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Evaluation of thermally crosslinkable chitosan-based nanofibrous mats for the removal of metal ions

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ABSTRACT

Environmentally sensitive composite nanofibrous mats capable of metal ion adsorption were successfully prepared via electrospinning. The composite nanofibers were fabricated with different ratios of chitosan to thermo-responsive polymer, poly(*N*-isopropylacrylamide-*co*-*N*-methylolacrylamide) (poly(NIPAAm-*co*-NMA), PNN). NMA provided the function of thermal crosslinking of the nanofibrous mats to form water-stable nanofibers in aqueous solution. Subsequently, glutaraldehyde was used as a secondary crosslinking agent to increase the gel fraction of the nanofibrous mats. The morphology changes of the nanofibers in different environments were studied. Comparing the nanofibrous mats and films of the same material, the fibrous mats showed significantly increased adsorption of Cu(II). The adsorption amount of Cu(II) on the chitosan/PNN (50/50) nanofibrous mats could reach 79 ± 2 mg/g-mats, and its desorption was relatively effective. The incorporation of poly(NIPAAm-*co*-NMA) significantly improved the desorption of Cu(II) from the nanofibrous mats. The chitosan/PNN fibrous mats maintained the capacity of Cu(II) adsorption for 4-time regeneration.

1. Introduction

Heavy metals are highly toxic and exist in the aqueous waste streams of many industries. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Of all the heavy metal ions, copper (Cu) and nickel (Ni) ions are usually considered as the model ions (Bailey, Olin, Bricka, & Adrian, 1999). Treatment processes for waste streams include chemical precipitation, membrane filtration, ion exchange, and carbon adsorption (Babel & Kurniawan, 2003). Recently, cheap agricultural wastes such as rice straw, bark, wool, and coconut husks have been highlighted as potential adsorbents for metal ion removal from wastewater (Crini, 2005). Minamisawa, Minamisawa, Yoshida, and Takai (2004) used chitin and chitosan for the adsorption of metal ions such as Cu(II), Cd(II), and Pb(II). Chitin is universally present in the exoskeletons of arthropods and is manufactured on a large scale from crab and shrimp shell wastes. Chitin and chitosan are nontoxic and readily biodegradable and hence are environmentally acceptable.

Chitosan is one of the most extensively studied polysaccharides. It is generally derived from chitin by alkaline deacetylation. Chitosan is a random copolymer composed of (1 → 4) linked 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose units. It is a pH-responsive polymer because of its amino groups along the chain. It can be dissolved in acidic solution due to the protonation of its amino group on the C-2 position of pyranose, and it then becomes a cationic pH-sensitive polyelectrolyte. It is also a low-cost biosorbent with a high adsorption capacity for metal ions (Ngah, Teong, & Hanafiah, 2011).

Electrospinning is a technique for manufacturing nanofibrous mats from a variety of synthetic or natural polymers (Sill & von Recum, 2008). The process begins with a polymer solution in a syringe, held at the end of the needle by its surface tension. A high-voltage charge is then induced on the needle by an external electric field. As the applied electric field is increased, the created charges directly oppose the surface tension. At a critical value, these forces cause the formation of a protruding conical shape known as the Taylor cone at the tip of the needle (Reneker & Yarin, 2008). Beyond this critical value, the electric field causes the charges to overcome the surface tension, and a charged jet of solution is formed. As this jet travels in the air, it experiences instabilities and follows a spiral path as the solvent evaporates, leaving behind a charged polymer fiber that is deposited onto the collector.

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Poly(*N*-isopropylacrylamide) (PNIPAAm) is a thermo-responsive polymer; it has a phase transition temperature, also known as the lower critical solution temperature (LCST), at approximately 32 °C (Binkert, Oberreich, Meewes, Nyffenegger, & Ricka, 1991). The transition from a hydrophilic to a hydrophobic structure occurs dramatically at the phase transition temperature (Schild, 1992). However, the application of polymer nanofibers of PNIPAAm and chitosan has been hindered by their relatively rapid dissolution in water at room temperature. *N*-(methylol acrylamide) (NMA) is a bifunctional monomer containing a self-condensable methylol group and a reactive double bond (Huglin & Radwan, 1991). Therefore, it could be copolymerized with NIPAAm and provided the function of thermal crosslinking.

