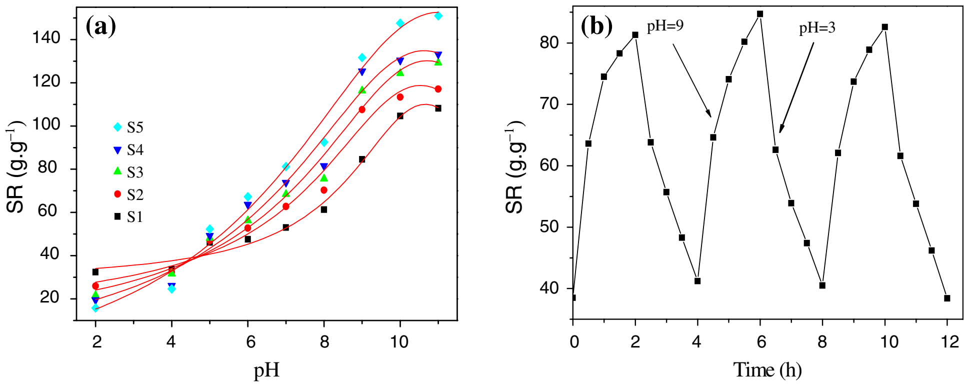

Fig. 3 (**a**) pH-sensitivity of PAM/PAC IPN hydrogels. (**b**) On–off effect of S5 in buffer solution of pH = 9.0 and 3.0

Deswelling of the hydrogels

It is well known that ionizable hydrogels consisting of carboxylic, amine, ammonium, and sulfonic groups can chelate with multivalent cations, such as Ca^{2+}, Cu^{2+}, and Fe^{3+} ions, which results in the deswelling of hydrogels. Here, the deswelling kinetics of PAM/PAC IPN hydrogel (S5) in Ca^{2+}, Cu^{2+}, and Fe^{3+} salt solution are investigated and the results are shown in Fig. 4. It can be seen that the DR increases rapidly in the first few hours and then becomes slower until reaching an equilibrium state. At the same time, the DR is higher in higher salt concentrations. It is understood that when the PAM/PAC IPN hydrogel is immersed into salt solutions, carboxylic group or carboxylate ion on the hydrogel chelate with cation ions in the solution, which results in the invalidation of hydrophilic groups, increasing of crosslinking density, and decreasing of water affinity of the hydrogel. Thus the holding water ability of the hydrogel decreases, the superfluous water is expeled from the hydrogel, and the PAM/PAC IPN hydrogel shrinks. With the further diffusion of cations in the solution to the inner of the hydrogel, the whole hydrogel will be chelated and shrinked. To observe the morphology of the chelate complex, the images of PAM/PAC IPN hydrogel after chelations of Ca^{2+}, Cu^{2+}, and Fe^{3+} ions are photographed using a scanning electron

