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Synthesis of polyacrylate/polyethylene glycol interpenetrating network hydrogel and its sorption for Fe^{3+} ion

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Abstract A simple two-step aqueous polymerization method was introduced to synthesize polyacrylate/polyethylene glycol (PAC/PEG) interpenetrating network (IPN) hydrogel. The sorption behaviors and mechanism were studied by the sorption of PAC/PEG IPN hydrogel to Fe^{3+} ion from aqueous solution. The experimental results revealed that the adsoption amount of Fe^{3+} ion using swollen hydrogels was much higher than that using the dried composite, they were 75.69 mg/g and 14.25 mg/g, respectively. The parameters, such as neutralization degree, acrylic acid (AA) dosages and temperature, on the sorption amount of PAC/PEG IPN hydrogel were detailedly investigated.

Introduction

Crosslinked hydrogels materials are a central component in numerous applications, such as separation membranes, biosensors, artificial muscles, chemical valves, superabsorbents, and drug delivery devices [1–4]. Interpenetrating network (IPN) hydrogels have attracted more attention because of their fancy structures, their properties in response to environmental stimuli: pH [5–8], temperature [9–12], ionic strength [13, 14], electric field [15], photics [16], etc., which are shown in volume phase transitions, swollen, or contractive. Among the various hydrogels, thermo-sensitive hydrogels are potentially used in drug delivery, cell encapsulation, and tissue engineering [17, 18]. The removal of metal ions from industrial and living waste water is attracting more attentions. Traditional treatment techniques to remove the dissolved metal ions from waste water disposal by chemical treatment, ultrafiltration or combination of chemical treatment and ultrafiltration do not always provide a sufficient contaminant removal to meet pollution control limits [19–24]. Recently, many hydrogels such as acrylic acid (AA), acrylic acid grafted cellulose, and macroporous poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) have been reported for the removal of Cu(II), Cd(II), and Cr(III) under competitive conditions [25–27].

Polyacrylate, typical 3D network, has been used to synthesize smart or intelligent hydrogels and functional hydrogels with IPN structures by graft or copolymerization [28–31]. However, the actual preparation methods are complicated and weakly repeatable, which restricts the wide application of IPN hydrogels.

In the article, a novel two-step method was introduced in synthesizing polyacrylate/polyethylene glycol (PAC/PEG) IPN hydrogel. The sorption behavior and mechanism were carried out by the sorption of the IPN to Fe^{3+} ion. The influences of parameters on the sorption amount of Fe^{3+} ion were detailedly investigated.

Experimental

Materials

Acrylic acid monomer was distilled under reduced pressure prior to use. Ammonium persulfate (APS) and PEG

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(M_n = 20,000) were used as received. Crosslinker *N*,*N*′-methylene bisacrylamide (NMBA) was purified by recrystallization from 66 wt% ethanol/water solution. Potassium hydroxide (KOH) was used to neutralize AA monomer. All the materials were purchased from Shanghai Chemical Reagents Co., China. All aqueous solutions were prepared in 18 MΩ water obtained by purification of deionized water with a Millipore Milli-Q system.

Synthesis of PAC/PEG IPN composite

A solution of AA monomer and acrylate (AC) monomers was prepared by agitating AA (15 g) and KOH of necessary concentration in deionized water (15 mL) at ambient temperature. Under a nitrogen atmosphere, the solution was stirred and heated to 80 °C in a water bath for 10 min, and then the initiator (APS, 0.045 g) was added to the reaction mixture. The polymerization reaction mixture was stirred for 10 min to prepare PAC prepolymer solutions.

Another solution (10 mL) of PEG and the crosslinker (PEG 2.5 g, NMBA 0.006 g) was poured into each PAC prepolymer solution, and the initiator (APS, 0.045 g) was added. Under a nitrogen atmosphere, the solution was stirred until the dilute reactant solution was ropy. Then the reactant was cooled to room temperature for about 30 min to allow copolymerization to take place. Half of the product was washed with distilled water and then dried under vacuum at 80 °C for more than 12 h until it reached a constant weight to remove low-molecular-weight polymers and impurities. After milling and sifting using a 40-mesh screen, a powdered PAC/PEG composite was obtained.

