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Shing -Yi Suen[a]; Hsin -Cheng Chiu[a]; Yi -Da Tsai[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, NATIONAL CHUNG HSING UNIVERSITY, TAICHUNG, TAIWAN, REPUBLIC OF CHINA

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Polysaccharide-Modified Poly(Ether Sulfone) Hollow Fibers as Solid Supports for Affinity Adsorption: Equilibrium Adsorption Study

SHING-YI SUEN,* HSIN-CHENG CHIU, and YI-DA TSAI
DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL CHUNG HSING UNIVERSITY
TAICHUNG, TAIWAN 402, REPUBLIC OF CHINA

ABSTRACT

Poly(ether sulfone) hollow fibers modified with various polysaccharides were used to immobilize Cibacron Blue 3GA for affinity adsorption. Characterization of modified hollow fibers with respect to their activation using ethylene glycol diglycidyl ether, conjugation with polysaccharides, and immobilization with Cibacron Blue 3GA indicates that the surface modification was successfully achieved. This work also studied the adsorption behavior of lysozyme onto immobilized Cibacron Blue 3GA using the polysaccharide-modified fibers as solid supports. The optimal adsorption capacity was observed from the hollow fibers conjugated with hydroxyethyl cellulose or dextran derivative and with high density of immobilized Cibacron Blue 3GA. Moreover, the effect of temperature on lysozyme adsorption was investigated. The results show that the lysozyme-ligand binding on the polysaccharide-modified hollow fibers tends to be endothermic.

INTRODUCTION

Adsorptive membranes have received increasing attention in applications of biomolecule purification and fractionation owing to their advantage of smaller mass transfer limitations than the conventional chromatography columns (1–5). Different types of membranes have been utilized for adsorption, including membrane disks, hollow fibers, spiral-wound shapes, tubular

* To whom correspondence should be addressed. FAX: 886-4-2854734. E-mail: sysuen@nchu.edu.tw

membranes, and so on (3–5). Adsorptive membrane disks have become commercialized in the market and are most often studied in the literature. In particular, their separation performances have received extensive interest (2, 3, 6–8). However, membrane disks also suffer from several disadvantages in applications such as membrane fouling for crude solutions or broth, flow maldistribution, and disk edge leaking in large-scale designs. These problems rather restrict the practical applications of membrane disks.

In this study, hollow fibers were selected as the solid supports for affinity adsorption due to their higher specific surface area than flat-sheet membranes. Larger available surface area of the adsorbent increases relative adsorption capacity. In addition, the hollow fiber holder is often designed in a crossflow manner to facilitate efficient filtration. This crossflow design gives the adsorptive hollow fibers a dual function of filtration and adsorption in a cycle and hence allows an effective separation of crude solutions or broth. Moreover, the leakage problem in large-scale membrane disks does not occur in the effective hollow fiber design with an increasing number of fibers.

Hollow fiber-related applications in affinity or ion-exchange separations have received increasing interest. Most of research has investigated methods of surface modification and ligand immobilization and the related adsorption properties (9–18). Some studies also examined the transport phenomena within affinity hollow fibers and the related separation performance (17, 19, 20). The hollow fiber materials reported in literature include polysulfone, poly(ether sulfone), polycaprolactam, poly(ethylenevinyl alcohol), polyamide, polyethylene, glass, and hydrazide. Ligands that have been tested for affinity adsorption include protein A, metal-iminodiacetate, histidine, antibody, IgG, and hydrophobic amino acids.

In this study, poly(ether sulfone) hollow fibers were adopted as solid supports for affinity adsorption. Polysulfone and poly(ether sulfone) membranes have excellent mechanical properties of rigidity, strength, and toughness. However, owing to their good chemical stability, an appropriate chemical activation is required prior to ligand immobilization. Klein et al. successfully conjugated polysulfone and poly(ether sulfone) fibers with polysaccharides (hydroxyethyl cellulose and chitosan) and immobilized affinity ligands onto the fibers (15, 16). Polysaccharide acts not only as a modifier to provide sufficient hydroxyl groups for ligand immobilization, but also as a spacer to reduce mass transfer resistance and the steric hindrance for binding.

This study largely focuses on modifying poly(ether sulfone) hollow fibers with various polysaccharides and evaluating the effects of modification on ligand immobilization. The modification strategy developed by Klein et al. (15) was employed with slight modification. The polysaccharides adopted in this study are hydroxyethyl cellulose, hydroxyethyl starch, dextran, and a dextran derivative. The ligand used in this work is Cibacron Blue 3GA, a triazine dye

which can be covalently bound with the hydroxyl groups of polysaccharide. The intense blue color of Cibacron Blue 3GA facilitates a clear observation of the ligand distribution on the outer surface of the hollow fiber. To determine an optimal ligand density, different concentrations of Cibacron Blue 3GA were used for immobilization and the pertinent adsorption results compared. The extent to which temperature affects the adsorption properties of lysozyme is also described.

EXPERIMENTAL

Materials

Most commercially available polysulfone or poly(ether sulfone) hollow fibers are placed in a holder, and it is difficult to achieve a uniform surface modification and ligand immobilization. Therefore, a single polysulfone or poly(ether sulfone) hollow fiber is the first choice. The commercial product that meets our requirements in this study is the poly(ether sulfone) hollow fiber with a nominal pore size of 0.65 μm from A/G Technology (Needham, MA, USA). The fibers are 15.5 cm in length, 0.75 mm in inner diameter, and 1.3 mm in outer diameter. Their thermal stability is up to 50°C and the pH stability ranges from pH 2 to 13. The porosity of the fiber is about 0.8, according to the manufacturer. Morphologic pictures of the hollow fiber from a scanning electron microscope, including the inner surface (1A), the outer surface (1B), the cross section of the entire wall (1C), and the cross section of the entire hollow fiber (1D), are illustrated in Fig. 1.