The aim of this study was to develop water-stable chitosan/poly(NIPAAm-*co*-NMA) (PNN) nanofibrous mats as adsorbents for the removal of metal ions. First, the thermally crosslinkable copolymer PNN was synthesized. Subsequently, chitosan/PNN nanofibers were fabricated via electrospinning. The morphologies of the chitosan/PNN nanofibers were observed by SEM. Additionally, Cu(II) and Ni(II) were used as model ions, and the adsorption and desorption of metal ions on the chitosan/PNN nanofibrous mats were studied in aqueous solution.

2. Experimental

2.1. Material

Chitosan (degree of deacetylation 83% (Desai, Kit, Li, & Zivanovic, 2008), molecular weight (*Mw*) 223 kDa) and *N*-methylol acrylamide (NMA; 48 wt% in water) were obtained from Sigma-Aldrich (St. Louis, MO, USA). *N*-isopropylacrylamide (NIPAAm), 2,2′-azobisisobutyronitrile (AIBN), trifluoroacetic acid (TFA), dichloromethane (DCM), glutaraldehyde solution (GA; 25 wt%), $CuSO_4{\cdot}5H_2O$, $NiSO_4{\cdot}6H_2O$, and nitric acid (70%, trace metals basis) were acquired from Acros Organic (Geel, Belgium). AIBN was recrystallized from ethanol. All other chemicals were at least of analytical grade and were used without the need of further purification.

2.2. Synthesis of poly(NIPAAm-co-NMA) (PNN)

To maintain the nanofibrous structure of the soaked nanofibers, a thermally crosslinkable monomer, NMA, was introduced into the copolymer. NIPAAm (30.55 g) and NMA solution (48 wt%; 6.32 g) were dissolved in 118 mL of methanol; the molar ratio of NMA to NIPAAm was 10:90. The solution was purged with nitrogen and heated to 60 °C. AIBN (0.0616 g) was dissolved in 2 mL of methanol and poured into the solution. Polymerization was carried out at 60 °C for 24 h. The resulting solution was subjected to dialysis (3000 Da molecular weight cut-off) at room temperature for 72 h in a series of methanol/deionized (DI) water mixtures (100%, 70%, 50%, and pure water for 3 times, 12 h for each step) to remove the residual initiator and unreacted monomer. The final dialyzed product was dried by lyophilization. The total monomer conversion (*X*, %) was calculated by gravimetric analysis using the following equation:

$$X = \frac{W_{\text{dry}}}{W_{\text{NIPAAm}} + (0.48 \times W_{\text{NMA}})} \quad (1)$$

where W_{NIPAAm} and W_{NMA} are the weights of NIPAAm monomer and NMA solution in the feed, respectively. The number of 0.48 is the weight concentration of the NMA solution. W_{dry} is the weight of the PNN polymer after lyophilizing for 72 h.

2.3. Preparation of the chitosan/PNN nanofibrous mats

The chitosan/PNN nanofibers were fabricated via electrospinning using TFA/DCM as a cosolvent, in which the weight ratio of TFA to DCM was 73 to 27. First, PNN and chitosan were separately dissolved in the cosolvent at equal concentrations of 2.5 wt%. The two solutions were blended at different weight ratios (CS/PNN = 100/0; 75/25; 50/50; 25/75; 0/100). The viscosities of the electrospun solutions were measured by viscometer (Brookfield DV-E, USA). The solution was filled in a syringe and pumped into a needle at a rate of 1 mL/h by a syringe pump (KD Scientific Model 100, USA). A high-voltage charge (14 kV) was then induced on the needle via a high voltage supply (Chargemaster CH30P, SIMCO, USA). As the applied electric field was increased, a charged jet of solution was formed. As this jet traveled in the air, it experienced instabilities and followed a spiral path while the solvent evaporated, leaving behind a charged polymer nanofiber that was deposited onto the collector. The distance from the needle tip to the collector was 12 cm. All electrospinning was carried out at room temperature.

2.4. Crosslinking of the nanofibers

In this study, two crosslinking reactions were carried on: thermal crosslinking for the PNN copolymer and the crosslinking of chitosan chains by glutaraldehyde vapor. PNN is a thermally crosslinkable copolymer, which led to the formation of a bis(methylene ether) and then of a methylene bridge by eliminating water and formaldehyde, respectively. First, the chitosan/PNN nanofibrous mats were baked at 110 °C for 48 h. Second, the chitosan/PNN nanofibrous mats were crosslinked via GA vapor. The nanofibrous mats were placed in a vacuum chamber with a bottle containing 10 mL of 25 wt% glutaraldehyde solution, and then the chamber was evacuated until the first bubble was present in the solution at 25 °C. After 7 h, the weights of the crosslinked nanofibrous mats were measured and noted as W_o. Sequentially, the mats were washed and brought to a pH of 4 for 2 days; the weights of the swollen mats were noted as W_s. Finally, the chitosan/PNN nanofibrous mats were dried by lyophilization and made ready for the adsorption studies; the weights of the dried mats were noted as W_d. The swelling ratio and gel fraction were calculated by Eqs. (2) and (3).