Fe^{3+} ion sorption

Sorption agent samples (dry PAC/PEG composite or swollen PAC/PEG hydrogel) were immersed in 0.05 M $FeCl_3$ solutions. The residual solutions were analyzed to determine for the concentration of rejected ions by spectrophotometrical method using KSCN and a UV-vis spectrophotometer (Shimadzu Corporation, Japan). The amount of absorbed Fe^{3+} ion was determined using Eq. 1 [32]:

$$\text{Adsorption capacity (mg/g)} = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where C_0 and C_t are the concentrations (mg/L) of Fe^{3+} ion at the beginning and after t min in solution, V is the solution volume (L) and m is the weight of dried PAC/PEG IPN composite (g).

Deswelling property

For the deswelling property of the PAC/PEG IPN hydrogel, the measurements were carried out in 0.1 M $FeCl_3$ solution for 8 h to reach a deswelling equilibrium. The dried PAC/PEG composite of 10 g were immerged in enough deionized water for 24 h to reach sorption saturation. The unadsorbed water was removed by filtrating over a 40-mesh stainless steel screen and hanging up for 5 min, and the obtained hydrogels of 30 g were put in above mentioned solutions. Weights of the deswelled hydrogels were measured at intervals. Deswelling ratios were obtained using Eq. 2:

$$\text{Deswelling ratio} = \frac{m_0 - m_t}{m_0 - m_d} \times 100\% \tag{2}$$

where m_0 and m_t are masses (g) of hydrogels at time 0 and t, m_d is mass (g) of dry composites.

Characterizations

The swollen PAC/PEG IPN hydrogel samples in the equilibrium swelling state were quickly frozen in liquid nitrogen and then freeze-dried under vacuum at −42 °C for 3 days until all the water sublimed. The freeze-dried hydrogel was fractured carefully, and its morphology was studied by scanning electron microscopy (SEM, Hitachi S-5200, Japan). The hydrogel specimens were fixed on aluminum stubs and coated with gold for SEM. The hydrogel samples were analyzed using a Nicolet Impact 410 Fourier infrared spectroscopy (FTIR) spectrophotometer in the region of 500–3,700 cm^{-1}. Prior to the measurement, the hydrogel samples were dried under vacuum overnight until they reached a constant weight. The dried hydrogel was pressed into a powder, mixed with 10 times as much KBr powder and then compressed into a pellet for characterization by FTIR.

Results and discussion

Synthesis

The PAC/PEG IPN hydrogel with an IPN structure was synthesized by a simple two-step aqueous solution polymerization. The synthetic pathway of the PAC/PEG IPN hydrogel is shown in Fig. 1. Polymerization takes place in

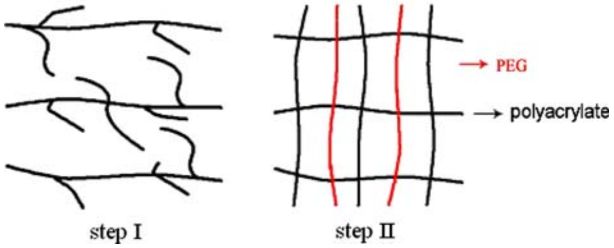


Fig. 1 Sketch of synthesis course of the PAC/PEG IPN hydrogel

step I to form a PAC prepolymer. Then, copolymerization between the PAC prepolymer and PEG occurs in step II to form an IPN structure.

Characterizations

The SEM images of the PAC/PEG IPN hydrogel were shown in Fig. 2a. Swollen PAC/PEG IPN hydrogel was frozen in liquid nitrogen and then freeze-dried before SEM morphological investigation [33]. As can be seen from the images, the IPN hydrogel exhibited regular network structures. No phase separation was observed in the SEM images, which implied the formation of a complete IPN structure consisting of a PAC network and PEG chains. Figure 2b, which was a high magnification of part of Fig. 2a, showed a connective, oriented, and even porous structure, which was expected to have infiltration, sorption, swelling, and drug release properties.