The chemical reagents and polysaccharides used for the surface modification of hollow fibers were obtained from commercial sources: ethylene glycol diglycidyl ether (EGDGE, 31% in purity) [TCI, Tokyo, Japan]; BF_3 etherate (Lancaster, Morecambe, England); hydroxyethyl cellulose (HEC, MW $> 10^6$) [SHOWA, Tokyo, Japan]; hydroxyethyl starch (HES, MW $> 10^6$) [Sigma, St. Louis, MO, USA]; dextran (T-70, Amersham Pharmacia Biotech, Uppsala, Sweden). A dextran derivative, *o*-(4-hydroxylbutyl carbamoyl) dextran, was also used for conjugation with poly(ether sulfone) hollow fibers (see the next section for its preparation). Cibacron Blue 3GA (C9534, 55% in purity) and chicken egg white lysozyme (L6876, MW 14300) were purchased from Sigma Chemical.

Synthesis of *o*-(4-Hydroxylbutyl Carbamoyl) Dextran Derivative

To a dextran (1 g) solution in 16 mL of DMSO/pyridine solvent (1:1 v/v), 4-nitrophenylchloroformate (685 mg) and 4-dimethylaminopyridine (as a catalyst, 76 mg) were added under 0°C with stirring. After 2 hours, ca. 6.3 mmol

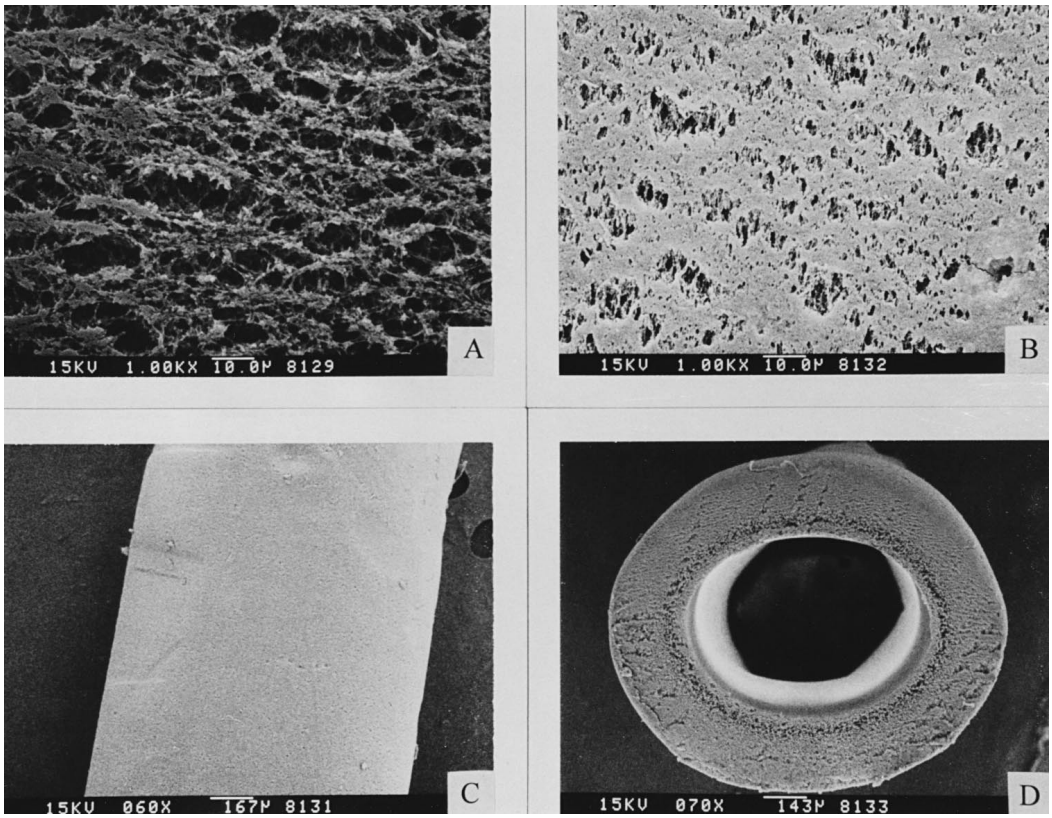


FIG. 1 Scanning electron photomicrographs for morphology of poly(ether sulfone) hollow fibers used in this work. (A) Inner surface. (B) Outer surface. (C) Cross section of fiber wall. (D) Cross section of entire hollow fiber.

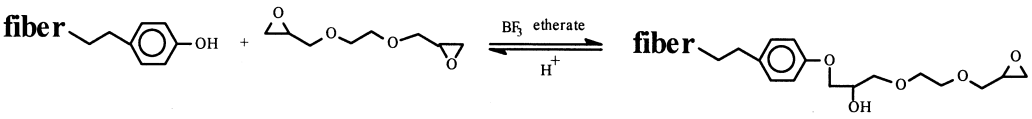
4-amino-1-butanol was added. The reaction was conducted at room temperature for 2 days. The product, *o*-(4-hydroxylbutyl carbamoyl) dextran, was precipitated in ethanol and collected by filtration.

Surface Modification Procedures

Reaction of Poly(Ether Sulfone) Hollow Fiber with EGDGE

To a solution of 0.3 M EGDGE and 120 μL BF_3 etherate (as a catalyst) in 60 mL of isopropanol–water azeotrope (87.8:12.2 w/w), one dry fiber was immersed. The reaction was performed in vacuo at room temperature to reduce air trapping in fiber pores. After 2 hours the fiber was removed from the EGDGE solution and immediately put into a vacuumed desiccater for further reaction. A visible liquid film of EGDGE was observed on the outer surface of the fiber. The existence of this thin film was found helpful as an indication of the reaction of EGDGE with the phenol groups of the fiber and, conse-

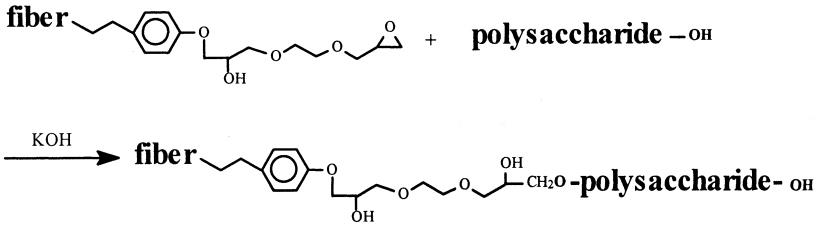
quently, to an increase in the extent of ligand immobilization. After 5 hours of reaction the fiber was rinsed with excess deionized water to remove the unreacted EGDGE.



