# A Novel Method for Obtaining a High-Concentration Chitosan Solution and Preparing a High-Strength Chitosan Hollow-Fiber Membrane with an Excellent Adsorption Capacity

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**ABSTRACT:** The biopolymer chitosan (CS) has been widely studied for various environmental and biomedical applications. However, the production of homogeneous CS solutions with high concentrations and the preparation of CS hollow-fiber membranes with high mechanical strengths for practical applications have been a great challenge so far. In this study, a novel dilute-dissolution and evaporating-concentration method was developed to allow highly concentrated homogeneous CS solutions to be easily prepared (up to 18 wt % as compared to ≤5 wt % prepared by the conventional method). CS hollow-fiber membranes prepared from high-concentration CS solutions showed greatly improved mechanical strengths (with tensile strengths up to 3.4 MPa), comparable to or even better than other hollow fibers made from many conventional industrial synthetic polymers. The prepared hollow-fiber membranes were found to possess very high adsorption capacities for heavy-metal ions (up to 206.6 mg of $Cu^{2+}$/g of CS fiber at pH 5), which were attributed to the low crystallinity of CS and the porous structure achieved in the hollow-fiber membranes. As a potential application example, the performance of the prepared hollow fibers for the adsorption of copper ions in real wastewater from a wafer fabrication factory in Singapore was also examined. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1913–1921, 2010

**Key words:** adsorption; biopolymers; fibers; membranes

## INTRODUCTION

In recent years, adsorptive membrane technology has attracted increasing interest in many separation applications because of its economical advantages, particularly, in the separation of small and low-concentration substances from bulk solutions, over conventional membrane technology, which works on the mechanism of size exclusion.[1] Adsorptive membranes carry reactive functional groups on the surfaces to capture targeted substances through specific interactions. Hence, the pore sizes of adsorptive membranes are much less crucial for separation, compared to conventional membranes, and can be much larger than the sizes of the targeted substances. This could significantly reduce the resistance of flow through the membrane and, thus, lower the energy consumption of the process.

However, most commercially available or conventional membranes are prepared from inert industrial synthetic polymers that do not have reactive functional groups. These membranes are, therefore, usually not suitable as adsorptive membranes. The common method for obtaining adsorptive membranes has been by surface modification of conventional membranes.[2,3] A major problem in the surface modification method is that the harsh physical or chemical treatment conditions used can often result in the deterioration of the polymer material and also in the alternation of the structures of the membranes.[2]

An alternative method for preparing adsorptive membranes is to use polymers containing reactive functional groups as the membrane materials, either partly or entirely.[4–6] Among materials with reactive functional groups, chitosan (CS) has been mostly studied.[7–9] CS is a natural biopolymer, readily available from sources such as seafood-processing waste.[10] CS possesses a high content of amine groups (up to 7 wt %), which are highly reactive, and has been found to show affinity to many water contaminants and bioproducts. Considerable efforts have been made in

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research to use CS or modified CS as an adsorbent or for composite membranes to remove heavy metal ions or to separate bioproducts.[11–18]

Although CS flat-sheet membranes or CS composite membranes (supported on other flat sheets or hollow fibers) have been prepared,[8,19–21] these membranes have appeared to be relatively less attractive because of their small specific surface areas or the small amount of CS contained and, hence, low adsorption capacity for adsorptive separation.[8] To increase the specific surface area, hollow-fiber membranes are usually the preferred membrane configuration (because of the high packing density).[21] Unfortunately, CS has encountered significant difficulty in the preparation of hollow-fiber membranes with adequate mechanical strength so far. CS solutions have very high viscosities, and the polymer dope solutions used to spin the hollow-fiber membranes usually unavoidably have a low CS concentration (often ≤5 wt %). There have been three representative reports in the literature about the preparation of CS hollow-fiber membranes.[22–24] The authors of the first two studies[22,23] prepared CS dope solutions with about 3–5 wt % concentrations, and the spun hollow-fiber membranes did not seem to have good self-supporting capability in wet state. The third study reported[24] CS dope solutions with concentrations up to 7 wt % by using "Low-viscosity" CS, and the strength of the spun hollow-fiber membranes was increased by increasing the crystallinity of CS in the spinning process. Not only does the requirement for low-viscous CS limit the choice of CS products in the market, a higher crystallinity also reduces the adsorption capacity of CS and is, therefore, not desirable for adsorptive CS membranes.

The major obstacle in preparing CS hollow-fiber membranes with a high mechanical strength arises, to a large extent, from the practical difficulty of obtaining highly concentrated homogeneous CS dope solutions to spin the hollow-fiber membranes. In this study, a novel method was developed to prepare homogeneous and high-concentration CS dope solutions (up to 18 wt %). CS hollow-fiber membranes fabricated from these high concentration CS solutions showed good mechanical strengths. Adsorption studies for copper-ion removal with the prepared CS fibers showed very high adsorption capacities (copper ions were used in this study as a model heavy metal for easy comparison with some early results reported in the literature).

## EXPERIMENTAL

### Materials

CS, which was practical grade from crab shells, was supplied by Aldrich (St. Louis, MO). The molecular weight of CS was 319,000 g/mol, as calculated through the Mark–Houwink equation,[25] and the *N*-deacetylation degree was 79%. Glacial acetic acid from Merck (Darmstadt, Germany) was used as the solvent for CS. Sodium hydroxide from BDH (London, United Kingdom) was used to prepare the inner and outer coagulant solutions. Urea provided by Riedel-de Haën (Seelze, Germany) was used to evaluate the permeating properties of the hollow-fiber membranes for nonadsorptive water-soluble components. Copper sulfate pentuhydrate ($CuSO_4{\cdot}5H_2O$) from Nacalai Tesque (Kyoto, Japan) was used to prepare copper-ion solutions for the adsorption evaluation experiments. Wastewater from a wafer fabrication factory in Singapore was also used to test the capability of the prepared adsorptive hollow fibers for the removal of copper ions from real industrial wastewater.

