Preparations and Properties of Sodium Alginate Formed-in-Place Membranes

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SYNOPSIS

Sodium alginate formed-in-place membranes were formed on a macroporous titanium dioxide membrane substrate at pH 3.3, 6.5, and 10.5. To investigate the rate and the mechanism of the membrane formation, the dependence of the pressure-to-flux ratio, P/J, on time, t, during the formation was evaluated using diagnostic graphs; $(P/J)^2$, $(P/J)^{1/2}$ and $-\ln(P/J)$ vs. t. The microfiltration properties of the membranes were investigated by determining the permeability, J/P, and the rejection of a protein, bovine serum albumin (BSA), in 1 g/L solutions as a function of the concentration of added KCl. The stability of the membranes was evaluated by comparing the ratio of the resistances of the membranes at the end of the formation, R, after crossflow rinsing, R_m, and after crossflow rinsing following the BSA microfiltration experiment, R_a. The linearity of the graphs of $(P/J)^2$ vs. t of the membranes formed in neutral or basic conditions indicated that the membranes were formed by deposition of a layer, or cake, of the polyelectrolyte on the substrate, while the membrane formed at lower pH was initially deposited as a layer followed by a more complex mechanism. Only the membranes formed pH 3.3 were stable to the crossflow water rinse and retained high BSA rejection at high ionic strength. Their permeabilities were about 50% lower than the permeabilities obtained with the membranes formed at higher pH. The BSA rejection results imply that a continuous sodium alginate membrane is present for the membranes formed at pH 3.3 and that membranes retaining a macroporous structure are present for the membranes formed at pH 6.5 and 10.5. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A formed-in-place (FIP) membrane is dynamically generated by depositing either organic or inorganic polymers on or in the pores near the surface of macroporous substrates, usually made of stainless steel, ceramics, and plastics that have excellent chemical and mechanical stability. FIP membranes were first developed in Oak National Laboratory in 1966.[1] FIP membranes, partly due to their reformation capabilities, have attracted attention for ultrafiltration and microfiltration applications involving separation, concentration, and purification in textile, biotechnology, food processing, and pharmaceutical fields.[2,3]

In this research, sodium alginate was deposited to form microfiltration membranes on a macroporous TiO_2 layer sintered on the inner surface of a porous stainless steel support tube. Sodium alginate is a natural biopolymer produced from marine algae.[4] Chemically, it is a linear copolymer of β-D-mannuronate and α-L-guluronate arranged with 1,4-linkage.[5] Sodium alginate is a weak acid polyelectrolyte that can be easily removed from the TiO_2 substrate by circulating basic solutions through the module at low pressure.[6]

The TiO_2 membranes have been used as a final filter of glucose solutions obtained from the enzymatic hydrolysis of starch for use as sweeteners. Proteins can be an impurity in the sweetener stream originating from the enzymes added to the process or entering as an impurity in the starch. Dynamic formation of an alginate membrane on the TiO_2

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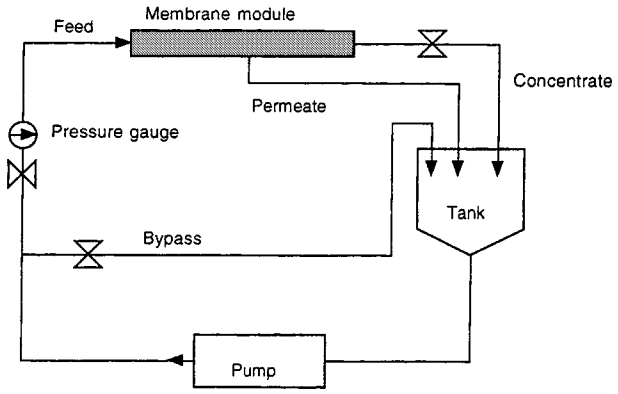

Figure 1 Schematic diagram of the filtration system.

substrate membrane should increase the rejection of the proteins.