The FTIR spectra of PAC, PEG, PAC/PEG IPN, and PAC/PEG-Fe were shown in Fig. 3. The bands of PAC at 3,635 cm^{-1} (O–H stretching due to polymeric association), 1,690 cm^{-1} (C=O stretching), 2,923 cm^{-1} (C–H bending), and 1,319 cm^{-1} (C–C stretching) were observed. In the PAC/PEG IPN composite, the vibration sorption peak at 1,109 cm^{-1} corresponding to the C–O–C stretching vibration of PEG was detected, which indicated that PEG had been introduced to the composite.

The peaks at 1,570 and 1,407 cm^{-1} relative to C=O bending in the –COOH and –COOK groups of PAC have moved to 1,592 cm^{-1} in –COOH and 1,424 cm^{-1} in –COOK for PAC/PEG-Fe composites. Peaks at 1,250 cm^{-1} and 1,456 cm^{-1}, attributed to O–H distorting in –COOH and $–COO^-$ stretching, respectively, have disappeared in the PAC/PEG-Fe composite, which indicates the chelation of $–COOH/–COO^-$ groups with Fe^{3+}.

Ion-exchange or sorption properties of polyelectrolyte hydrogels arise by redistribution of a salt solution [34]. In the present study, we mainly investigated the influences of neutralization degree, temperature, and AA dosages on Fe^{3+} ion sorption. Generally, the chelation was a gradual change process from hydrogel surface to interior. To reveal the gradual process, the profile morphology was shown in Fig. 4. There were three different regions; they were chelation area, transition area, and hydrogel, respectively. It was known that Fe^{3+} was first attracted to the PAC/PEG IPN hydrogel surface. Due of the active points in –COOH, $–COO^-$, and –OH groups, the chelation occurred in active groups and Fe^{3+} ions. Once the exterior groups lost their activities, the metal ions would transfer to interior by the network channels. Step by step, the whole hydrogel system was all chelated.

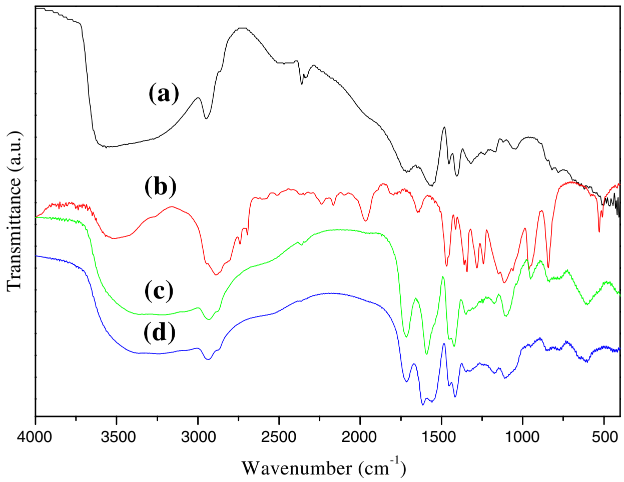


Fig. 3 FTIR spectra of PAC (a), PEG 20,000 (b), PAC/PEG IPN (c), and PAC/PEG-Fe (d)

Influence of neutralization degree on Fe^{3+} sorption

It was well known that neutralization degree (i.e., pH value of solution) was an important factor for heavy metal ions removal [35]. The effects of the neutralization degree of the AA monomer on Fe^{3+} sorption value are shown in Fig. 5. It can be seen that Fe^{3+} sorption value increased with increasing of neutralization degree. In fact, the PAC polymer backbone contains $–COO^-$ and –COOH groups, and $–COO^-/–COOH$ ratio increases with increasing