### Preparation of the highly concentrated CS dope solution and spinning CS hollow-fiber membranes

CS was first dissolved in a 1% acetic acid solution to obtain a 2 wt % CS solution. The solution was stirred with a magnetic stirrer for 2 h and then filtered through 2.5-μm-pore filter paper to ensure the homogeneity of the solution. The dilute CS solution was collected in a glass beaker and subsequently placed in a water bath with the temperature maintained at 60°C. The solution in the beaker was slowly stirred, and the solvent (i.e., acetic acid and water) in the solution was gradually evaporated off to give a more and more concentrated CS solution. When the concentration of the CS solution was about to reach the level needed to spin the hollow-fiber membrane, as determined from the weight of the content in the beaker, heating was stopped, and the solution was allowed to slowly cool to room temperature (23–24°C). The beaker was then covered with Parafilm, and the content was degassed in a centrifuge (9000 rpm) for 5 min to remove any air bubbles trapped in the solution. The final concentration of CS in the solution reached as high as 18 wt %, and the solution could be readily used as the dope solution to spin the CS hollow-fiber membranes.

The hollow-fiber membranes were prepared through a wet-spinning method, similar to that described elsewhere.[26] In brief, the clear CS dope solution was forced through a stainless steel spinneret comprising an annular ring (o.d. = 1.72 mm, i.d. = 0.72 mm) under high-pressure $N_2$ gas and protruded directly into a coagulation bath (with no air gap) under zero drawing force. A bore liquid coagulant was delivered simultaneously through the inner core of the spinneret by a high-pressure syringe pump. A 10 wt % NaOH solution was used as both the external coagulant (in the coagulation bath) and the internal coagulant (the bore flow). Although an 18 wt % CS dope solution could be prepared, this led to highly dense or nonporous membranes, which is not desirable for adsorption membranes. In this study, two specific types of CS hollow-fiber membranes were, therefore, prepared from dope solutions with CS concentrations of 8 and 12 wt % and were examined to demonstrate the workability of the method and the performance of the prepared adsorptive membranes.

## Characterization analyses

A field emission scanning electron microscope (JEOL JSM-6700F, Japan) was used to characterize the morphologies and structures of the CS hollow-fiber membranes. The wet samples were treated with propanol and hexane to retain the original structures of the fibers for the surface scan. The dried hollow-fiber membranes were also snapped in a liquid nitrogen environment to give a generally clean break of the cross section for the cross-section scan. As the polymer was nonconductive, the samples were coated with platinum powder on the surface for 40 s at 40 mbar vacuum before the scanning analysis. The electrical voltage was controlled below 10 kV to prevent possible collapse of the samples caused by the electron beam in the analyses.

The mechanical properties of the hollow-fiber membranes were evaluated through the measurement of tensile strength, elongation ratio, and Young's modulus. Tests were conducted with an Instron-5542 (Norwood, MA) materials testing machine equipped with Bluehill Version 2.5 software at room temperature and a relative humidity of about 60%. The initial gauge length was set to 20 mm, and the drawing speed was set at 2 mm/min. The sample hollow fiber was cut into a 50 mm long piece and attached onto the two clamps of the machine. The test data were recorded, and the values of the tensile stress, elongation ratio, and Young's modulus of the hollow-fiber membranes were calculated by the software. For reliability, five measurements were made for each sample, and the average values are reported.

The porosities of the CS hollow-fiber membranes were estimated through the dry–wet weighing method. We took out a certain amount of the hollow fibers stored in deionized water in a measuring cylinder, removed the water in the lumen with a rubber pipette bulb, removed the surface water by placing the fibers on a few pieces of tissue paper for 2 min, and then weighed the fibers, using a beam balance, to obtain the initial weight ($W_h$). The weighed hollow fibers were subsequently dried in a vacuum desiccator (at about 1 mTorr) at room temperature for 3 days. The weight of the dried hollow fibers ($W_d$) was weighed again with the same beam balance. The porosity ($P$) of the hollow fibers was then calculated approximately by

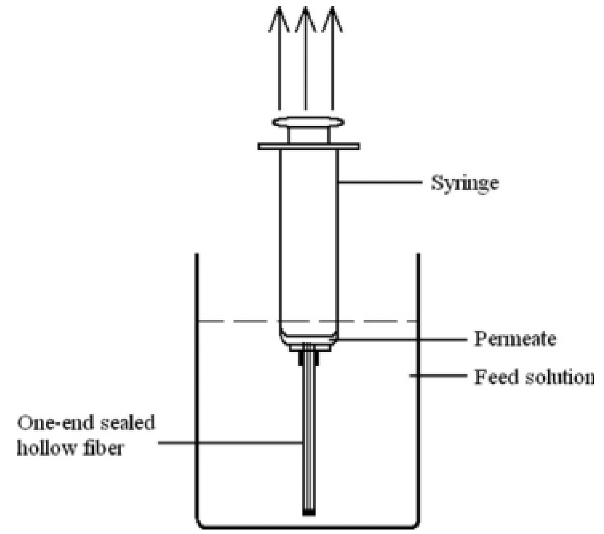

**Figure 1** Schematic representation of the permeation experimental setup for urea.

$$P = \frac{(W_h - W_d)/\rho_w}{W_d/\rho_{CS} + (W_h - W_d)/\rho_w}$$

where $\rho_w$ ($\rho_w \approx 1.0$ g/cm$^3$) is the density of water and $\rho_{CS}$ ($\rho_{CS} = 1.4$ g/cm$^{3}$ [27]) is the density of the CS.