$$\text{Swelling ratio} = \frac{W_s}{W_d} \quad (2)$$

$$\text{Gel fraction} = \frac{W_d}{W_o} \quad (3)$$

2.5. Morphology

The morphologies of the crosslinked nanofibrous mats were observed by scanning electron microscopy (SEM; JOEL JSM-6700F). A small section of the fibrous mats was placed on the SEM sample holder and sputter-coated with platinum. Furthermore, morphology changes of the mats which were soaked at various pH values and temperatures were studied. The mats were immersed in various environments (25 °C pH 2, 70 °C pH 2, and 25 °C pH 10) for 24 h. Then, the mats soaked at 25 °C were dried by lyophilization, and those soaked at 70 °C were dried by vacuum oven at 70 °C.

2.6. Phase transition temperature

The phase transition temperature was measured by differential scanning calorimetry DSC (TA Q20 System, USA). The PNN copolymer was dissolved in deionized water adjusted to pH 4 by HCl at

the concentration of 2 wt% polymer. In addition, the crosslinked nanofibrous mats were put into DSC cells and wetted by an amount of 50 times of water for 24 h. DSC thermograms were obtained at a heating rate of 10 °C/min from 0 to 90 °C. The transition temperature was defined as the onset temperature of transition zone.

2.7. Elemental analysis

An Agilent 7700e inductively coupled plasma mass spectrometer (ICP-MS) was used for the quantitative determination of the metal ion concentration. Standard solutions (0, 25, 50, 75, 100 μg/L) for the calibration curve were prepared. The sampling solutions were diluted to the detection range (0–100 μg/L). All samples and standard solutions were acidified by adding proper amounts of concentrated HNO_3 to produce 2.0 wt% HNO_3 in the final solution.

2.8. Adsorption kinetics and equilibrium studies

The electrospun chitosan/PNN nanofibrous mats were used as adsorbents for the removal of Cu(II) and Ni(II) from aqueous solution. The stock solutions (1 g/L) were prepared by dissolving $CuSO_4{\cdot}5H_2O$ and $NiSO_4{\cdot}6H_2O$ in deionized water and adjusting to pH 4 by HCl. Each of the nanofibrous mats (0.06 g) was immersed in 12.0 mL of a 1000 mg/L or 100 mg/L ion solution and continuously shaken in a water batch shaker at 100 rpm and 25 °C for 24 h. For dynamic studies, 0.1 mL of the ion solution was drawn out from the system after a predetermined period and serially diluted to the detection rage (0–100 ppb). The adsorbed amount was calculated as follows:

$$A_n = C_0V_0 - C_nV_n - \sum_{k=1}^{n} C_kV_{k,\text{sampling}} \quad (4)$$

$$V_n = V_{n-1} - V_{n-1,\text{sampling}} - \left(V_{n,\text{swelling}} - V_{n-1,\text{swelling}}\right) \quad (5)$$

where A_n is the amount of ion adsorbed (mg/g), C_0 and C_n are the initial and nth operation's concentration of the ion solution, respectively, V_0 and V_n are the initial and nth operation's volume of the ion solution, respectively, $V_{n,\text{sampling}}$ is the volume of the ion solution drawn out of the system for analysis, and $V_{n,\text{swelling}}$ is the volume of the solution swollen into the mat.

Chitosan/PNN films were prepared with the same composition to compare them to the nanofibrous mats in the adsorption and desorption studies. First, PNN and chitosan were separately dissolved in 90 wt% acetic acid solution at a concentration of 2.5 wt%. The two solutions were blended at different weight ratios (CS/PNN = 100/0; 75/25; 50/50; 25/75; 0/100) overnight. The mixed solutions were poured into plate dishes and dried at 50 °C in an oven. Next, the films were crosslinked at 110 °C in an oven for 48 h and then crosslinked using 1 wt% GA solution for 4 h at 25 °C. Finally, the films were washed with a pH 4 solution several times until the pH value of solution was unchanged and dried by lyophilization.