Fig. 2 SEM morphologies of the PAC/PEG IPN hydrogel

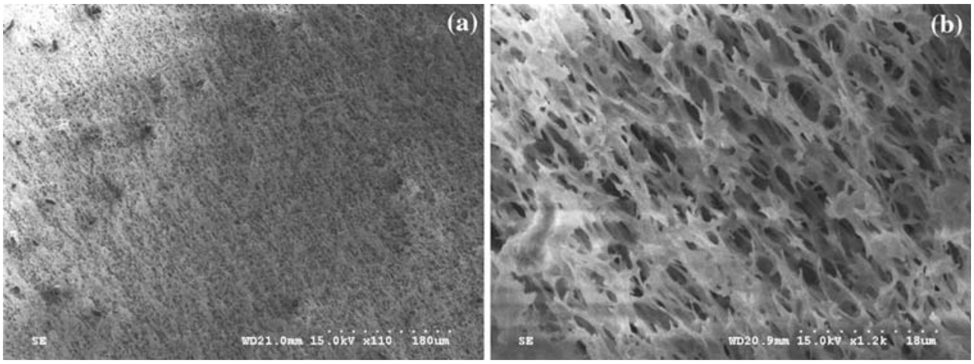


Fig. 4 Profile morphology of chelate PAC/PEG IPN hydrogel

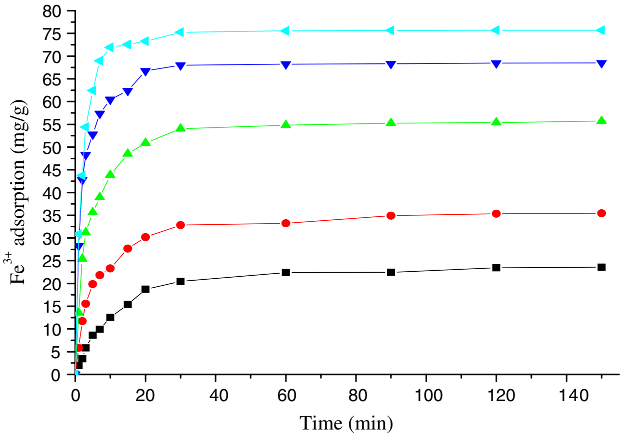


Fig. 5 Fe^{3+} ion sorption versus neutralization degree of AA at room temperature (The mass ratio of AA to PEG 20,000 is 15: 2.5). Neutralization degree of AA: (■) 20%, (●) 40%, (▲) 60%, (▼) 80%, and (◀) 100%

neutralization degree. Since the coordination ability and electrostatic affinity of the –COO^- group to Fe^{3+} are higher than those of the –COOH group, Fe^{3+} sorption value increases with increasing neutralization degree.

The metal complexes tend to be structural stability. Due to the intermolecular and intramolecular interactions, the PAC/PEG-Fe complex presented five- and six-membered rings, which was shown in Fig. 6a. The orientating network structures become circular cavities. The sorption of Fe^{3+} not only attributed to the chelation but also aggradation and accumulation of $FeCl_3$. The surface of the PAC/PEG-Fe was shown in Fig. 6b. As can be seen from Fig. 6b, lots of superfluous $FeCl_3$ crystals adhered to the surface of the PAC/PEG-Fe complex. In fact, the total Fe^{3+} sorption of the PAC/PEG IPN hydrogels includes two parts: chelation and crystallization metal ions. In our experiments, we only measured the amounts of chelation Fe^{3+} regardless of crystallization.

In order to reveal the diffusion mechanism of Fe^{3+} in PAC/PEG IPN hydrogels, Fickian diffusion theory [Eq. 3] was introduced [36].

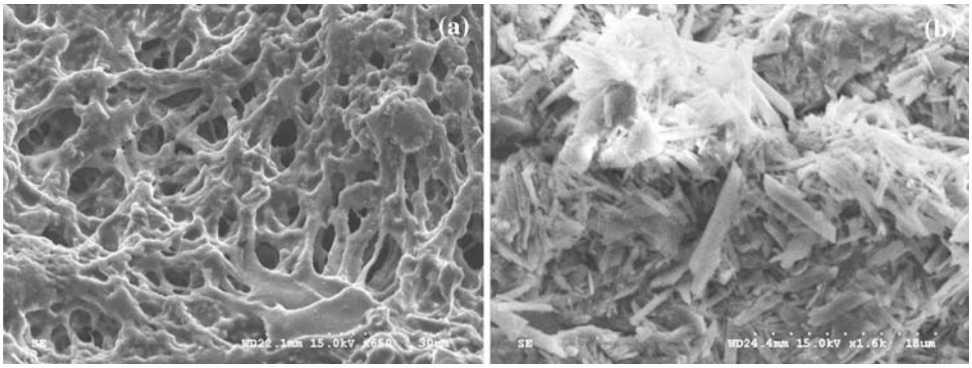
$$\frac{M_t}{M_\infty} = kt^{1/2} \tag{3}$$