Urea was used as a model molecule to test the permeating properties of the hollow-fiber membranes for small water-soluble components that do not have an affinity to CS. The urea solution at a concentration of 50 mg/L was fed from the outer surface to the lumen of the hollow-fiber membranes at 1 bar of pressure, and the concentrations of urea in the feed and permeate were analyzed with a Shimadzu TOC-500A analyzer (Kyoto, Japan). The permeation experiment was done with a syringe and a piece of hollow-fiber membrane that was fixed to the needle of the syringe at one end and was sealed with epoxy at the other end, as shown in Figure 1.

The crystallinity of the dry hollow-fiber membrane was measured with a Miniflex Rigaku X-ray diffractometer with nickel-filtered Cu K$\alpha$ radiation. The scanning was conducted at a speed of 2°/min over a 2$\theta$ range from 5 to 60°. A method developed by Singh and Ray[28] was used to calculate the crystallinity of the dry hollow-fiber membranes.

## Adsorption performance for copper ions

A primary evaluation of the adsorptive performance of the prepared CS hollow fibers was conducted with copper-ion solutions in a series of batch experiments. The hollow-fiber membranes were cut into pieces about 0.25 cm in length and used in the adsorption study. Adsorption performance was examined in terms of the effect of the solution pH values and the adsorption isotherms. To examine the effect of solution pH, adsorption experiments were conducted with copper-ion solutions with an initial concentration of 50 mg/L but different pH values in the range 3–5 (a higher pH was not used to prevent the possibility of precipitation). A certain amount of the wet hollow-fiber pieces (equivalent to 0.2 g of dry fibers) was added to 40 mL of a copper-ion solution in a 50-mL flask. The contents of the flask were shaken in an orbital shaker at 200 rpm and room temperature for a period of up to 24 h. The final copper-ion concentrations in the solutions were analyzed. An adsorption isotherm study was conducted at room temperature and an initial pH value of 5, with the initial copper-ion concentrations varied in the range 50–200 mg/L. A certain amount of the wet hollow-fiber pieces (equivalent to 0.2 g of dry fibers) was added to a number of 50-mL flasks, each containing 40 mL of the copper-ion solution with a different concentration. The contents of the flasks were shaken in an orbital shaker at 200 rpm at room temperature for a period of 24 h, and the final concentrations of copper ions in the solutions were measured.

The adsorption of copper ions from real industry wastewater was also investigated to examine the adsorptive performance of the prepared CS hollow-fiber membranes, especially at low copper-ion concentrations. The CS hollow-fiber membrane prepared from an 8 wt % CS solution was used in the experiments. The wastewater was supplied by a semiconductor company in Singapore with copper-ion concentrations around 12.1 mg/L. The wastewater had a pH value of about 6.2 and contained organic carbon as total organic carbon (TOC) at 32.5 mg/L. In the isotherm adsorption tests, different amounts of hollow-fiber pieces were added to each 40-mL wastewater sample in a number of 50-mL flasks. The contents in the flasks were shaken in an orbital shaker at 200 rpm at room temperature until the adsorption equilibrium was reached (in 2 h). The initial and final concentrations of copper ions in the solutions were analyzed. In the regeneration/reuse study, amounts of 0.02 and 0.25 g of wet hollow-fiber pieces were used, respectively. After adsorption, the hollow-fiber pieces were separated and regenerated in 40 mL of 0.01*M* ethylene diamine tetraacetic acid (which was reused for 10 cycles) with a pH of about 10 adjusted by the addition of NaOH solution. The mixture was stirred at 200 rpm at room temperature for 1 h to remove the copper ions adsorbed. Then, the hollow-fiber pieces were washed in deionized water and reused in the subsequent adsorption test. The adsorption and desorption cycle was conducted 10 times.

In this study, the concentrations of copper ions in all of the samples were analyzed with an inductive coupled plasma spectrometer (Perkin Elma DV3000, OES optical).

## RESULTS AND DISCUSSION

### CS concentration in the solutions

The first step for the preparation of a hollow-fiber membrane is to obtain a homogeneous dope solution of adequate polymer concentration to ensure enough strength and a uniform structure for the spun hollow-fiber membranes. The polymer (which may include some additives as well) is usually dissolved in a solvent, and the solution is well mixed to achieve homogeneity. In general, a higher polymer concentration in the solution is desired for a stronger hollow-fiber membrane. Higher polymer concentrations can allow the polymer chains to overlap or entangle one another to achieve better strength, but they also cause polymer dissolution and solution homogeneity to be more difficult to achieve. For most synthetic polymers, the critical polymer concentration has been found to be in the range 0.2–0.3 (or 20–30 wt %)[29] for successful preparation of a homogeneous polymer solution to fabricate hollow-fiber membranes. CS has high swelling rates, and the solution usually has a very high viscosity. For degraded low-molecular CS, it was reported that the concentration can be as low as about 0.0118[30] for a homogeneous solution. For normal CS with a molecular weight of 100,000–300,000 g/mol, homogeneous solutions with CS concentrations at a maximum of 3–5 wt % have been successfully obtained.[22,23,26] To further increase the CS concentration, it has been found that CS could not be adequately dissolved, even after a dozen days, because of the extremely high viscosity, which prevented the polymer chains from being fully opened. However, evidence has indicated that CS hollow-fiber membranes prepared from solutions of CS concentrations up to 3–5 wt % had tensile strengths less than 0.1 MPa and were not strong enough even for self-support in their wet state.[22]