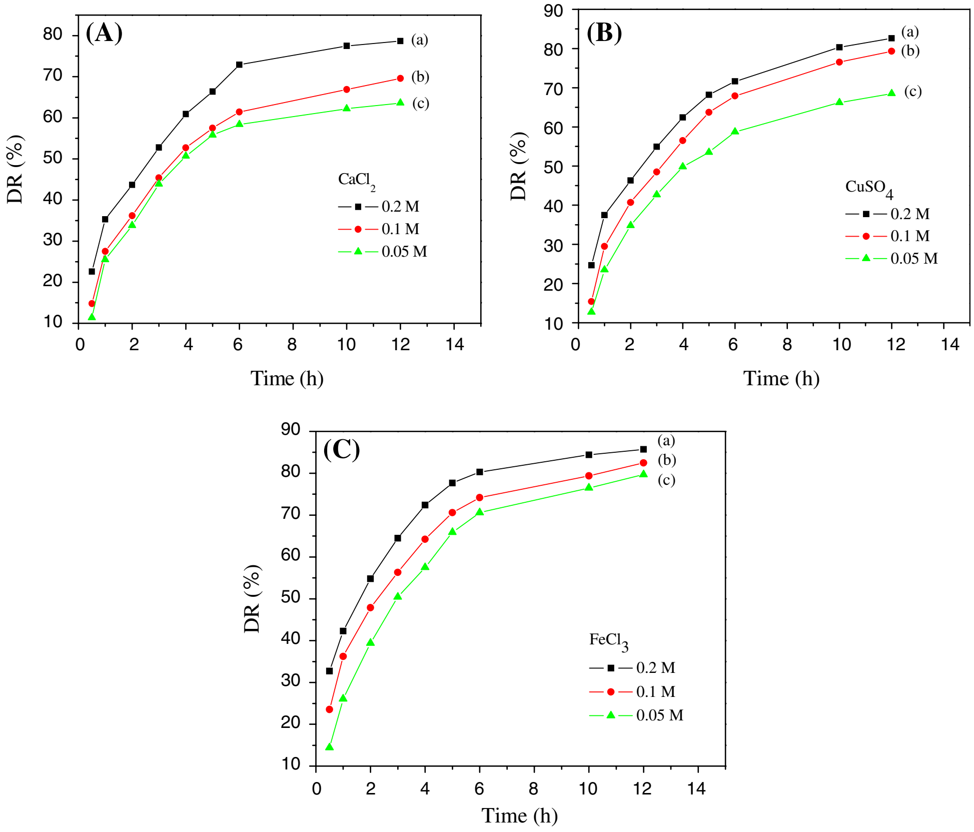

Fig. 4 The DRs of S5 samples in (**A**) $CaCl_2$, (**B**) $CuSO_4$ and (**C**) $FeCl_3$ solutions with the concentration of 0.2 M (a), 0.1 M (b) and 0.05 M (c)

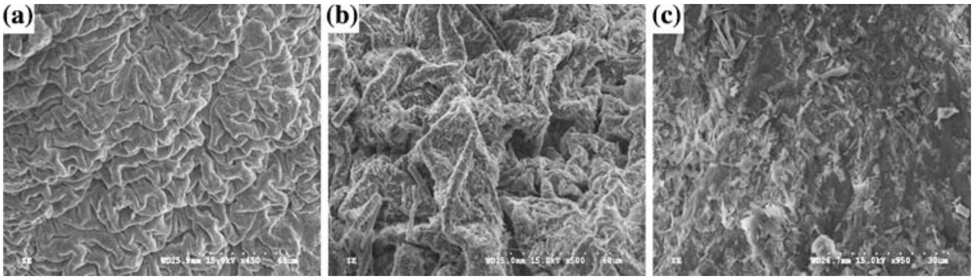

Fig. 5 Morphologies of PAM/PAC IPN hydrogels after chelations of (**a**) Ca^{2+}, (**b**) Cu^{2+} and (**c**) Fe^{3+} ions

microscopy and shown in Fig. 5. The hydrogels are shrinked and large amount of salt deposition appear on the surface of the hydrogel. Owing to that, the hydrogel containing carboxylic, amine, ammonium, and sulfonic groups can be applied as a remover for metal ions and heavy metal ions in solution [6, 19–22].

MO removal

The PAM/PAC IPN dried sample is immersed in 0.2 M MO solution to reach a swelling equilibrium and then the swollen hydrogels absorbed MO are put in salt solutions. Under the effect of the chelation of metal ions, the MO will be released from the hydrogels; thus, the dye removal is achieved. Figure 6 plots the MO release in multivalent salt solutions. It can be seen from Fig. 6a that release in 0.05 M $CaCl_2$ solution is rapid in the beginning, especially for S5, the cumulative released is more than 80% in 30 min and nearly 100% in 180 min. The release of MO in salt solutions is due to the chelation effect of the carboxylic group/carboxylate ions on the hydrogel with cations in solution is the stronger than the hydrogen bonds or Van der Waals interaction between carboxylic/carboxylate groups with MO/water molecules [20]. In the presence of multivalent cations,