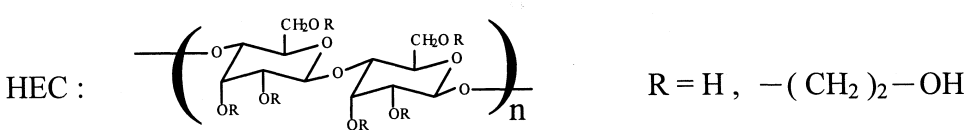
The chemical attachment of EGDGE on poly(ether sulfone) hollow fiber was checked by the ninhydrin method (21). First, a fiber 1 cm in length after EGDGE activation was placed into a 10-mL solution of 0.5% (w/v) 1,10-diaminodecane. The reaction was performed at 50°C for 2 hours under shaking. The reaction of free epoxide groups at one end of the immobilized EGDGE with the excess amino groups of 1,10-diaminodecane led to the formation of free amino end groups for ninhydrin reaction. The aminated hollow fiber was thoroughly rinsed with deionized water and then placed into a ninhydrin solution (10 mL, 1% w/v) in acetone. An intense purple color of the hollow fiber was observed at 50°C after 1 hour, indicating that the activation of EGDGE onto the hollow fiber had been successfully achieved.

Reaction with Polysaccharide

A single hollow fiber after EGDGE activation was immersed into a polysaccharide solution (60 mL, 2% w/v) containing 1.2 mL of 1 M KOH. The reaction was conducted at 50°C for 3 days. After the reaction, the hollow fiber was thoroughly washed with deionized water to remove any unreacted polysaccharide. The conjugation of polysaccharide with poly(ether sulfone) fiber was assayed by titration of the carbohydrate content by using the phenol-sulfuric acid method (22). A clear orange color in the reaction solution was displayed.



Polysaccharide :



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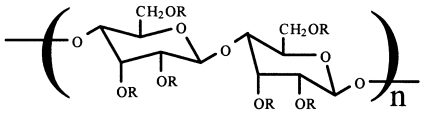
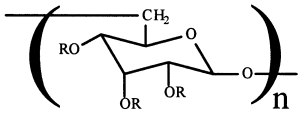
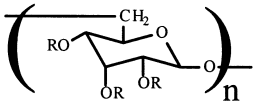
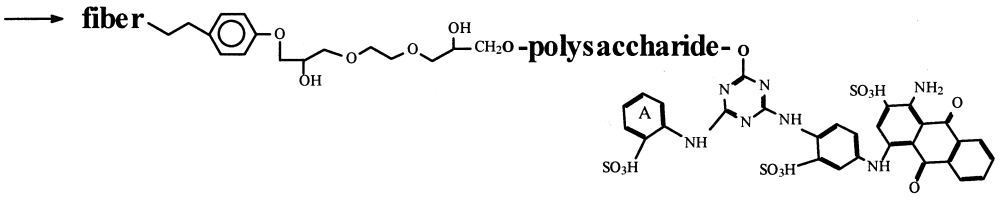
HES :  R = H , $-(CH_2)_2-OH$

Dextran :  R = H

Dextran derivative :  R = H , $-C(=O)-NH-(CH_2)_4-OH$

Cibacron Blue 3GA Immobilization

The immobilization of Cibacron Blue 3GA onto polysaccharide-modified hollow fiber was carried out by reaction of the triazine group of Cibacron Blue 3GA with the hydroxyl groups of polysaccharide. Twenty milliliters of Cibacron Blue 3GA solution with a given concentration were reacted with a polysaccharide-modified fiber at 50°C for 1.5 hours. Different Cibacron Blue 3GA concentrations were tested in this work: 3, 0.3, 0.03, and 0.003% (w/v). Twenty milliliters of 7.5% (w/v) NaCl solution and 20 mL of 7.5% (w/v) Na_2CO_3 solution were then added to the mixture. The reaction was continuously conducted for 1 day under the same temperature. After the reaction, the fiber was thoroughly rinsed with deionized water until no blue Cibacron Blue 3GA was eluted.



Batch Adsorption Equilibrium Experiments

The loading buffer for adsorption was 50 mM Tris-HCl, pH 7, with 0.005% NaN_3. At this pH, lysozyme would be positively charged based on

its isoelectric point of 11, which allows an electrostatic interaction of the protein with Cibacron Blue 3GA. In addition, a loading buffer with a high salt concentration (1 M KCl in Tris-HCl) was used as the elution buffer. Both buffers were filtered through 0.2 μm nylon membranes (Lida Manufacturing, Kenosha, WI, USA). Lysozyme solution was prepared in the loading buffer and filtered by 0.45 μm filters (Millex-HV, Millipore, Bedford, MA, USA).

Twenty-five milliliters of lysozyme solution of a given concentration and a Cibacron Blue 3GA-immobilized dry hollow fiber were placed in a centrifuge tube for batch adsorption equilibrium study. The protein solution with the fiber was incubated at a fixed temperature for 12 hours. Lysozyme concentration was determined using a UV/Vis spectrophotomer (UV-1601, Shimadzu, Auburn, Australia) at 280 nm. The extinction coefficient for lysozyme ($E^{280\ \mathrm{nm}}_{1\ \mathrm{mg/mL}}$) is 2.65 (23). After each batch of protein adsorption the fiber was washed thoroughly with elution buffer to remove the bound protein. The experiments were performed at 4, 25, and 37°C, respectively.