2.9. Desorption and regeneration studies

Desorption studies were performed using deionized water adjusted to pH 2 by HCl with two different processes: 25-70-25 and 70-25-70. In the first one, 25-70-25 is the metal ion containing nanofibrous mats (0.06 g) were immersed in 35 mL of the deionized water and continuously shaken at 25 °C for 30 min. After that, the fibrous mat was removed to fresh deionized water at 70 °C for another 30 min and then 25 °C, sequentially. In the second process, 70-25-70, the temperature order was changed. The metal ion containing nanofibrous mats were immersed in 35 mL of the deionized water at 70 °C, then 25 °C, and 70 °C for 30 min each, sequentially. All of the deionized water mentioned in this section was at pH 2. The amount of metal ion desorbed was analyzed by ICP–MS after each step.

After desorption, the fibrous mats were neutralized by 1 M of K_2CO_3 aqueous solution for regeneration, and then it was washed to pH 4 and dried by lyophilization for adsorption.

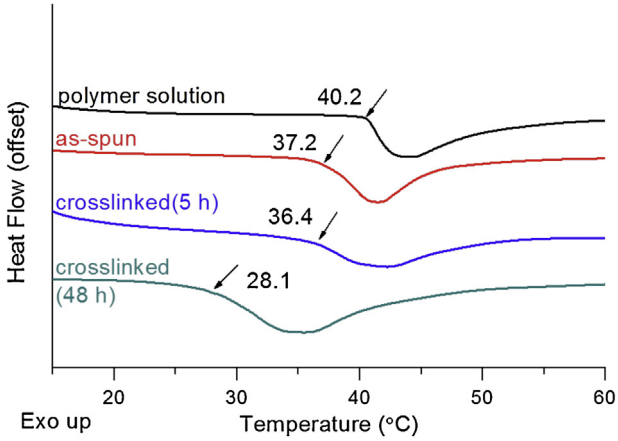

Fig. 1. The phase transition temperature of PNN solution and PNN fibrous mats under various crosslinking times (pH 4).

3. Results and discussion

3.1. Characteristics of the PNN

The NIPAAm and NMA copolymer (PNN) was synthesized by free radical polymerization in methanol using AIBN as an initiator. The monomer conversion was estimated as 92.6% using Eq. (1). The number average molecular weight (Mn) of the copolymer was 28,355, and the weight average molecular weight (*Mw*) was 33,272, characterized by GPC using tetrahydrofuran as the mobile phase. The composition of the PNN was determined from the ^{1}H NMR spectra recorded in CD_3OD. The NMA molar content in the polymer was 10.95 mol%, similar to the monomer feeding concentration of 10 mol%.

3.2. The phase transition temperature of PNN

The PNN nanofibers were fabricated by electrospinning and crosslinked at 110 °C for 5 or 48 h. The thermal properties of the nanofibers were measured by DSC. As shown in Fig. 1, the phase transition temperatures of the PNN solution and as-spun nanofibers were 40.2 °C and 37.2 °C, respectively. After 5-h and 48-h thermal crosslinking, the transition temperature shifted to 36.4 °C and 28.1 °C, respectively. This was because the hydrophilic hydroxyl groups of NMA were eliminated during the crosslinking reaction that the crosslinked PNN was more hydrophobic than uncrosslinked one.

3.3. Formation of the chitosan nanofibers

The chitosan nanofibers were fabricated by electrospinning with different concentrations in the cosolvent. Below 2 wt%, the nanofibers consisted of beads and broken fibers. With an increase in the concentration, continuous nanofibers were obtained. However, the viscosity was significantly increased at a concentration of 3.5 wt%. The high viscosity restricted the flow of the electrospun solution in the needle, and the Taylor cone at the tip of the needle became unstable. Therefore, a concentration of 2.5 wt% was used for the further studies of the chitosan/PNN electrospinning.

3.4. Crosslinking of the chitosan nanofibers

The chitosan was crosslinked under glutaraldehyde vapor via a Schiff base reaction (Schiffman & Schauer, 2007). With an increase in the contact time with the GA vapor, the gel fraction of the chitosan nanofibers increased and the swelling ratio decreased because of the increase of the crosslinking degree (Fig. 2). The adsorption of metal ions was attributed to the amino group of the chitosan. Therefore, with the increase in the gel fraction, the adsorption of Cu(II) decreased. Because the gel fraction significantly increased during the first 7 h, the chitosan/PNN nanofibrous mats were crosslinked for 7 h by GA vapor in the further studies.