In this study, the dilute-dissolution method allowed CS molecules to be easily and fully dissolved at first. Because of the relatively low viscosity of the solution, the process also provided another advantage for easily removing any insoluble impurities in the CS product from the solution through filtration separation. The subsequent evaporating-concentration process with slow stirring increased the concentration of CS in the solution because of the loss of the solvent from the system. Homogeneous CS solutions with concentrations as high as 18 wt %

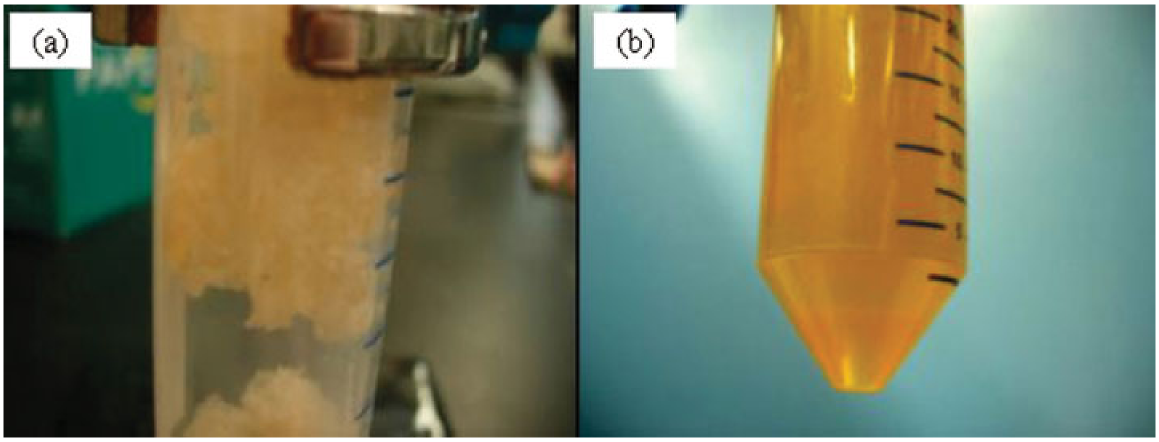

**Figure 2** Photos showing 18 wt % CS solutions: (a) prepared by the conventional method (direct dissolution) and (b) prepared by the new method (dilute dissolution and evaporation-concentrating). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

were successfully achieved in this study. In Figure 2, the photos show the 18 wt % CS solutions prepared by the conventional method (direct dissolution) and by the method developed in this study. It is clear that the conventional method could not achieve the homogeneity (particles are still observed) and the CS solution prepared by the new method was essentially very uniform with a high homogeneity.

## Morphological properties

The structures and morphologies of the CS hollow-fiber membranes prepared from 8 and 12 wt % CS solutions were examined (and are referred to as 8CSHF and 12CSHF, respectively). The outer diameters of 8CSHF and 12CSHF were 1630 ± 100 and 1650 ± 100 μm, respectively, in the wet state and changed to 750 ± 80 and 760 ± 80 μm after drying. The inner diameters of 8CSHF and 12CSHF also changed from 680 ± 70 and 670 ± 60 μm, respectively, in the wet state to 430 ± 50 and 440 ± 60 μm after drying. Figure 3 shows typical field emission scanning electron microscopy images on the cross section and surface morphologies of these CS hollow-fiber membranes (dry). Both types of hollow-fiber membranes had a spongelike porous cross-

