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# Mechanical, swelling and adsorptive properties of dry–wet spun chitosan hollow fibers crosslinked with glutaraldehyde

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ABSTRACT

Chitosan (CS) hollow fiber (HF) membranes were successfully prepared according to the dry–wet spinning technique. A post-treatment with glutaraldehyde (GA) aqueous solution was carried out to perform the cross-linking reaction. The effect of GA concentration in the range 50–1000 mg $l^{-1}$ on the swelling, mechanical and adsorptive properties was investigated. The morphology and chemical structure of the fibers were examined by means of SEM and FTIR. The degree of swelling and adsorption capacity decreased as the GA concentration increased. CS hollow fibers swelled the most in acidic solution as compared with distilled water and saline solution. The adsorption capacity of CS HFs increased while decreasing of initial pH from 7.5 to 3.5. Desorption experiments showed that CS HFs were reusable as adsorbent. Mechanical properties were strongly affected by GA post-treatment: tensile strength and elastic modulus increased at low GA concentration (50 mg $l^{-1}$), to sharply decrease when concentration was $\geqslant$500 mg $l^{-1}$. Breaking elongation decreased with increasing GA concentration.



## 1. Introduction

In recent years, adsorptive membranes have emerged as powerful means for removal of pollutants from effluents [1]. Adsorptive membrane is a type of membrane bearing functional groups such as —COOH, —$SO_3H$, and —$NH_2$ on its external and internal surfaces. These functional groups can bond with pollutants through the mechanism of surface complexation or ion exchange [2].

Chitosan has attracted more attention among materials with reactive functional groups for preparing adsorptive membranes. The presence of a considerable percentage of free amine and hydroxyl groups on chitosan endows it with a good capability in the sorption of pollutant [3].

Chitosan is a biopolymer that can be easily obtained by deacetylation of chitin present in the shells of crustaceans such as shrimps, crabs and lobsters which are widely available from the seafood processing wastes [4–6].

The required characteristics for an adsorptive membrane are large specific surface area, high density of reactive functional groups and good mechanical and chemical resistance [7].

Flat sheet chitosan membranes [8,9] and coated chitosan membranes [10,11] have been reported. These membranes are not suitable for adsorption process because of their small specific surface areas or the small amount of CS contained [12].

To increase the specific surface area, hollow fibers are usually the preferred membrane configuration. However, there are few articles in literature dealing with the preparation of chitosan hollow fiber adsorptive membranes to remove pollutants in the solution.

The weak mechanical properties and the solubility of chitosan in acidic media are the major obstacle for using chitosan hollow fibers as adsorbent [13].

The chemical modification of CS by using crosslinking reaction offers an alternative pathway for producing chemically more stable chitosan, which can extend the potential applications of this biopolymer to more areas [14].

So far, in this work we describe the preparation of CS hollow fiber membranes aimed at studying the influence of crosslinking agent on their swelling, mechanical and adsorptive properties. The potential of CS hollow fibers to adsorb RB19 as a model of reactive dyes was studied. Reactive dyes are the most important class of dyes for cellulose fabrics. However, the fixation of the reactive

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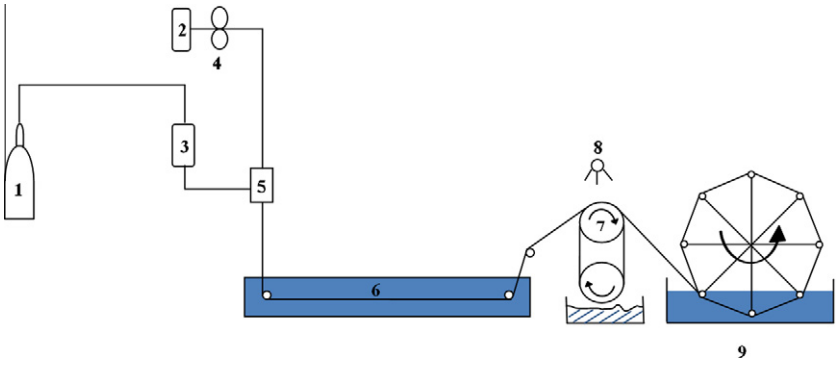


**Fig. 1.** Schematic drawing of the spinning setup. (1) $N_2$ gas cylinder, (2) bore fluid reservoir, (3) dope tank, (4) bore fluid pump, (5) spinneret, (6) external coagulation bath, (7) take-up roller, (8) water spraying device and (9) spool.

dyes on cellulose fabrics is lower and a lot of unfixed dyes may be lost with the effluent during dyeing processes [15].