where M_t and M_∞ are the masses (g) of diffusion at time t (min) and equilibrium state, respectively. It can be considered that the relative diffusion of the Fe^{3+} is linear with the square root of time. Peppas extended the Higuchi model [Eq. 4] to a more generalized form:

$$\frac{M_t}{M_\infty} = kt^n \tag{4}$$

where n is the diffusional exponent. Information about the diffusion mechanism can be gained by fitting the sorption data and comparing the values of n to the semi-empirical values for various geometries reported by Peppas [37, 38]. For a cylindrical geometry, values of n of 0.45 (or less) correspond to a purely Fickian diffusion mechanism. Values of n greater than 0.89 indicate a relaxation controlled mechanism, and n values between 0.45 and 0.89 indicate an anomalous diffusion mechanism. Despite the approximations, it has been found that these relationships can be applied to sorption data, indicating that the diffusion-based models of Higuchi and Peppas describe diffusion of ions from a polymeric system quite well. According to Eq. 4

Fig. 6 Profile (**a**) and surface (**b**) morphologies of the PAC/PEG-Fe complex



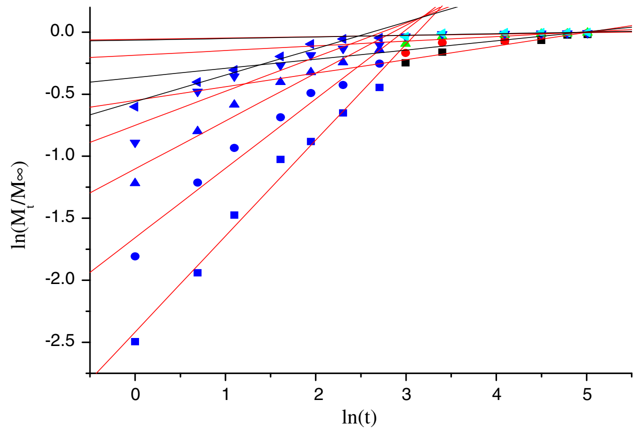


Fig. 7 The relation of ln M_t/M_∞ – ln t for PAC/PEG IPN hydrogel with different neutralization degree (The mass ratio of AA to PEG 20,000 is 15: 2.5). The slopes of two lines under different neutralization degree were: (■) 0.7727 and 0.1094 (20%), (●) 0.5618 and 0.0759 (40%), (▲) 0.3861 and 0.0376 (60%), (▼) 0.2747 and 0.0129 (80%), (◀) 0.2137, and 0.0106 (100%), respectively

and Fig. 5, the relationship of ln (M_t/M_∞) versus ln t was plotted in Fig. 7.

The values of the diffusion exponent n for the PAC/PEG IPN hydrogel at different neutralization degrees were 0.7727 and 0.1094 (20%), 0.5618 and 0.0759 (40%), 0.3861 and 0.0376 (60%), 0.2747 and 0.0129 (80%), and 0.2137 and 0.0106 (100%), respectively. It can be seen from Fig. 7 that there was two slopes for every curve. Diffusion exponent decreased with increasing of neutralization degree in the both two stages. From Fig. 7, n was higher than 0.45 in acidic condition (when the neutralization degree was about 45%, the whole hydrogel system was neutral), and an anomalous diffusion mechanism for Fe^{3+} sorption was observed. Whereas in basic environment, n was lower than 0.45 which revealed a purely Fickian diffusion mechanism. At the second stage, all n values were lower than 0.45 and a Fickian diffusion was found, which may be the cooperation effect of electrostatic force and chelation.