RESULTS AND DISCUSSION

Surface Modification and Ligand Immobilization of Poly(Ether Sulfone) Hollow Fibers

This study employed conjugation of polysaccharides to immobilize Cibacron Blue 3GA (as an affinity ligand) onto the poly(ether sulfone) hollow fibers. Figure 2 illustrates the HEC-modified hollow fibers after the immobilization of Cibacron Blue 3GA. In this figure, four different concentra-

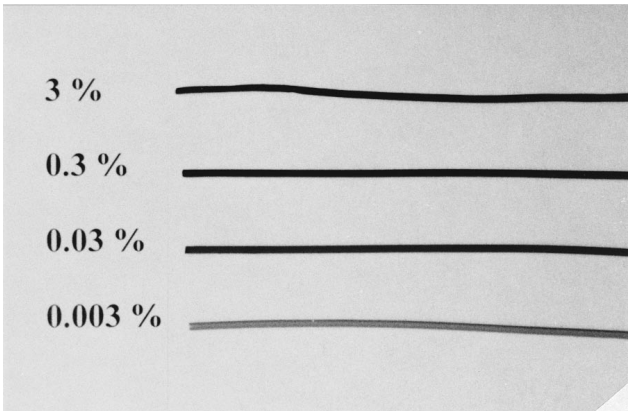


FIG. 2 Photographs for hydroxyethyl cellulose-modified hollow fibers using different concentrations of Cibacron Blue 3GA for immobilization.

tions (3, 0.3, 0.03, and 0.003%, w/v) of Cibacron Blue 3GA were used. Similar results were observed from hollow fibers conjugated with different polysaccharides after immobilization with the affinity ligand. Figure 2 reveals that the blue color was displayed on all the modified hollow fibers and the distribution pattern was rather uniform, indicating a successful surface modification and immobilization. Moreover, the intense blue on the outer surface of fiber signified a higher density of immobilized Cibacron Blue 3GA. This indicates that when a higher ligand concentration was used in the reaction, the density of immobilized ligand increased. However, the difference in immobilization determined by visual observation between concentrations of 3 and 0.3% of Cibacron Blue 3GA was insignificant due to the intense blue color displayed on both fibers.

This study also compared the colors on the inner and outer surfaces of all the fibers (results not shown). A lighter blue color on the inner surface than on the outer surface was observed for all fibers, suggesting that the surface area available for ligand immobilization on the inner surface region was less than on the outer surface. This finding agreed with the observation from the SEM photomicrographs (Fig. 1). The SEM results indicate that the pore size increases from the outer to the inner surface. The increasing pore size reduces porosity, subsequently reducing the specific surface area in the inner surface compared to the outer surface. Similar observations have been reported for derivatization of poly(ether sulfone) hollow fiber (19).

In addition, the stability of dye-immobilized membranes is crucial for practical applications in affinity separation. This stability was investigated by repeatedly using the above Cibacron Blue 3GA-immobilized hollow fibers. No leakage of blue dye from the fibers was observed, clearly verifying the success of the methods of surface modification and ligand immobilization studied in this work.

Adsorption of Lysozyme to Immobilized Cibacron Blue 3GA

Adsorption Isotherms

Figures 3 to 5 summarize the results for lysozyme adsorption to immobilized Cibacron Blue 3GA using different polysaccharide-modified hollow fibers as solid supports at 4, 25, and 37°C, respectively. The adsorption capacity, q, was calculated based on the solid volume of the fiber. In addition, the Langmuir isotherm model was used for curve fitting from the experimental data:

$$q = \frac{q_m c}{K_d + c} \tag{1}$$

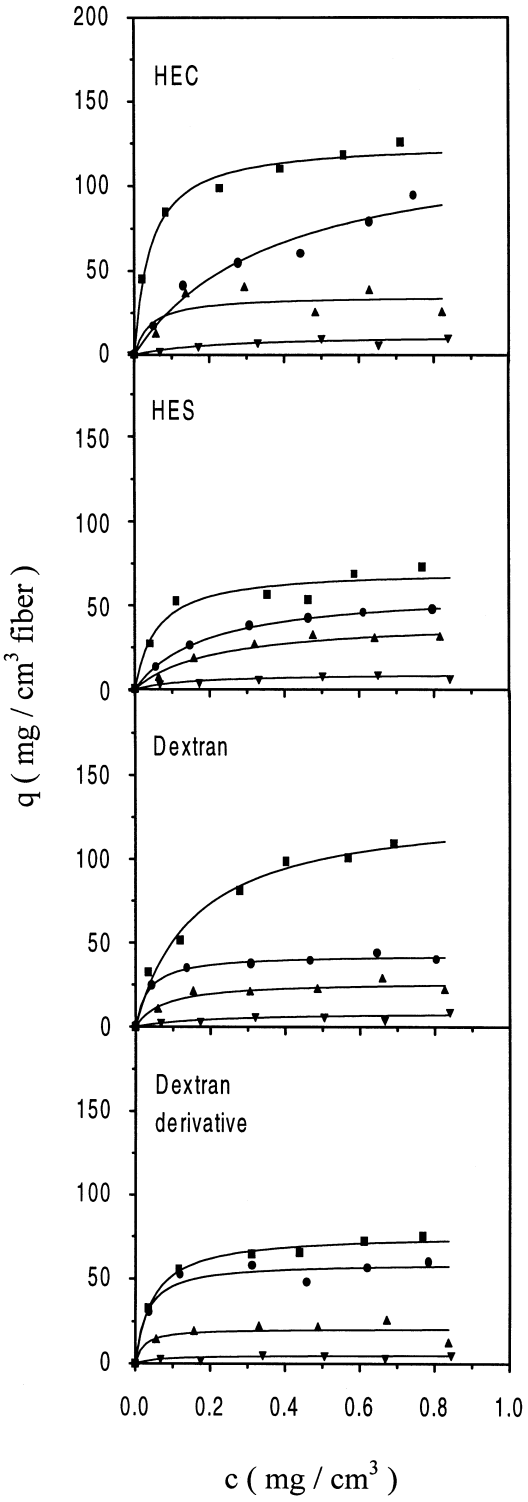


FIG. 3 Adsorption isotherms of lysozyme to polysaccharide-modified and Cibacron Blue 3GA-immobilized hollow fibers at 4°C. Cibacron Blue 3GA concentrations used: (■) 3%, (●) 0.3%, (▲) 0.03%, (▼) 0.003%.