## 2. Experimental

### 2.1. Materials

Chitosan low viscous grade was purchased from Sigma–Aldrich. The degree of deacetylation as reported by the supplier was bigger than 75%. Glutaraldehyde (5% by weight in water) was obtained and used as crosslinking agent from Amersham Biosciences. Reactive blue 19 also known as Remazol Brilliant Blue R (Color Index Number: 61200, chemical formula: $C_{22}H_{16}N_2Na_2O_{11}S_3$, $M_W$: 626.54 g mol$^{-1}$, $\lambda_{max}$: 598 nm) was purchased from Sigma–Aldrich, and was used without purification. Other chemical agents used were all analytical grade and all solutions were prepared with distilled water.

### 2.2. Preparation of chitosan hollow fibers

The polymer solution (dope) has been prepared by dissolving the chitosan in a 3 wt.% acetic acid aqueous solution, under mechanical stirring at 30 °C. The polymer concentration in the dope was 5.5 wt.%. Before spinning, the dope was filtered on a 40 μm stainless steel filter and left standing for at least 30 min in the feeding reservoir under vacuum to remove air bubbles. The degassed dope was then fed to the spinneret having the outer and the inner diameter of 2.0 and 1.0 mm, respectively. As the bore fluid, a 20 wt.% NaOH aqueous solution was used. The dope and the bore fluid flow rate were 6.0 and 3.0 g/min, respectively. The polymer solution leaving the spinneret entered an air gap of 5 cm before dipping into the coagulation bath of 10 wt.% NaOH. The formed hollow fiber was continuously pulled out the coagulation bath by a couple of driving rolls and finally collected on a spool. A scheme of the spinning set-up is depicted in Fig. 1.

The as-spun CS hollow fibers were stored in distilled water. When required, the fibers were crosslinked by immersing in glutaraldehyde aqueous solution at different concentration (50, 200, 500, 1000 mg l$^{-1}$) for 1 h. After removal from the glutaraldehyde solution, the hollow fibers were rinsed with distilled water and then dried. Removing water directly from a wet membrane in the air may cause changes of its morphology. Therefore, solvent exchange drying in a two-step procedure was used as an effective method to minimize these changes.

First, the water contained in the fibers was removed by immersion in an ethanol bath for 15 h. Then, ethanol was replaced by *n*-hexane in which the fibers were kept for 3 h. Finally, they were dried at room temperature.

### 2.3. Characterization of CS hollow fibers

FT-IR spectra were recorded on Perkin-Elmer FT-IR spectrophotometer (4000–600 cm$^{-1}$). KBr pellet technique was used to prepare sample for recording FT-IR spectrum.

The morphology of CS hollow fibers was studied by SEM (Cambridge Stereoscan 360). Hollow fibers were freeze fractured, using liquid $N_2$ to produce a clean brittle fracture and were subsequently sputter-coated with gold before SEM observation.

Mechanical properties of the dry hollow fibers were investigated through the measurement of tensile strength, elongation at break point and Young's modulus using the Zwick Roell (Germany) single-column Universal testing machine (model Z2.5) with a 50 N maximum load cell and the test data were analyzed by the TestXpert V11.0 Master software. The initial gauge length was set to 20 mm and the drawing speed at 50 mm min$^{-1}$. The hollow fibers were cut into a 60 mm length and fixed onto the clamps of the machine. For reliability, five measurements for each sample were made and the average value was reported.

The degree of swelling of CS hollow fibers was calculated through a series of gravimetric measurements [16] as follow:

$$\text{Degree of swelling } (\%) = \frac{W_w - W_d}{W_w} \times 100 \quad (1)$$

A certain amount of the hollow fiber was dipped into a cylinder filled with a solution for 24 h at room temperature. Afterward, the water on the inner surface was removed by flushing the lumen with air, while the outer surface of the hollow fiber was wiped with adsorbing paper. Then, hollow fiber was weighed to obtain the wet weight ($W_w$). The weighed hollow fiber was subsequently dried in a vacuum desiccator for 2 days and weighed again ($W_d$).

### 2.4. Adsorption and desorption experiments

Adsorption experiments were conducted in a flask into which 50 ml of dye aqueous solution and a known amount of chitosan hollow fibers were added. The hollow fiber membranes were cut into pieces of about 30 mm and used in the adsorption studies. The pH value was adjusted by adding a few drops of dilute NaOH or HCl if necessary. The samples were kept under stirring at 25 °C. The concentration of the residual RB19 was analyzed by UV–vis spectrophotometer (UV-160A Shimadzu) at 598 nm corresponding to the maximum absorbance.

Adsorption capacity of CS hollow fibers, $q_t$, was calculated at various conditions by the following equation:

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