Influence of acrylic acid dosage on Fe^{3+} sorption

The effect of AA dosage on the sorption of Fe^{3+} is shown in Fig. 8. It is clear that the amount of adsorbed Fe^{3+} ions increased quickly with increasing AA dosage. In the PAC/PEG IPN hydrogel, PEG is a hybrid agent for constructing the IPN structure. The –O– and –OH groups on the PEG chains have some coordination ability and electrostatic affinity to Fe^{3+} ions, which however are less than those of the –COOH and –COOK groups in the PAC network. Therefore, a greater amount of PAC in the PAC/PEG IPN hydrogel is favorable for improving the sorption ability of the hydrogel for Fe^{3+} ions.

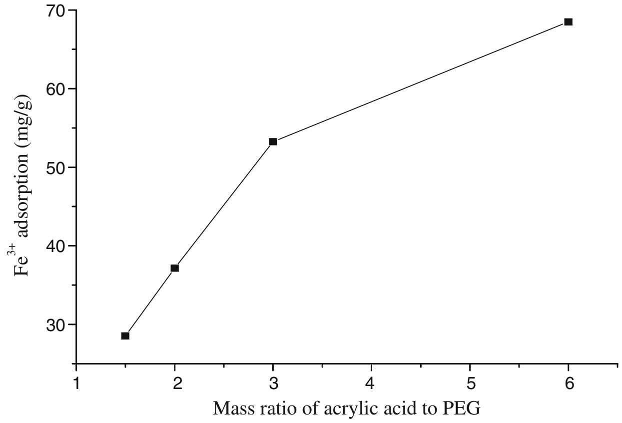


Fig. 8 Fe^{3+} ion sorption versus AA dosage at neutralization degree of 80% and room temperature

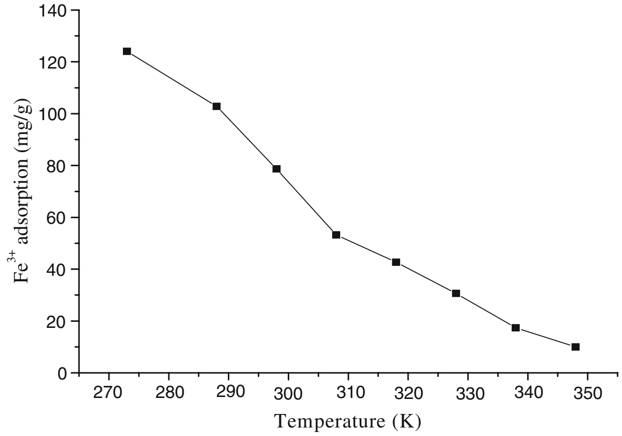


Fig. 9 Fe^{3+} ion sorption versus temperature for 15:2.5 PAC/PEG IPN hydrogel at neutralization degree of 80%

Influence of temperature on Fe^{3+} sorption

The effect of temperature on Fe^{3+} ion sorption from 273 to 348 K was depicted in Fig. 9. An increase in temperature beyond 298 K adversely affected the sorption behavior of the polymeric supports. The results were of technical interest, at lower temperatures these hydrogels exhibited the higher efficiency. The same phenomenon was also observed by another group [32]. At higher temperatures, the Fe^{3+} ions have higher velocity and activation energy. Thus it was easier for Fe^{3+} ions to escape from the restrictions due to electrostatic affinity and chelation, which resulted in decrease in the amount of Fe^{3+} sorption.

Swelling mechanism of hydrogel in $FeCl_3$ solution

The swelling behavior of the dried PAC/PEG composite for Fe^{3+} sorption was presented in Fig. 10. To reveal the sorption process of the PAC/PEG IPN hydrogel in $FeCl_3$ solution, we depicted the experimental curve and an ideal