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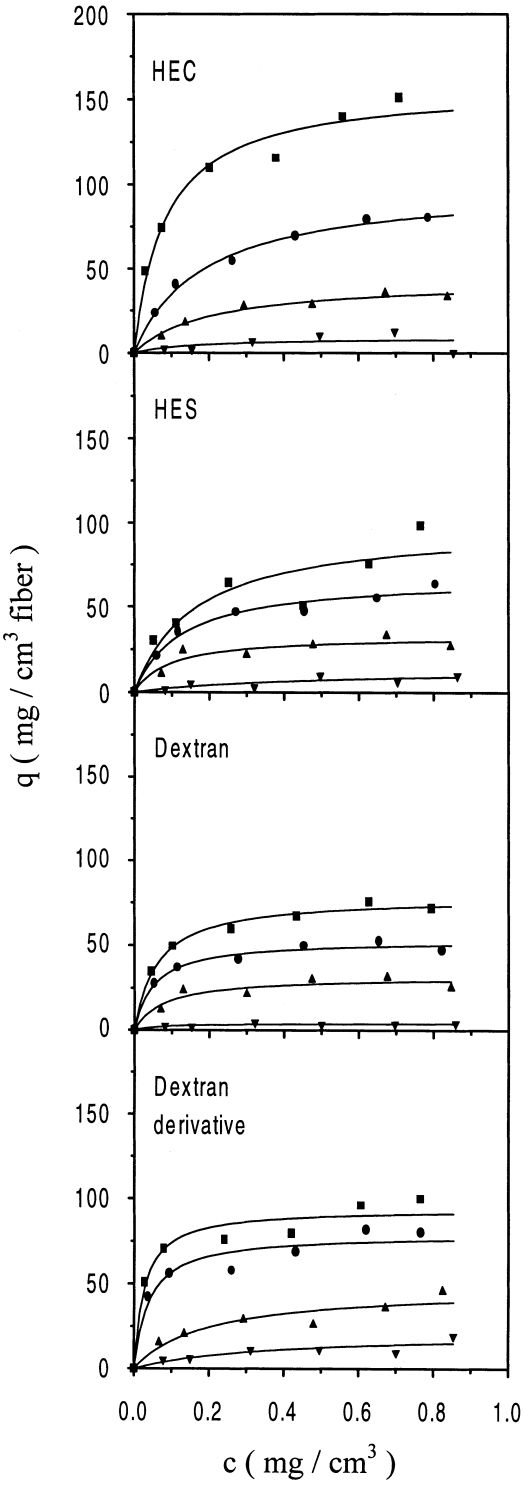

FIG. 4 Adsorption isotherms of lysozyme to polysaccharide-modified and Cibacron Blue 3GA-immobilized hollow fibers at 25°C. Cibacron Blue 3GA concentrations used: (■) 3%, (●) 0.3%, (▲) 0.03%, (▼) 0.003%.

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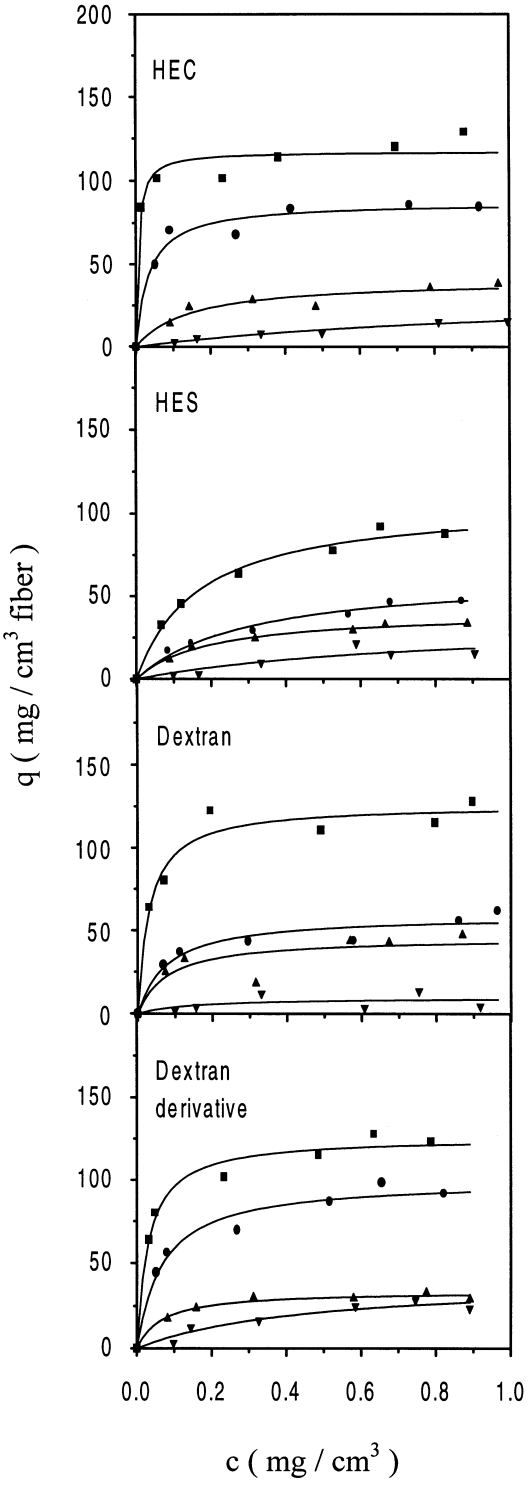

FIG. 5 Adsorption isotherms of lysozyme to polysaccharide-modified and Cibacron Blue 3GA-immobilized hollow fibers at 37°C. Cibacron Blue 3GA concentrations used: (■) 3%, (●) 0.3%, (▲) 0.03%, (▼) 0.003%.

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The fitted curves are plotted as solid lines in the figures, and the values of the fitted parameters are listed in Table 1.