The purpose of the present work is to investigate the effects of pH during formation on the course of the dynamic formation of the sodium alginate membranes and to describe the dependence of membrane stability and retentive microfiltration of a protein, bovine serum albumin, as a function of ionic strength on the formation procedures.

EXPERIMENTAL

Membrane Formation

Sodium alginate FIP membranes were formed using dilute solutions of sodium alginate on a microporous titanium dioxide (TiO_2) layer sintered on the inner surface of a stainless steel porous tube provided by Du Pont Separation systems, Inc., Seneca, SC. The tubular substrate was 0.61 m in length, 0.016 m in the inner diameter, with a membrane area of 0.030 m^2. The alginate (KELTONE HV) used in the formation was obtained from Kelco Division of Merck & Co. Inc. (Rahway, NJ) without further purification. The viscosity average molecular weight of the sodium alginate was 22 kDa, as determined by measuring the viscosity of solutions of the polyelectrolyte in 0.1*M* NaCl solution with an Ostwald viscometer at 25°C and utilizing the Mark–Houwink equation.[7] The mannuronate/guluronate ratio (M/G) determined by ^{13}C-NMR spectroscopy (Bruker AC300, Hitachi) was 1.5, a value characteristic of sodium alginate obtained from the Atlantic sea water adjacent to the USA.[8,9]

The membrane formations were performed under a constant pressure of 1.7 bar (25 psi) in an operating system shown in Figure 1. Identification of the membranes with the pH of the formation is given with the standard formation conditions in Table I. The volume fluxes, *J*, were measured before the formation, during the period of the formation, at the end of formation, and after two crossflow rinses.

Microfiltration of Dilute BSA Solutions

The microfiltration properties of the membranes were investigated by measuring the volume flux, *J*, and the rejection of bovine serum albumin (BSA) of a 1.0 g/L BSA solution as a function of ionic strength. The bovine serum albumin fraction V (BSA) was obtained from the United States Biochemical Corporation (Cleveland, OH). The molecular weight of BSA is 68 kDa and the molecular weight obtained by a laser matrix oblation time-of-flight mass spectrometer method in our laboratory was 66 kDa. The ionic strengths of the solutions used in the microfiltration experiments were adjusted by adding a 2*M* KCl solution and the pH was adjusted by adding a minimum amount of HCl or NaOH. The microfiltration experiments were run at complete recycle of permeate and concentrate at pH 6.5 ± 0.2 under a constant pressure of 1.9 bar (27 psi) and a temperature of 25 ± 1°C. BSA rejections were determined by the concentrations of the protein in the permeate and in the feed using a UV-20101 PC, UV-VIS Scanning Spectrophotometer (SHIMADZU) at the wave length of 280 nm. The solution flux was measured at regular intervals during each microfiltration experiment and water flux was determined after two crossflow rinses with water following the discharge of the BSA solution.

After BSA filtration, the membrane was cleaned by recirculating a mixture of NaOH (1%, w/v) and 30% H_2O_2 (1%, v/v) for 6–12 h and then concentrated HNO_3 (1%, v/v) for 1 to 4 h at 40°C. Two 10 min rinses with water followed these cleaning steps, and water permeability was determined to check the cleaning sequence efficiency. An additional cleaning

Table I Membrane Identification and Formation Conditions

Membrane Identification	pH
F-1	6.5 ± 0.3
F-7	10.5 ± 0.3
F 9	3.3 ± 0.3

Formed by deposition of 0.20 g/L sodium alginate solutions for 30 min at $T = 22 \pm 2$°C, $P = 1.7$ bar, and crossflow velocity of 0.32 ± 0.02 m/s.

cycle was executed whenever needed. The cleaning procedure was always concluded with the HNO_3 rinse to ensure the substrate surface was in the same state for each experiment.

All the water used in the experiments was deionized and then filtered through an FIP ultrafiltration membrane.