3.5. Morphologyies of the chitosan/PNN nanofibrous mats

The chitosan/PNN nanofibrous mats were crosslinked by two mechanisms: thermal crosslinking and GA crosslinking. First, the as-spun mats were thermally crosslinked at 110 °C for 48 h. Second, the chitosan/PNN nanofibrous mats were crosslinked via GA vapor. Fig. 3a–c shows the SEM images of the crosslinked chitosan/PNN nanofibers with different weight ratios of chitosan to PNN. A uniform fibrous structure is observed for each ratio. The diameter of the pure chitosan nanofibers was 214 ± 35 nm. With an increase in the PNN content, the diameter of the nanofibers first increased and then decreased as PNN/chitosan ratio was above 50/50.

To observe the morphology changes of the chitosan/PNN nanofibers in different environments, the crosslinked nanofibers were soaked in various environments (25 °C pH 2, 70 °C pH 2, and 25 °C pH 10) for 24 h. The SEM images of the chitosan/PNN (50/50) nanofibrous mats are shown in Fig. 3d–f. In Fig. 3d, both the PNN and chitosan swelled in the pH 2 solution at 25 °C. The fibrous structure remained but the diameter of the fibers increased. The surface of nanofibers was smooth and puffy with approximately average diameter of 550 nm. The fluctuation in cross section of the nanofibers was small. In the 70 °C pH 2 solution, the PNN shrank and chitosan swelled. The surface of the nanofibers was obviously wrinkled (Fig. 3e). It was suggested that the PNN shrank

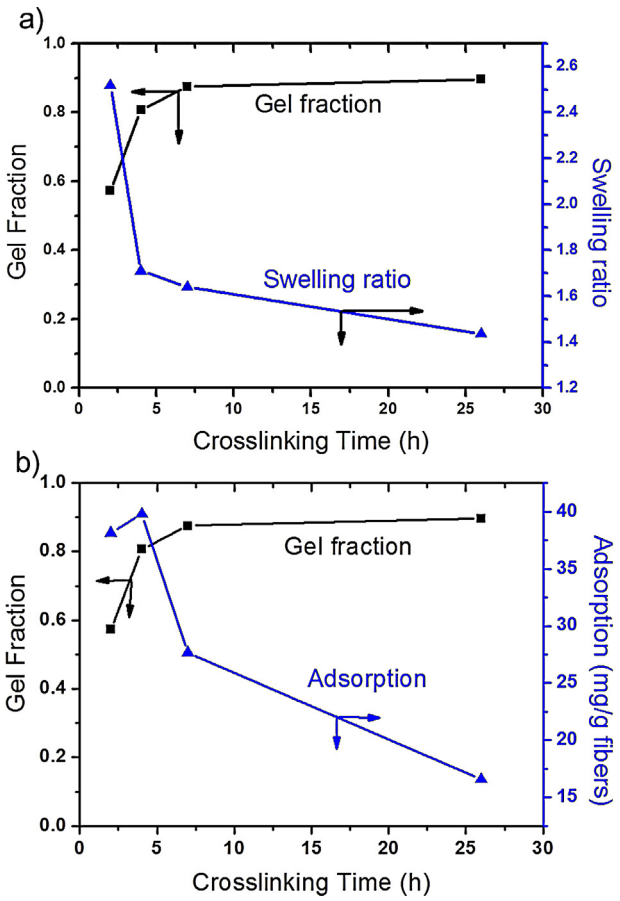

Fig. 2. Effect of the crosslinking time on the chitosan nanofibrous mats: (a) gel fraction and swelling ratio; (b) gel fraction and adsorption of Cu(II).