To distinguish the effects of specific and nonspecific binding, the hollow fibers modified solely with polysaccharide in the absence of Cibacron Blue 3GA were used for lysozyme adsorption at room temperature. According to our results, the nonspecific adsorption capacities at high equilibrium concentration were as follows: 2 mg/cm^3 for HEC and dextran, 4 mg/cm^3 for HES, and 2.5 mg/cm^3 for the dextran derivative. These values are relatively smaller than the results from Fig. 4 (the specific adsorption), except for the data of the 0.003% concentration. This result is not surprising since numerous free hydroxyl groups remained on the hollow fiber from unreacted polysaccharide

TABLE 1
The Fitted Parameters Using the Langmuir Isotherm Model[a]

			Cibacron blue 3GA concentration used for immobilization (w/v)			
			3%	0.3%	0.03%	0.003%
Hydroxyethyl cellulose	4°C	q_m	126 ± 5	130 ± 20	35 ± 5	10 ± 11
		K_d	0.042 ± 0.008	0.4 ± 0.1	0.04 ± 0.03	0.2 ± 0.6
	25°C	q_m	158 ± 5	100 ± 8	44 ± 8	9 ± 7
		K_d	0.08 ± 0.01	0.19 ± 0.04	0.2 ± 0.1	0.2 ± 0.4
	37°C	q_m	117 ± 3	87 ± 4	41 ± 7	34 ± 50
		K_d	0.006 ± 0.001	0.034 ± 0.009	0.14 ± 0.08	1 ± 3
Hydroxyethyl starch	4°C	q_m	71 ± 3	60 ± 6	42 ± 6	10 ± 5
		K_d	0.06 ± 0.01	0.19 ± 0.06	0.2 ± 0.1	0.2 ± 0.3
	25°C	q_m	100 ± 11	68 ± 9	33 ± 7	10 ± 26
		K_d	0.17 ± 0.06	0.13 ± 0.06	0.09 ± 0.09	0.5 ± 1.9
	37°C	q_m	108 ± 4	64 ± 7	41 ± 5	40 ± 19
		K_d	0.17 ± 0.02	0.30 ± 0.80	0.19 ± 0.07	0.8 ± 0.8
Dextran	4°C	q_m	132 ± 5	43 ± 2	27 ± 3	9 ± 5
		K_d	0.16 ± 0.02	0.03 ± 0.01	0.08 ± 0.04	0.2 ± 0.4
	25°C	q_m	78 ± 2	53 ± 2	32 ± 2	4 ± 2
		K_d	0.061 ± 0.008	0.05 ± 0.01	0.08 ± 0.03	0.1 ± 0.2
	37°C	q_m	126 ± 5	59 ± 6	46 ± 7	10 ± 9
		K_d	0.031 ± 0.007	0.08 ± 0.04	0.08 ± 0.05	0.1 ± 0.5
Dextran derivative	4°C	q_m	76 ± 3	59 ± 2	21 ± 2	5 ± 3
		K_d	0.046 ± 0.009	0.030 ± 0.008	0.02 ± 0.02	0.1 ± 0.2
	25°C	q_m	94 ± 4	79 ± 4	48 ± 9	20 ± 16
		K_d	0.027 ± 0.007	0.04 ± 0.01	0.2 ± 0.1	0.4 ± 0.6
	37°C	q_m	126 ± 3	100 ± 4	34 ± 4	40 ± 14
		K_d	0.031 ± 0.004	0.07 ± 0.01	0.07 ± 0.04	0.4 ± 0.3

[a] q_m = mg/cm^3 fiber. K_d = mg/cm^3.

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because 0.003% of Cibacron Blue 3GA was used, and consequently increased the extent of nonspecific binding. Although the effect of nonspecific binding may be significant for the results of 0.003% Cibacron Blue 3GA concentration, the following analyses neglect the adsorption capacity from nonspecific binding.

Figures 3 to 5 clearly demonstrate that lysozyme adsorption capacity increases with the increased concentration of Cibacron Blue 3GA used for immobilization, regardless of the kind of polysaccharide employed. This behavior agrees with the observation from Fig. 2. Polysaccharide conjugated with hollow fibers provides plenty of hydroxyl groups for Cibacron Blue 3GA immobilization. With a higher concentration of Cibacron Blue 3GA, a higher extent of Cibacron Blue 3GA was immobilized onto the fibers. Consequently, more lysozyme molecules were adsorbed and the measured capacity was increased.

To compare adsorption effects from different polysaccharides, the saturation capacity data (q_m) shown in Table 1 were analyzed. The highest adsorption capacity occurred from the fiber conjugated with HEC at 4 and 25°C, whereas *o*-(4-hydroxylbutyl carbamoyl) dextran-derivatized fiber dominated at 37°C. However, the adsorption capacities for HEC at 37°C approached those for the dextran derivative. Consequently, this study considers HEC to be an ideal choice of polysaccharide for the surface modification of poly(ether sulfone) hollow fibers. This work also tested chitosan, a polysaccharide used in the literature (16). However, its conjugation with EGDGE-activated fibers failed owing to the low solubility of chitosan in water.

The adsorption capacity onto affinity hollow fiber was compared with other affinity supports using the same ligand and protein to further explore its practical application. In the author's previous work (24), the saturation capacities of lysozyme from Blue Sepharose CL-6B gel beads and Cibacron Blue 3GA-immobilized membrane disks (without spacer arm) at room temperature were investigated. The capacity values of 1300 to 1600 μM for Blue Sepharose CL-6B and 1300 to 1400 μM for membrane disks were determined. In terms of the amount of lysozyme adsorbed per cubic centimeter of the solid supports, the adsorption capacities for gel beads and membrane disks ranged from 19 to 23 mg/cm^3. The adsorption capacities from polysaccharide-modified hollow fibers using 3% Cibacron Blue 3GA were 3 to 8-fold greater (Table 1). These findings demonstrate that the polysaccharide-modified hollow fibers in this study provide more reactive sites for ligand immobilization and hence lead to higher adsorption capacity.

Scatchard Plots

To analyze the adsorption homogeneity, Scatchard plots of the adsorption data are shown in Figs. 6 to 8. The figures also include Scatchard plots of the