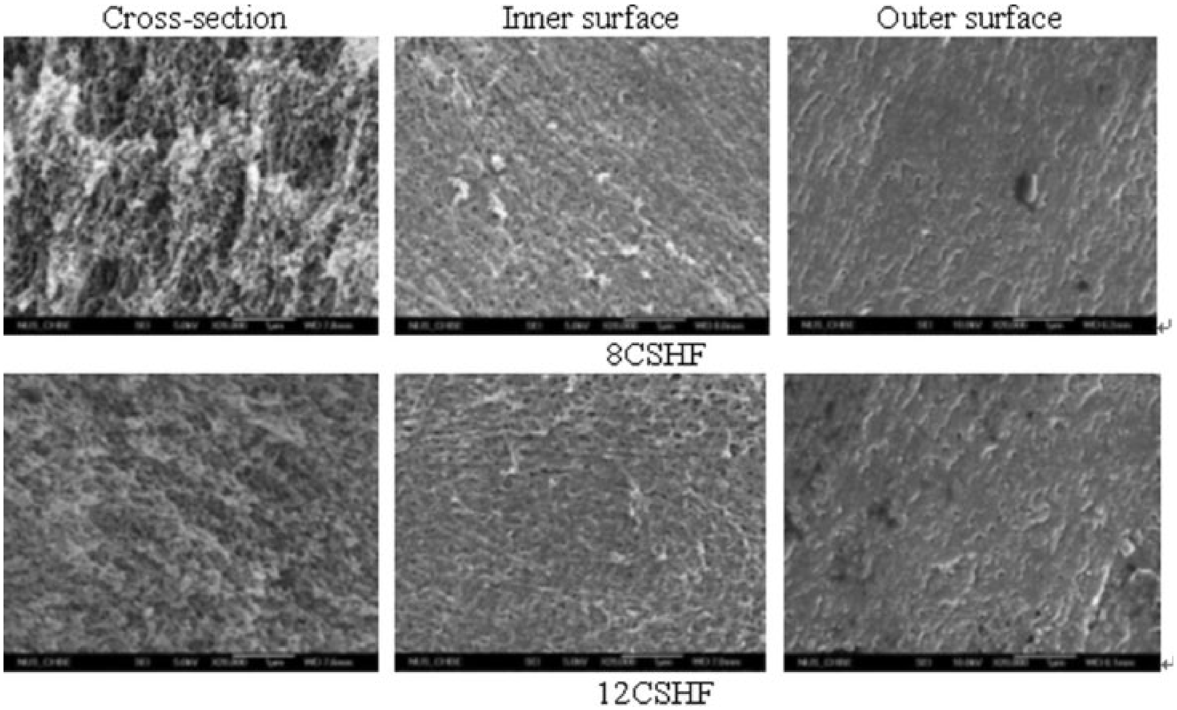

**Figure 3** Morphologies of the CS hollow-fiber membranes prepared from an 8 wt % CS solution (8CSHF) and a 12 wt % CS solution (12CSHF).

**TABLE I**
**Mechanical Strength Values of the CS Hollow-Fiber Membranes Prepared in This Study**

| Hollow-fiber type | Tensile stress at break (MPa) | Elongation ratio at break (%) | Young's modulus (MPa) |
|---|---|---|---|
| 8CSHF | 2.17 | 84% | 3.55 |
| 12CSHF | 3.45 | 125% | 4.69 |

section structure, and the pore sizes became smaller with higher CS concentrations in the dope solution. The inner surfaces of the hollow-fiber membranes were also porous, but the outer surfaces appeared to be much denser. Although the 10% NaOH solution was used as both the inner and outer coagulant, it coagulated CS at different rates on the outer and inner sides in the coagulation process.[26] The small amount of the NaOH solution in the lumen was rapidly neutralized by the acetic acid solution extracted from the CS dope solution, which reduced the coagulation rate of CS in the inner side of the hollow-fiber membrane and favored the formation of larger pores and, thus, the more porous inner surface. The preparation method for the hollow-fiber membranes, therefore, provided the membrane with an interesting structure: a porous and macrovoid-free cross section and inner surface but a relatively dense outer surface, ideally to be used as a membrane for both filtration (removal of particles through the outer surface) and adsorption (removal of soluble species by the internal surfaces) functions.

The porosities of 8CSHF and 12CSHF were found to be around 91.2 and 89.0%, respectively, in the wet state and 77.6 and 73.1%, respectively, in the dry state; this indicated a denser polymer content in 12CSHF than in 8CSHF. The urea permeation experiments indicated that about 99.1 and 98.8% of the urea molecules passed 8CSHF and 12CSHF, respectively. The results suggest that the prepared hollow-fiber membranes were permeable to small water-soluble components that had no affinity to CS.

## Mechanical strength

With the highly concentrated CS dope solutions, the CS hollow-fiber membranes were found to become mechanically strong. Table I summarizes the measured values of the tensile strength, elongation ratio, and Young's modulus of the wet CS hollow-fiber membranes prepared in this study. In general, both types of CS hollow-fiber membranes showed high tensile strengths that were comparable to or even higher than those obtained from other hollow-fiber membranes made of typical industrial synthetic polymers (see Table II). The improvements in the mechanical properties of the CS hollow-fiber membranes, to a large extent, resulted from the use of highly concentrated CS solutions to spin the CS hollow-fiber membranes.

## Adsorption performance

Adsorption data for copper-ion removal with the prepared CS hollow fibers were collected to evaluate their adsorptive performance. Figure 4 shows the results of copper-ion adsorption on 8CSHF and 12CSHF at different solution pH values. In general, the adsorption uptakes increased with increasing solution pH values. At pH values below 3, no significant adsorption occurred. In the pH range 3–5, the adsorption uptake increased significantly with the solution pH value and reached the highest uptakes at pH 4.6 or above in the pH range examined. It is advantageous for the maximum adsorption uptake to be achieved at a pH closer to the neutral level, as this can reduce the need for pH adjustment in many cases of applications where water or wastewater usually has a pH at or near the neutral point. The trend of the changes in the adsorption uptake of the copper ions on the CS hollow-fiber membranes with solution pH was similar to those that used CS as the adsorbent for heavy-metal removal.[40] The phenomenon of lower uptake amounts at lower pH values was attributed to the protonation of the amine groups of CS at lower solution pH values, which created greater electrostatic repulsion on the metal ions to be adsorbed and, therefore, reduced the amount of adsorption at a lower solution pH.

An adsorption isotherm study is commonly conducted to evaluate the adsorption capacity and adsorption pattern of an adsorbent for an adsorbate. Figure 5 shows the experimental isotherm adsorption results obtained at room temperature and pH 5. The adsorption uptake amounts in general increased with the equilibrium copper-ion concentration in the solution and approached a maximum at higher

**TABLE II**
**Comparison of the Tensile Strength Values of the CS Hollow-Fiber Membranes Prepared in This Study with Those from Industrial Synthetic Polymers**

| Hollow-fiber type | 8CSHF | 12CSHF | Cellulose acetate[31] | Polysulfone[32] | Nylon[33,34] |
|---|---|---|---|---|---|
| Tensile strength (MPa) | 2.17 | 3.45 | 1.05–1.90 | 1.36–3.27 | 0.97–4.22 |
| Hollow-fiber type | PVB[35] | PES[36] | PVC[37] | PVDF[38] | PAN[39] |
| Tensile strength (MPa) | 0.1–0.4 | 0.94–1.65 | 1.3–4.3 | 0.6–1.7 | 1.1–3.1 |