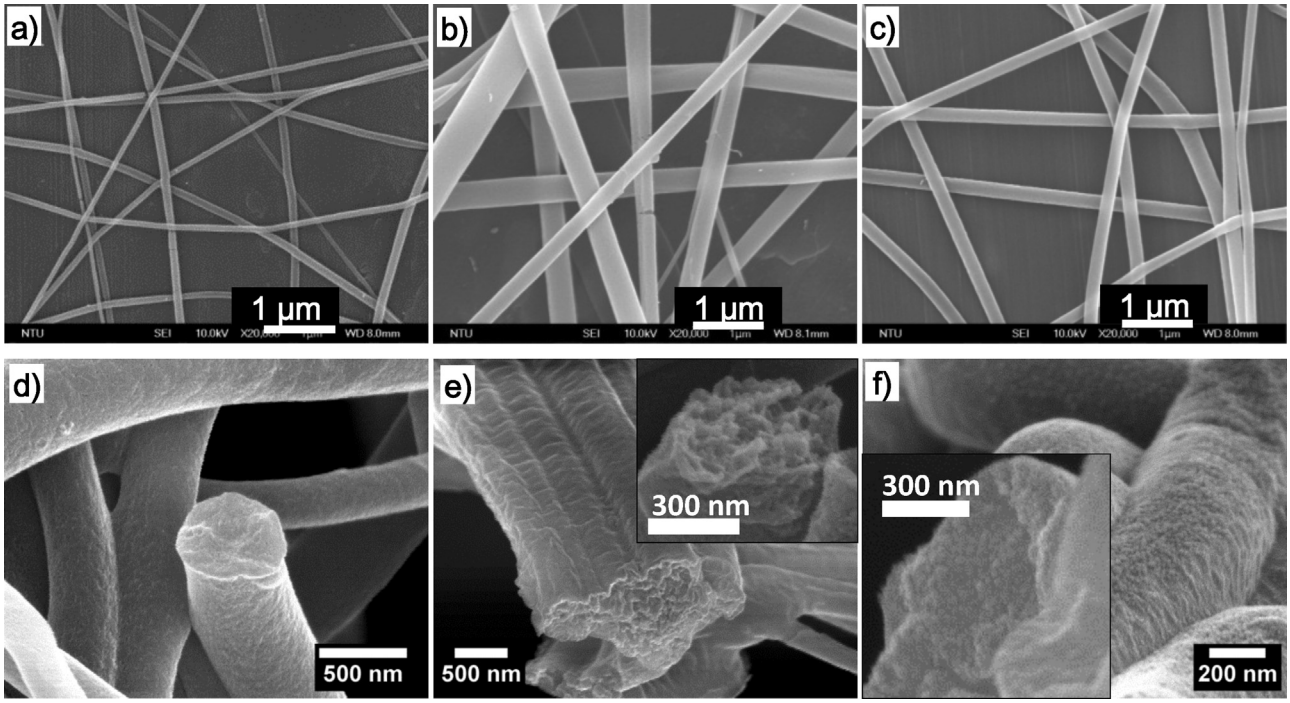

Fig. 3. SEM images of the crosslinked chitosan/PNN nanofibers with different weight ratio (CS/PNN = (a)100/0, (b) 50/50, and (c) 0/100;) and the soaked CS/PNN (50/50) nanofibers in (d) 25 °C pH 2, (e) 70 °C pH 2, and (f) 25 °C pH 10 water.

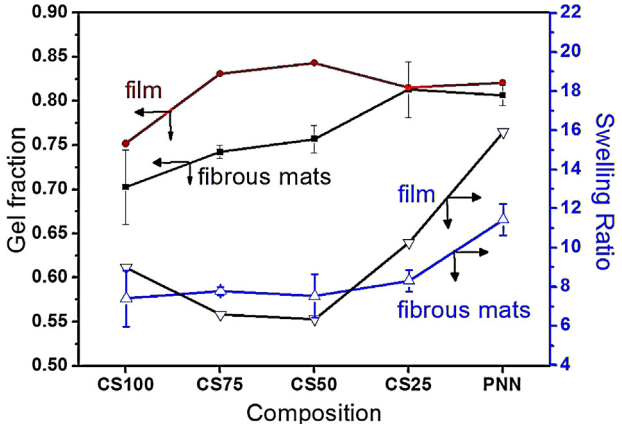

Fig. 4. Swelling ratio and gel fraction of the chitosan/PNN fibrous mats and composite films.

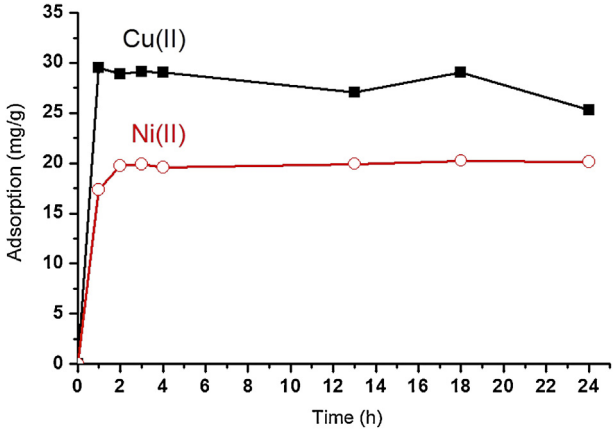

Fig. 5. Effect of the shaking time on the adsorption of Cu(II) and Ni(II) on the chitosan/PNN fibrous mats (chitosan/PNN = 50/50) with an initial concentration of 100 ppm (pH 4, 25 °C).