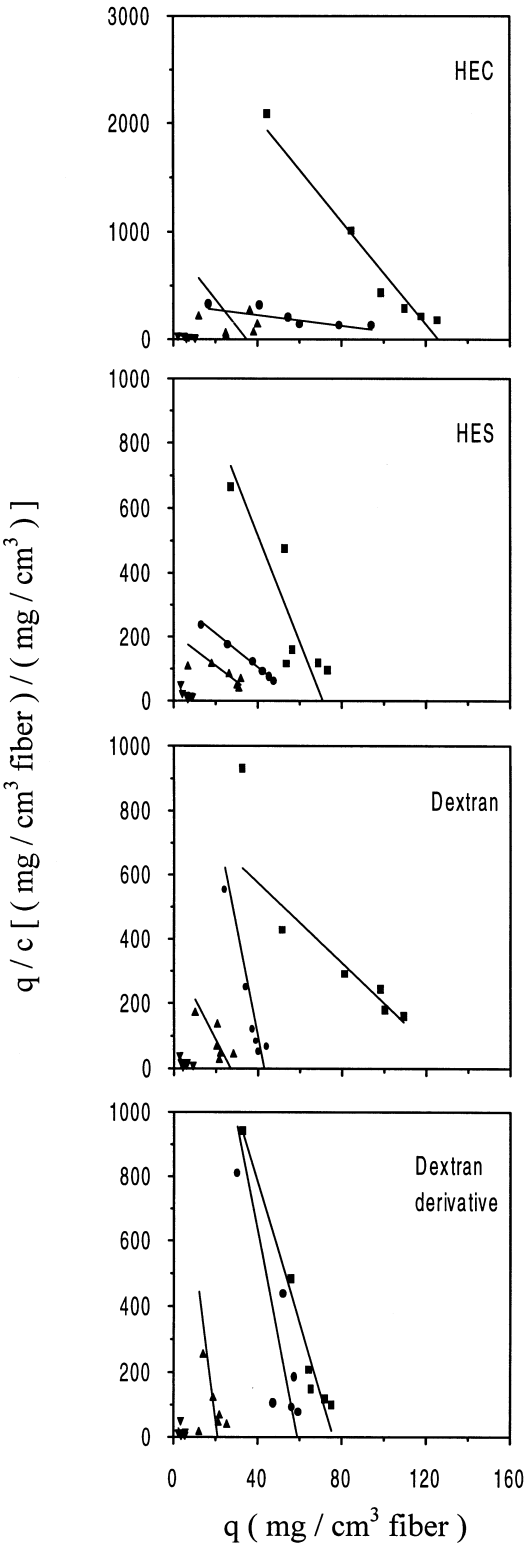

FIG. 6 Scatchard plots for adsorption isotherms of lysozyme to polysaccharide-modified and Cibacron Blue 3GA-immobilized hollow fibers at 4°C. Cibacron Blue 3GA concentrations used: (■) 3%, (●) 0.3%, (▲) 0.03%, (▼) 0.003%.

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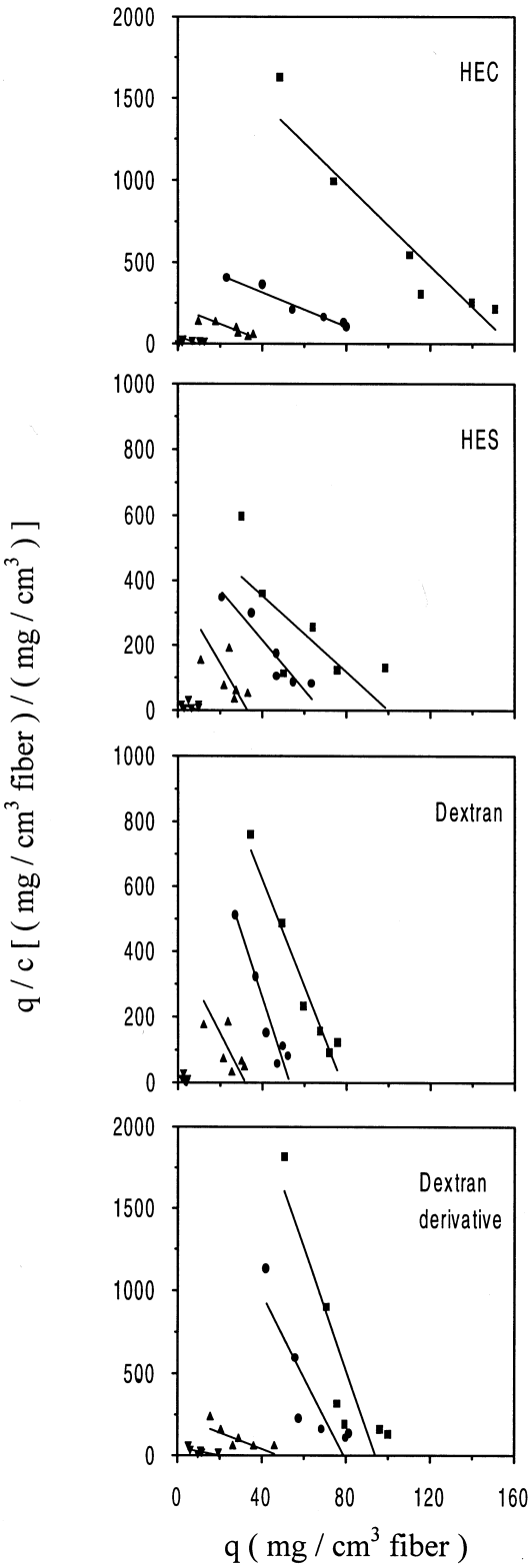

FIG. 7 Scatchard plots for adsorption isotherms of lysozyme to polysaccharide-modified and Cibacron Blue 3GA-immobilized hollow fibers at 25°C. Cibacron Blue 3GA concentrations used: (■) 3%, (●) 0.3%, (▲) 0.03%, (▼) 0.003%.