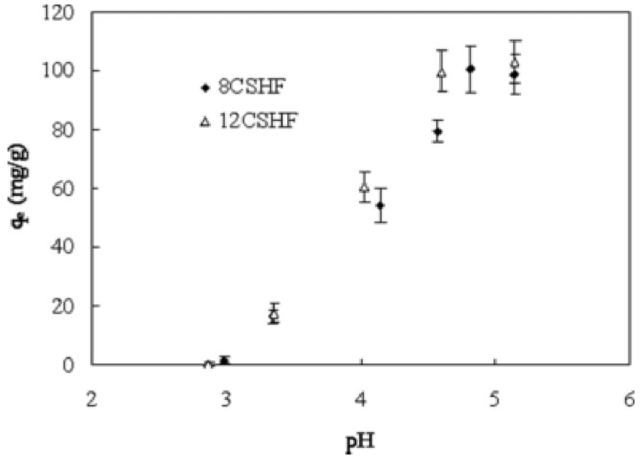

**Figure 4** pH effect of the copper-ion adsorption on the prepared CS hollow-fiber membranes [equilibrium adsorption amount ($q_e$) is in terms of per gram of dry CS hollow-fiber pieces, $C_0 = 150$ mg/L]. The error bars were determined from three repeated experiments with errors of less than 7%.

equilibrium concentrations. The Langmuir and Freundlich isotherm models were used to fit the experimental isotherm adsorption data in this study because of their relative simplicity. The Langmuir model ($R^2 = 0.9938$ and 0.9940 for 8CSHF and 12CSHF, respectively) was found to fit the data better than the Freundlich model ($R^2 = 0.9678$ and 0.9835 for 8CSHF and 12CSHF, respectively), which indicated that the surface properties of the hollow-fiber membranes played a crucial role in the adsorption performance. The fitted results from the two models are also included in Figure 5. From the Langmuir model fitting analysis, the maximum adsorption amount or adsorption capacity for copper ions on 8CSHF and 12CSHF in this case were calculated to be 186.7 and 206.6 mg of $Cu^{2+}$/g dry hollow fibers, respectively.

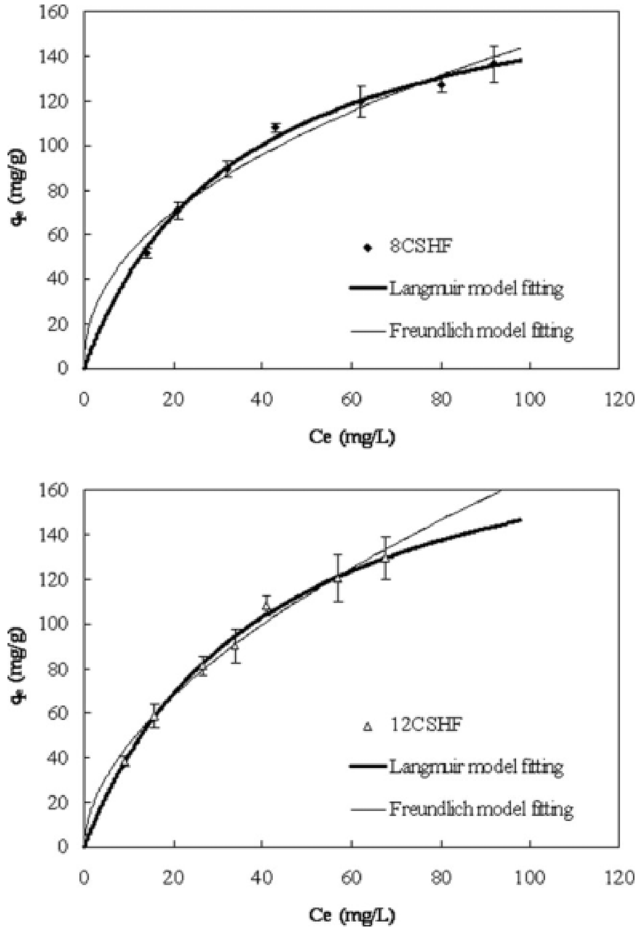

**Figure 5** Experimental adsorption isotherm data and the fitted results by adsorption isotherm models to the experimental results [$t$ (temperature) $t = 23°C$, pH 5, $C_0 = 50$ to 200 mg/L].

**TABLE III**
**Comparison of the Copper-Ion Adsorption Capacity on CS Reported in the Literature and Obtained in This Study**

| Copper-ion adsorption capacity (mg/g) in terms of CS | Form of CS | Authors |
|---|---|---|
| 15.4 | Powder | Chu[40] |
| 33.4 | Gel beads | Wan Ngah et al.[47] |
| 42.4 | Particles | Bal et al.[48] |
| 80.7 | Gel beads | Wan Ngah et al.[42] |
| 105.4 | Membrane | Han et al.[41] |
| 150 | Gel beads | Zhao et al.[49] |
| 163.9 | Gel beads | Li and Bai[43] |
| 186–202 | Membrane | This study |

The capacities of 186–206 mg of $Cu^{2+}$/g CS fibers from this study appeared to be high compared to those from earlier reports; see Table III. For example, in terms of copper-ion adsorption on CS, 103–105 mg of $Cu^{2+}$/g CS in CS/CA (cellulose acetate) blend hollow-fiber membranes[41] and around 80–160 mg of $Cu^{2+}$/g CS in CS gel beads[42,43] were obtained. Interestingly, the CS in the hollow fibers prepared from the dilute-dissolution preparation method in this study had a much lower crystallinity (13.7%), as indicated in Figure 6 by the lower peak at 2θ around 20°. In the literature, the crystallinity of CS ranges from about 30 to 60% for CS flakes,[28,44] CS flat-sheet membranes,[45] and CS hollow-fiber membranes[24] prepared by other methods. It is known that a lower crystallinity of CS can contribute to a greater adsorption capacity of CS.[46] Hence, the low crystallinity of CS, together with the porous structure, achieved in the prepared hollow-fiber membranes in this study probably contributed to the observed high adsorption capacities shown in Figure 5.