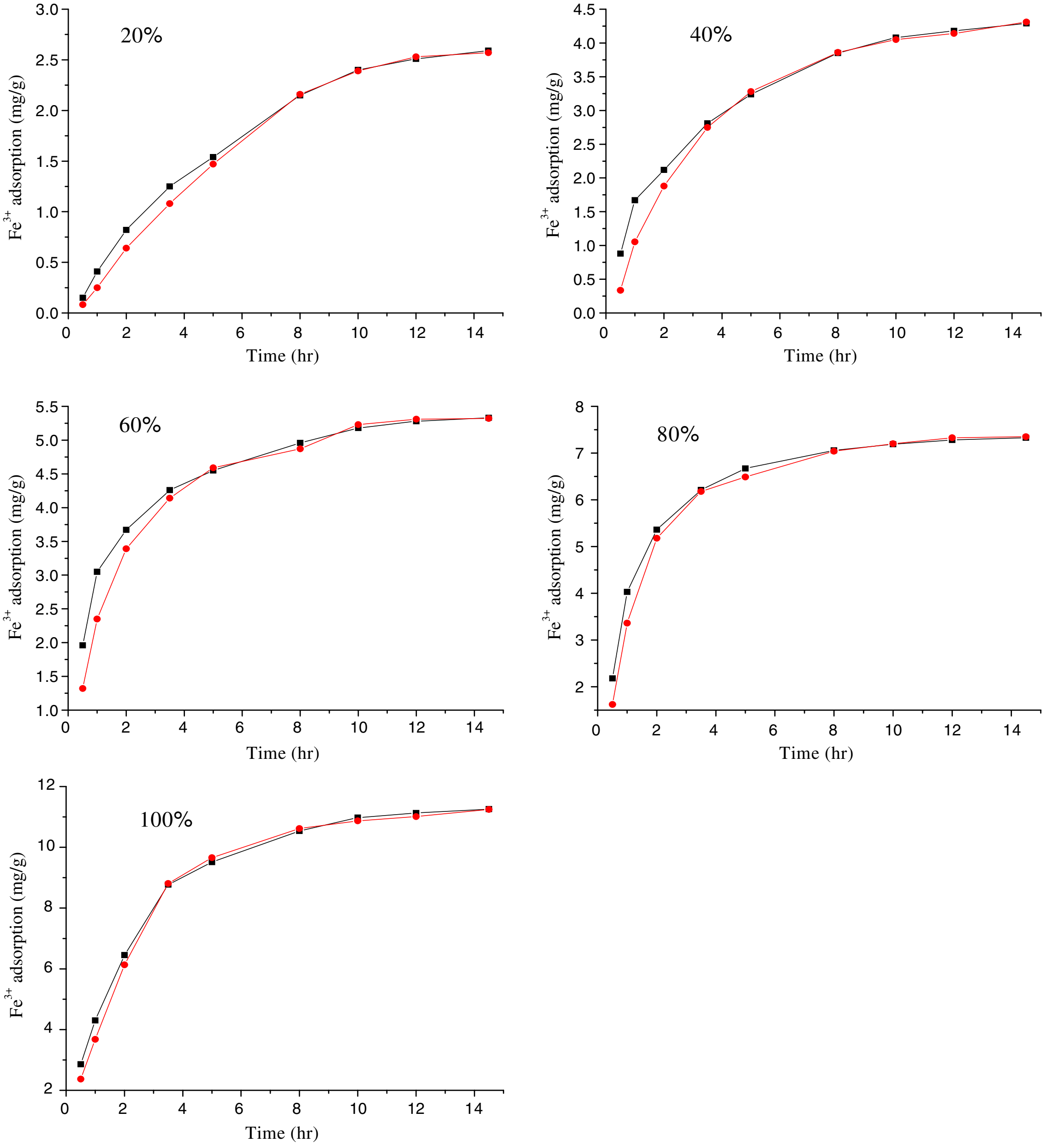


Fig. 10 The sorption of 15:2.5 IPN hydrogel under different neutralization degrees on Fe^{3+} sorption at room temperature (■) plotted the sorption curves according to concentration of 0.05 M $FeCl_3$ solution; (●) plotted the actual sorption curves

Fe^{3+} sorption curve supposing the invariability of concentration of $FeCl_3$ solution. Interestingly, the curves under ideal and actual conditions were not accordant in the first few hours, with the proceeding of chelation, the experimental data tended to be consistent with ideal ones. It was also discovered the swelling time became shorter with increasing of neutralization degree.