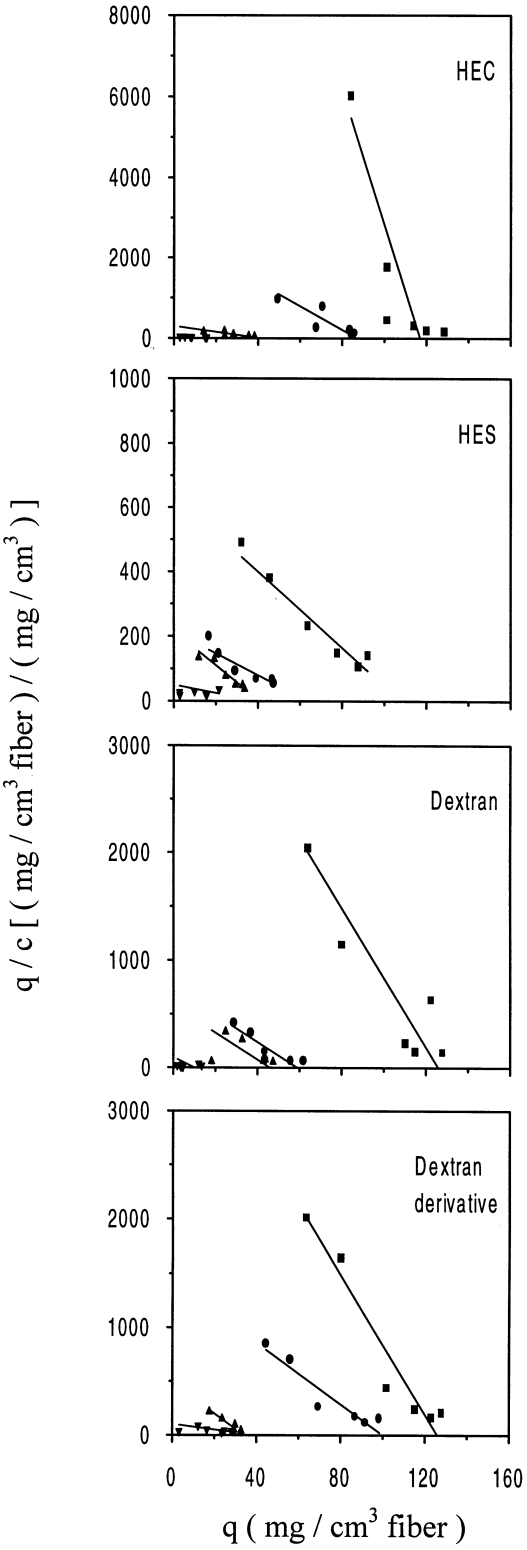

FIG. 8 Scatchard plots for adsorption isotherms of lysozyme to polysaccharide-modified and Cibacron Blue 3GA-immobilized hollow fibers at 37°C. Cibacron Blue 3GA concentrations used: (■) 3%, (●) 0.3%, (▲) 0.03%, (▼) 0.003%.

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fitting isotherm results with the Langmuir model as solid lines. The corresponding equation for the Scatchard plot of the Langmuir model is

$$\frac{q}{c} = \frac{q_m}{K_d} - \frac{1}{K_d} q \tag{2}$$

The linearity with a negative slope from Eq. (2) is an index for adsorption homogeneity. Deviation from the negative-slope straight line of the Scatchard plot represents heterogeneous adsorption. Most of the Scatchard curves from the adsorption of lysozyme onto hollow fibers agreed fairly well with the negative-slope lines from the Langmuir model, although some data were slightly scattered. As a consequence, lysozyme adsorption onto Cibacron Blue 3GA-immobilized hollow fibers in this study can be considered to be homogeneous adsorption. Moreover, the adsorption behavior described by the Langmuir model follows a one-to-one binding pattern in a single adsorption layer. This may imply that as long as the Langmuir model applies, the protein-ligand affinity adsorption is primarily a consequence of single-site interaction. Otherwise, multivalent, multisite, multilayer, or other complicated binding mechanisms may occur. From the adsorption study in this work, the lysozyme adsorption onto hollow fibers is more likely to be a single-site and single-layer binding.

Temperature Effect

Previous investigations (23, 25) have indicated that the binding of lysozyme onto Cibacron Blue-immobilized particle matrices results from both ionic and hydrophobic interactions, and the increase in binding strength with increasing temperature was mainly attributed to an elevated hydrophobic effect. In this study the reciprocal of the dissociation equilibrium constant ($1/K_d$) is a measure of the association strength. Accordingly, the data of the dissociation equilibrium constant in Table 1 were compared to evaluate the temperature effects on binding strength.

For HEC, K_d values decreased with increasing temperature at higher Cibacron Blue 3GA concentrations (3 and 0.3%) whereas K_d values showed an opposite trend for low ligand concentrations (0.03 and 0.003%). Since the fitted parameter values have larger deviations and nonspecific binding effect is more significant for lower Cibacron Blue 3GA concentrations, the K_d values for 3 and 0.3% concentrations are considered more reliable. Therefore, the binding strength ($1/K_d$) results from HEC-modified fibers indicate an endothermic adsorption. As for HES, K_d values generally increased slightly with increasing temperature, indicating an exothermic-like adsorption process. This pattern is different from that in which the hydrophobic effect plays a key role in binding. Perhaps the lysozyme-ligand binding was dominated by the

electrostatic force while HES was adopted. In the case where dextran was used, K_d values significantly decreased with increasing temperature for 3% Cibacron Blue 3GA concentration, whereas K_d values varied only slightly for the other three concentrations. Similar to HEC, the protein-ligand binding from dextran-modified fibers should be endothermic. For the dextran derivative, most K_d values at different temperatures fell within the same order of magnitude when the same concentration of Cibacron Blue 3GA was employed. This pattern suggests that the temperature effect on the binding strength was rather insignificant.

The temperature effect on the saturation capacity was also investigated. The temperature for the highest adsorption capacity for dextran and the dextran derivative was 37°C, whereas no significant effect of temperature on HEC and HES was observed (Table 1). Moreover, the saturation capacity generally increased with temperature for dextran and the dextran derivative, possibly indicating an endothermic process for lysozyme adsorption onto the dextran or dextran derivative-modified hollow fibers. Combining the analyses for the dissociation equilibrium constant and saturation capacity, lysozyme adsorption onto polysaccharide-modified hollow fibers tends to be an endothermic process in this work.

CONCLUSIONS

This study investigated the adsorption behaviors of lysozyme onto immobilized Cibacron Blue 3GA in poly(ether sulfone) hollow fibers using different polysaccharides for surface modification and different ligand concentrations in the immobilization process. The results indicate that the polysaccharide modification method is successful, and the employment of HEC achieved the highest adsorption capacity at room temperature. In addition, increasing ligand concentration may optimize adsorption capacity. Our results demonstrate that the saturation capacities of lysozyme onto hollow fibers were significantly greater than the use of membrane disks and traditional chromatographic gel beads. The advantages of high capacities and the crossflow design for hollow fibers may allow the applications of hollow fibers in bioseparation processes to overtake the traditional chromatographic and other adsorptive membrane techniques.

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