and squeezed the aqueous solution out because PNN became hydrophobic above the phase transition temperature. Furthermore, the cross section of the nanofibers was very rough with some projections which were the PNN domains after phase separation. In the 25 °C pH 10 solution, the PNN swelled and chitosan was deprotonated. As shown in Fig. 3f, granular projections were observed throughout the surface and cross section of the nanofibers. Deprotonated chitosan was easily precipitated in aqueous solution due to intermolecular H-bonding; therefore, the chitosan coagulated and formed a granular projection in PNN swelling networks. The overall results indicated that chitosan was uniformly dispersed in PNN networks.

3.6. Gel fraction and swelling ratio

The swelling ratio and gel fraction were calculated using Eqs. (2) and (3). The swelling ratio increased with the PNN content because of the hydrophilic nature of PNN at room temperature (Fig. 4). Due to the difference in the crosslinking mechanisms, the gel fraction increased with an increase of the PNN content. It was suggested that the thermal crosslinking of PNN was more effective than the GA crosslinking for chitosan. Therefore, the incorporation of PNN increased the gel fraction of the composite fibrous mats.

3.7. Adsorption of metal ions

The chitosan/PNN nanofibrous mats (50/50) were immersed in 100 ppm metal ion solutions and shaken continuously. As shown in Fig. 5, it was found that the adsorption of Cu(II) was approximately 29 mg/g and that of Ni(II) was approximately 20 mg/g. The results showed that equilibrium could be reached quickly. The adsorption of Cu(II) and Ni(II) reached equilibrium within 2 h. For the equilibrium studies, the chitosan/PNN fibrous mats and films were shaken overnight in the Cu(II) solution. As shown in Fig. 6, the adsorption amount of Cu(II) increased with an increase in the initial Cu(II) concentration, and the adsorption amount of Cu(II) on the fibrous mat was higher than that on the film in each group. This result suggested that the fibrous mats have a great capacity for the adsorption of Cu(II) because of their high surface area and porosity. The adsorption amount of Cu(II) on the CS/PNN (50/50) nanofibrous mats which was washed to pH 4 was 38 ± 7 mg/g-mats. In order to increase the adsorption capability, another set of nanofibrous mats were washed to pH 7 to reduce the protonation of chitosan. Then, the adsorption amount of Cu(II) was increased to 79 ± 2 mg/g-mats on CS/PNN (50/50) nanofibrous mats.

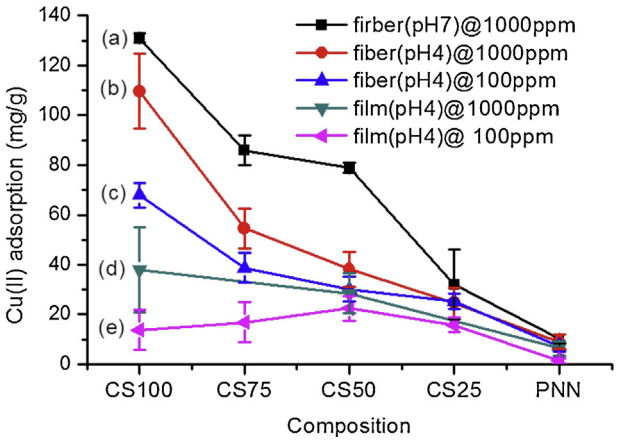

Fig. 6. Effect of the chitosan content on the adsorption of Cu(II) on the chitosan/PNN fibrous mats and films at pH 4 with various initial Cu(II) concentrations. (a) fiber washed to pH 7, 1000 ppm; (b) fiber washed to pH 4, 1000 ppm; (c) fiber washed to pH 4, 100 ppm; (d) film washed to pH 4, 1000 ppm; (e) film washed to pH 4, 100 ppm.

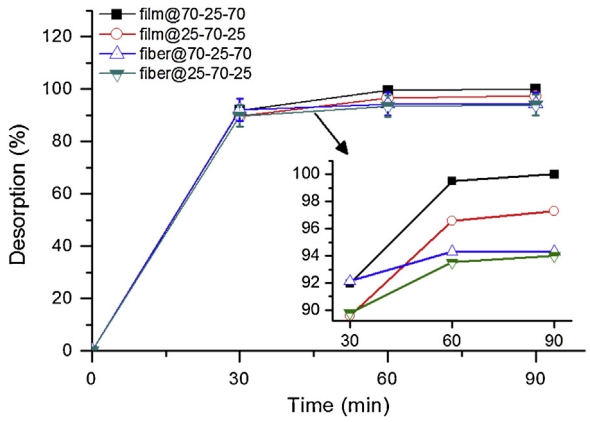

Fig. 7. Effect of temperature on the desorption of Cu(II) from the chitosan/PNN (50/50) nanofibrous mats and the films at pH 2.