### Copper-ion removal from real industrial wastewater

Typical results with 8CSHF for the removal of copper ions from the real industrial wastewater are shown in Figure 7. The results show that the adsorption uptake increased with the increase of equilibrium concentration, a similar phenomenon to that observed in Figure 5. The TOC of the wastewater remained at 32.5 mg/L before and after the adsorption test. Therefore, the hollow-fiber membrane prepared in this study did not show significant adsorption for the TOC in the wastewater but selectively adsorbed the copper ions from the wastewater. Experiments indicated that the concentration of copper ions in the wastewater could be effectively reduced to below 1 mg/L, which meets the maximum contaminant level goal and treatment technique to control the corrosiveness of water established by the U.S. Environmental Protection Agency.[50] The reusability test results also indicated that the capacity of the hollow-fiber pieces remained at about 90% of the initial capacity even after 10 rounds of adsorption–desorption cycles. These results show the potential for the developed adsorptive hollow-fiber membranes to be used for copper-ion removal in the treatment of semiconductor industrial wastewater.

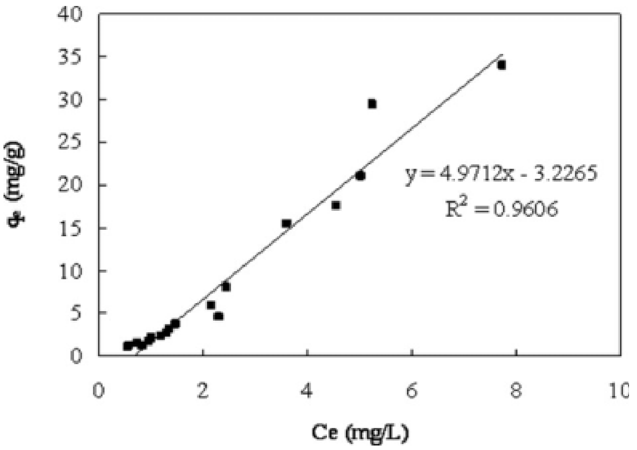

**Figure 7** Performance of the copper-ion adsorption on 8CSHF from semiconductor industrial wastewater (pH = 6.2, TOC = 32.5 mg/L, initial copper-ion concentration = 12.1 mg/L). $q_e$ is the equilibrium adsorption amount on the adsorbent and $C_e$ is the equilibrium concentration of the solute in the bulk solution.

## CONCLUSIONS

Homogeneous high-concentration CS solutions and high-strength CS hollow-fiber membranes were successfully prepared. The novel dilute-dissolution and evaporating-concentration method developed in this study allowed homogeneous CS solutions with a concentration at as high as 18 wt % to be practically obtained. This overcame the limitation of the conventional preparation method, which fails to obtain a high-concentration CS solution with homogeneity. From the prepared high-concentration CS solutions, CS hollow-fiber membranes with comparable or even higher mechanical strengths (in the wet state) than many industrial synthetic polymer membranes were fabricated. The prepared CS hollow-fiber membranes were found to have a porous and macrovoid-free structure on the cross section and inner surface but a much denser outer surface. This type of membrane structure may be beneficial for a membrane used to achieve both the filtration (the removal of larger particles) and adsorption (the removal of dissolved small components) separation functions. Adsorption experiments showed that the prepared CS hollow fibers had a very high adsorption capacity for copper ions. The low crystallinity of CS achieved in the prepared hollow fibers is considered to be one of the major factors that contributes to the high adsorption capacity. The prepared CS hollow fibers were also shown to effectively remove copper ions from real wastewater from the semiconductor industry. It is expected that there will be great potential for CS hollow-fiber membranes to be used in many separation applications in the future.

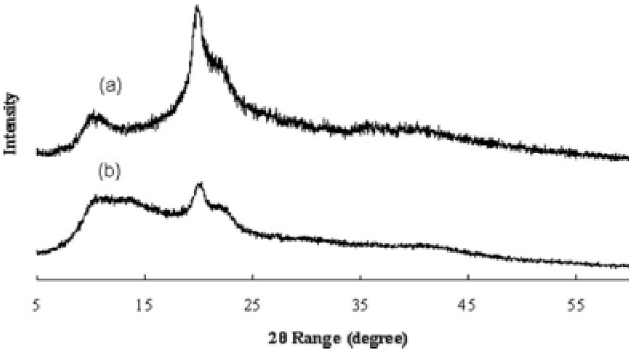

**Figure 6** X-ray diffraction spectra of (a) raw CS flake (with normal crystallinity) and (b) CS in 12CSHF prepared in this study. The peaks at 2θ around 20° indicated the extent of crystallinity.