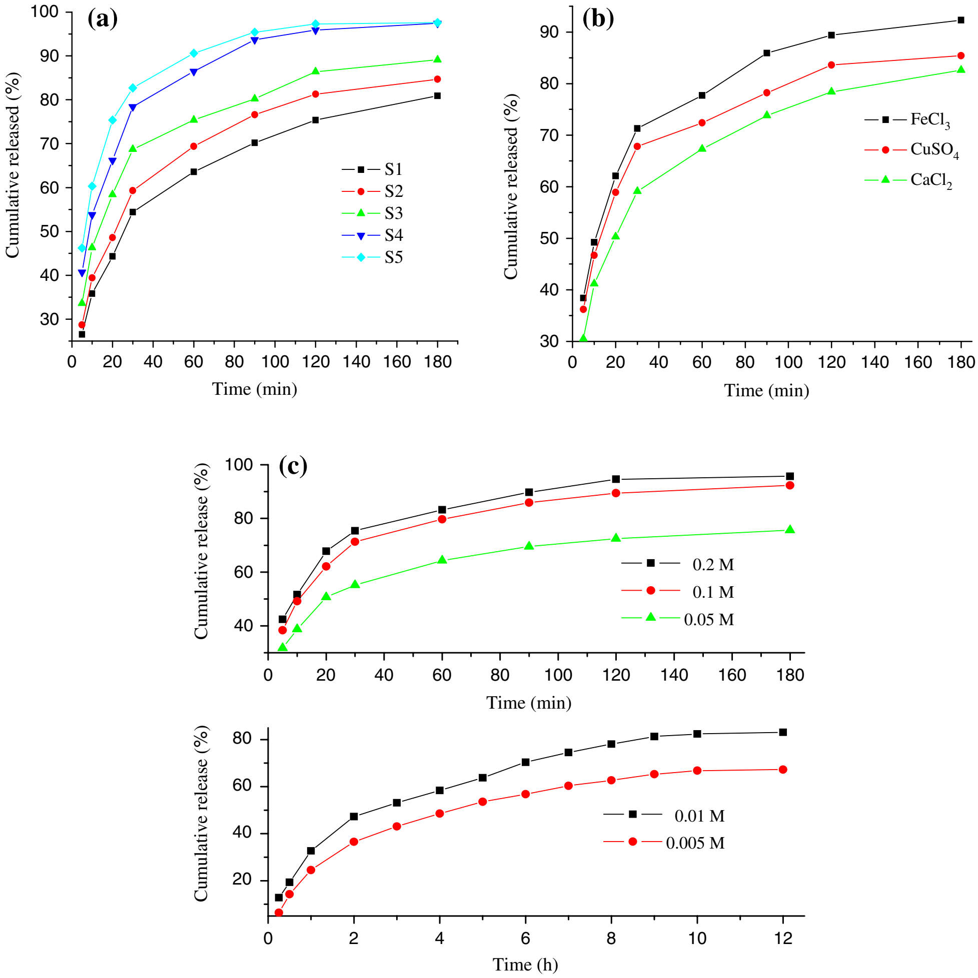

Fig. 6 (**a**) MO release from PAM/PAC IPN hydrogels in 0.05 M $CaCl_2$ solution. (**b**) MO release from S2 sample in salt solutions with concentration of 0.2 M. (**c**) MO release from S2 sample in $FeCl_3$ solution with a concentration ranging from 0.005 M to 0.2 M

hydrogen bonds or Van der Waals interactions between carboxylic group/carboxylate ions groups with MO/water molecules are destroyed, the hydrogel shrink and MO is released. Owing to the chelation occurring in –COOH and –COO^{-} groups, it is understandable that the cumulative release increases with increasing of acrylic acid dosages under the same conditions. Figure 6b shows the relations of cations species with MO release. It is obvious that valence of the cation is another important factor on the release of dye. A salt solution with higher valence cation will quicken the release rate. Furthermore, influences of the cation concentrations on the cumulative release are shown in Fig. 6c. It is clear that a higher concentration is advantageous for the release of dyes, which is consistent with DR in Fig. 4.