3.8. Desorption studies

Desorption studies were carried out to evaluate the possibility of regenerating the nanofibrous mats and films for subsequent reuse. Based on the thermal response of CS/PNN (50/50) nanofibers, two different processes, 25-70-25 and 70-25-70, were designed to

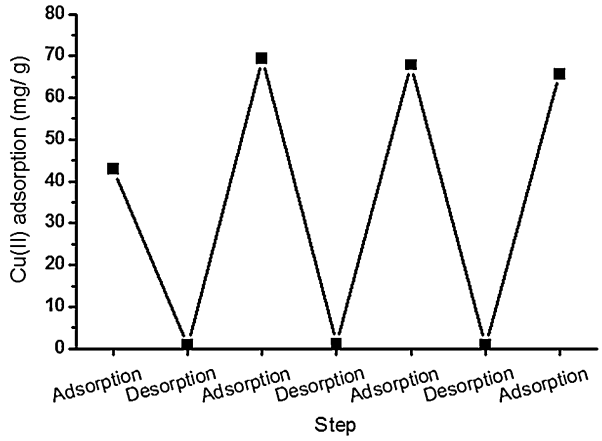

Fig. 8. The regeneration of the chitosan/PNN fibrous mats (chitosan/PNN = 50/50).

find a high efficient desorption process. In the first one, the nanofibrous mats/films was firstly immersed in 25 °C pH 2 water, and then it was removed to fresh pH 2 deionized water at 70 °C and 25 °C for 30 min each, sequentially. In the second process, 70-25-70, the temperature order was changed. The metal ion containing nanofibrous mats were immersed in 35 mL of the deionized water at 70 °C, 25 °C, and 70 °C for 30 min each, sequentially. In a 25 °C pH 2 solution, the PNN was swelled and chitosan was protonated. Then, Cu(II) was released from the positively-charged NH_3^+ of chitosan and diffused out. On the other hand, Cu(II) was squeezed out the mats/films in a 70 °C pH 2 solution due to the thermal response of PNN above phase transition temperature. As shown in Fig. 7, it was found that desorption was relatively effective for all groups. Moreover, the desorption efficiency of the 70-25-70 was slight better than that of the 25-70-25 because Cu(II) was squeezed out twice by the thermal response of the PNN at the two steps of 70 °C in the 70-25-70 process. In addition, there were infinitesimal differences (less than 6%) between films and nanofibrous mats. It was suggested that the porous structure of the nanofibrous mats reduced the shrinking effect of nanofibers at 70 °C. In conclusion, the incorporation of poly(NIPAAm-*co*-NMA) significantly improved the desorption of Cu(II) from the nanofibrous mats.

After desorption, the used fibrous mats were neutralized by 1 M of K_2CO_3 solution for regeneration and washed with a pH 4 solution several times until the pH value of solution was unchanged. As shown in Fig. 8, the chitosan/PNN (50/50) fibrous mats maintained the capacity of Cu(II) adsorption for 4 cycles.

4. Conclusion

Thermally responsive chitosan/PNN nanofibrous mats were successfully prepared via electrospinning and applied in the adsorption of metal ions. The fibrous structure of the soaked chitosan/PNN mats was preserved by crosslinking using NMA and GA vapor. The adsorption of Cu(II) on the chitosan/PNN fibrous mats was higher than that on the films with the same composition. The adsorption amount of Cu(II) on the CS/PNN (50/50) nanofibrous mats which was washed to pH 7 could reach 79 ± 2 mg/g-mats, and its desorption was relatively effective. The incorporation of poly(NIPAAm-*co*-NMA) significantly improved the desorption of Cu(II) from the nanofibrous mats. The chitosan/PNN (50/50) fibrous mats maintained the capacity of Cu(II) adsorption for at least 4 cycles. Because the chitosan/PNN (50/50) nanofibrous mats have a high surface area and thermal sensitivity, the chitosan/PNN fibrous mats exhibit great potential as materials for the removal of metal ions from waste water.

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