It was known that swelling of hydrogel was a complicated process. Generally, the three continuous processes are involved [39]: (a) water molecules enter inner of hydrogel; (b) relaxation of macromolecule chains; (c) stretch of whole macromolecule chains in water. Once the dried PAC/PEG composite was immerged in $FeCl_3$ solution, the water molecules will first enter the composite, then the chelation of Fe^{3+} and –COOH/–COO^- groups occurs. Thus, the concentration of the $FeCl_3$ solution is expected to increase in the initiator state (2–4 h), which can be proved by the decrease of Fe^{3+} sorption in the beginning lower than the ideal ones. Owing to the hydrophilic capability of –COO^- group higher than that of –COOH, obviously, the hydrophile of hydrogels increased with increasing of neutralization degree. Thus, water molecules were easier to enter network of PAC/PEG IPN hydrogel with a higher neutralization degree.

For PAC/PEG IPN hydrogel, it was expected to remove much more heavy metal ions. From Figs. 5 and 10, it was seen that the sorption amount of Fe^{3+} for PAC/PEG IPN hydrogel was higher than that for the dried composite under the same conditions. Once the chelation happened after step (a), the surface effective crosslink density increased [40], from Flory theory [41], the swelling ratio decreased. The compact hydrogel surface further stopped the movement of Fe^{3+} to inner of the IPN hydrogel, thus the Fe^{3+} sorption capability reduced.

Deswelling behavior

It is well known that there are three forms of water: free water, bound water, and bond water. Among them, bond water is bonded via hydrogen bonds between –OH in H_2O and –COOH in PAC, whereas free water and bound water are mobile. If the chelation of –COOH/–COO^- groups and Fe^{3+} occurred to form PAC/PEG IPN complex, the hydrogen bonds would be broken. Thus, the fixed charges in PAC/PEG IPN hydrogel and affinity to water decreased, and the crosslinking density increased. From Flory theory [41], the superfluous water was released which resulted in shrinkage of PAC/PEG IPN hydrogel. The influence of neutralization degree on deswelling ratio of PAC/PEG IPN hydrogel was plotted in Fig. 11. From Fig. 11 we can see that, the PAC/PEG IPN hydrogel shrank rapidly in the first few minutes. For example, the deswelling ratio of sample with a neutralization degree of 100% was around 80% when the hydrogel was immerged in 0.1 M $FeCl_3$ solution for 25 min. At the same time, the deswelling ratio was higher at high neutralization degree than that at lower ones. In the deswelling experiment, all the hydrogel samples could reach an equilibrium state.

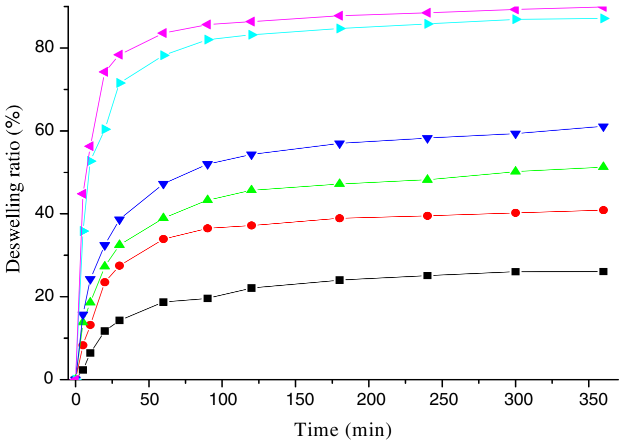


Fig. 11 Deswelling ratio of 15:2.5 PAC/PEG IPN hydrogels in 0.1 M $FeCl_3$ solution under different neutralization degrees 0% (■), 20% (●), 40% (▲), 60% (▼), 80% (▶), and 100% (◀)

Conclusions

PAC/PEG IPN hydrogel was synthesized by a simple two-step method. We investigated the effects of neutralization degree, acrylic acid dosage, and temperature on Fe^{3+} sorption onto IPN hydrogel. At higher neutralization degree, higher AA dosage and lower temperature, the IPN hydrogel exhibited higher sorption capacity. A comparative experiment on Fe^{3+} sorption by dried PAC/PEG composite and swollen PAC/PEG IPN hydrogel was carried out. The results of the experiment revealed that the sorption amount of PAC/PEG IPN hydrogel for Fe^{3+} was much higher than that of dried composite. The diffusion and sorption mechanisms were investigated using Fickian diffusion theory.

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