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## References

1. Avramescua, M. E.; Sager, W. F. C.; Wessling, M. J Membr Sci 2003, 216, 177.
2. Matsuyama, H.; Berghmans, S.; Loyd, D. R. J Membr Sci 1998, 142, 213.
3. Tan, K.; Obendorf, S. K. J Membr Sci 2006, 274, 150.
4. Urmenyi, A. M.; Poot, A. A.; Wessling, M.; Mulder, M. H. V. J Membr Sci 2005, 259, 91.
5. Bayramoğu, G.; Yılmaz, M.; Arıca, M. Y. Colloid Surf A 2004, 243, 11.
6. Han, B.; Carvalho, W.; Canilha, L.; da Silva, S. S.; Silva, J. B. A. E.; McMillan, J. D.; Wickramasinghe, S. R. Desalination 2006, 193, 361.
7. Varma, A. J.; Deshpande, S. V.; Kennedy, J. F. Carbohydr Polym 2004, 55, 77.
8. Guibal, E. Sep Purif Technol 2004, 38, 43.
9. Crini, G. Prog Polym Sci 2005, 30, 38.

10. Shahidi, F.; Arachchi, J. K. V.; Jeon, Y. Trends Food Sci Technol 1999, 10, 37.
11. Jeon, C.; Höll, W. H. Water Res 2003, 37, 4770.
12. Vieira, R. S.; Beppu, M. M. Water Res 2006, 40, 1726.
13. Jansson-Charrier, M.; Guibal, E.; Roussy, J.; Delanghe, B.; LeCloirec, P. Water Res 1996, 30, 465.
14. Machado, R.; José de Arruda, L. E.; Santana, C. C.; Bueno, S. M. A. Process Biochem 2006, 41, 2252.
15. Uzun, I.; Güzel, F. J Colloid Interface Sci 2004, 274, 398.
16. Yan, W. L.; Bai, R. B. Water Res 2005, 39, 688.
17. Adriano, W. S.; Veredas, V.; Santana, C. C.; Gonçalves, L. R. B. Biochem Eng J 2005, 27, 132.
18. Benesch, J.; Tengvall, P. Biomaterials 2002, 23, 2561.
19. Zeng, X.; Ruckenstein, E. Ind Eng Chem Res 1996, 35, 4196.
20. Tsai, H. A.; Chen, H. C.; Lee, K. R.; Lai, J. Y. Desalination 2006, 193, 129.
21. Gabelman, A.; Hwang, S. J Membr Sci 1999, 159, 61.
22. Pittalis, F.; Bartoli, F.; Giovannoni, G.; Milanese, G. U.S. Pat.4,464,321 (1984).
23. Vincent, T.; Guibal, E. Ind Eng Chem Res 2001, 40, 1406.
24. Modrzejewska, Z.; Eckstein, W. Biopolymers 2004, 73, 61.
25. Wang, W.; Bo, S.; Li, S.; Qin, W. Int J Biol Macromol 1991, 13, 281.
26. Liu, C.; Bai, R. B. J Membr Sci 2005, 267, 68.
27. Santos, H.; Veiga, F.; Pina, M.; Podczeck, F.; Sousa, J. Int J Pharm 2002, 246, 153.
28. Singh, D. K.; Ray, A. R. Carbohydr Polym 1998, 36, 251.
29. Teraoka, I. Polymer Solution: An Introduction to Physical Properties; Wiley: New York, 2002.
30. Desbrieres, J. Biomacromol 2002, 3, 342.
31. Ghatge, N. D.; Sabne, M. B.; Gujar, K. B.; Mahajan, S. S. J Appl Polym Sci 1984, 29, 1743.
32. Tsai, H.; Huang, D.; Ruaan, R.; Lai, J. Ind Eng Chem Res 2001, 40, 5917.
33. Lai, J. Y.; Chen, Y. C.; Hsu, K. Y. J Appl Polym Sci 1991, 43, 1795.
34. Unal, H.; Mimaroglu, A.; Alkan, M. Polym Int 2004, 53, 56.
35. Fu, X.; Matsuyama, H.; Teramoto, M.; Nagai, H. Sep Purif Technol 2005, 45, 200.
36. Chung, T.; Qin, J.; Gu, J. Chem Eng Sci 2000, 55, 1077.
37. Xu, J.; Xu, Z. J Membr Sci 2002, 208, 203.
38. Tomaszewska, M. Desalination 1996, 104, 1.
39. Yin, X.; Cheng, H.; Wang, X.; Yao, Y. J Membr Sci 1998, 146, 179.
40. Chu, K. H. J Hazard Mater 2002, 90, 77.
41. Han, W.; Liu, C.; Bai, R. B. J Membr Sci 2007, 302, 150.
42. Wan Ngah, W. S.; Endud, C. S.; Mayanar, R. React Funct Polym 2002, 50, 181.
43. Li, N.; Bai, R. B. Ind Eng Chem Res 2005, 44, 6692.
44. Trung, T. S.; Ng, C.-H.; Stevens, W. F. Biotechnol Lett 2003, 25, 1185.
45. Chao, A. C.; Yu, S. H.; Chuang, G. S. J Membr Sci 2006, 280, 163.
46. Kurita, K.; Sannan, T.; Iwakura, Y. J Appl Polym Sci 1979, 23, 511.
47. Wan Ngah, W. S.; Kamari, A.; Koay, Y. J. Int J Biol Macromol 2004, 34, 155.
48. Bal, Y.; Bal, K. E.; Laarbi-Bouamrane, O.; Lallam, A. Miner Eng 2006, 19, 1456.
49. Zhao, F.; Yu, B.; Yue, Z.; Wang, T.; Wen, X.; Liu, Z.; Zhao, C. J Hazard Mater 2007, 147, 67.
50. U.S. Environmental Protection Agency. National Primary Drinking Water Standards. http://www.epa.gov/safewater/contaminants/index.html. Washington, DC, 2003.