Conclusions

PAM/PAC IPN hydrogels are synthesized using a simple two-step polymerization technique. The swelling properties are investigated and a non-Fickian process is observed. As an ionic hydrogel, typical pH-sensitivity and on–off effect are found in buffer solutions. Owing to the chelation of the ionic hydrogel, deswelling experiments are also carried out and the influences on DRs are discussed. Based on the deswelling property, the heavy metal ions and dyes in wastewater can be reclaimed and reused.

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References

1. Buchholz F, Grajam A (1997) Modern superabsorbent polymer technology. Wiley-VCH, New York
2. Tang QW, Lin JM, Wu JH (2007) J Appl Polym Sci 104:735. doi:10.1002/app.25531
3. Fanta GF, Doane WM (1986) Grafted starches. In: Wurzburg OB (ed) Modified starches: properties and uses. CRC Press, pp 149–178
4. Tang QW, Lin JM, Wu JH (2007) Carbohydr Polym 67:332. doi:10.1016/j.carbpol.2006.05.026
5. Yetimoglu EK, Kahraman MV, Ercan O (2007) React Funct Polym 67:451. doi:10.1016/j.reactfunctpolym.2007.02.007
6. Yan WL, Bai RB (2005) Water Res 39:688. doi:10.1016/j.watres.2004.11.007
7. Ali AE, Shawky HA, Rehim HA (2003) Eur Polym J 39:2337. doi:10.1016/S0014-3057(03)00150-2
8. Owens DE, Jian Y, Fang JE, Slaughter BV, Chen YH, Peppas NA (2007) Macromolecules 40:7306. doi:10.1021/ma071089x
9. Zhang J, Peppas NA (2000) Macromolecules 33:102. doi:10.1021/ma991398q
10. Tang QW, Wu JH, Lin JM (2008) e-Polymers 21:1
11. Tang QW, Wu JH, Lin JM (2008) Carbohydr Polym 73:315. doi:10.1016/j.carbpol.2007.12.030
12. Yang ZW, Jiang YS, Xu LX, Wen B, Li FF, Sun SM et al (2005) J Mater Chem 15:1807. doi:10.1039/b418015c
13. Wu JH, Wei YL, Lin JM (2003) Polymer (Guildf) 44:6513. doi:10.1016/S0032-3861(03)00728-6
14. Omidan H, Hashemi SA, Sammes PG (1998) Polymer (Guildf) 39:6697. doi:10.1016/S0032-3861(98)00095-0
15. Li A, Wang AQ (2005) Eur Polym J 41:1630. doi:10.1016/j.eurpolymj.2005.01.028
16. Firestone BA, Siegel RA (1991) J Appl Polym Sci 43:901. doi:10.1002/app.1991.070430507
17. Pourjavadi A, Barzegar SH, Zeidabadi F (2007) React Funct Polym 67:644. doi:10.1016/j.reactfunctpolym.2007.04.007
18. Mullarney MP, Seery T, Weiss RA (2006) Polymer (Guildf) 47:3845. doi:10.1016/j.polymer.2006.03.096
19. Lin YH, Liang HF, Chung CK (2005) Biomaterials 26:2105. doi:10.1016/j.biomaterials.2004.06.011
20. Zimmermann H, Wahlisch F, Baier C (2006) Biomaterials 28:1327. doi:10.1016/j.biomaterials.2006.11.032
21. Singh B, Chauhan GS, Bhatt SS (2006) Carbohydr Polym 64:50. doi:10.1016/j.carbpol.2005.10.022
22. Chauhan GS, Singh B, Chauhan S (2005) Desalination 181:217. doi:10.1016/j.desal.2005.03.002