RESULTS AND DISCUSSION

The dependence of the flux on time during the deposition of the sodium alginate to form the membrane has been related to three flux-decline models; pore blockage, pore constriction, and cake filtration. The dependence of the pressure-to-flux ratio, P/J, on time differs for each of these mechanisms.[10] The pore blockage model assumes the number of blocked pores is proportional to the volume of permeate and the time dependence of P/J is $-\ln(P/J) \sim t$. The pore constriction model assumes the reduction of the pore radius is proportional to the volume of permeate and $(P/J)^{1/2} \sim t$. The cake filtration model assumes the hydraulic resistance is proportional to the mass of solute deposited and $(P/J)^2 \sim t$.

The dependence of the pressure-to-flux ratio, P/J, on time, t, during formation was evaluated using graphs of $(P/J)^2$, $(P/J)^{1/2}$, and $-\ln(P/J)$ vs. t. These graphs are diagnostic; a linear dependence of $(P/J)^2$ on t is consistent with the formation of a continuous layer or cake of polyelectrolyte on the substrate, a linear dependence of $(P/J)^2$ on t is consistent with pore constriction by deposition of the polyelectrolyte, and a linear dependence of $-\ln(P/J)$ on t over the major fraction of the formation period is consistent with deposition of the polyelectrolyte by random pore plugging to form a membrane.[10,11] The formation process was identified in terms of these interpretations when a linear graph was obtained. When all graphs were nonlinear, the membrane formation and resulting morphology was interpreted as being more complex than these identifiable processes. The graphs indicated that none of the three formations followed the random pore plugging or the pore constriction mechanisms. The $(P/J)^2$ vs. t plots in Figure 2 indicates that the formation of membrane F-7, formed at pH 10.5, and F-1, formed at pH 6.5, followed the cake or continuous layer depositing mechanism. However, the membrane formed at pH 3.3, F-9, showed a layer depositing mechanism only for the first 5–10 min followed by a more complicated mechanism. The slopes of the linear portions of the plots of $(P/J)^2$ vs. t are listed in Table II. The formation rate at pH 10.5 was much slower than the others, possibly due to the strong electrostatic repulsion between the alginate polyion and the TiO_2 substrate and also between alginate polyions. Both TiO_2 and alginate possess net negative charges at the high pH.

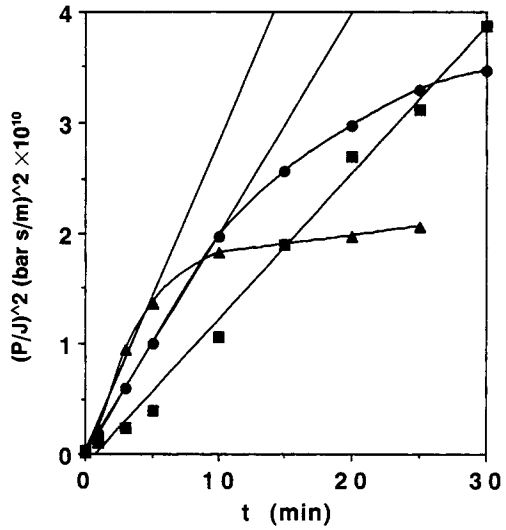

Figure 2 Square of the pressure to flux ratio vs. time for sodium alginate membranes formed at pH 3.3 (circles), 6.5 (triangles), and 10.5 (squares).

Table II Slopes of $(P/J)^2$ vs. t during Formation

Membrane	pH	Slope 10^{-7} (bar^2 s/m^2)
F-1	6.5 ± 0.3	4.02
F-7	10.5 ± 0.3	2.19
F-9	3.3 ± 0.3	4.18

The results of the steady state rejection of BSA, r(BSA), vs. $[KCl]^{1/2}$ obtained in the microfiltration experiments on the FIP membranes with 1.0 g/L BSA at neutral pH (6.5 ± 0.2) are shown in Figure 3. The extent of the decline of the rejection with the addition of KCl was dependent on the pH of the formation. Only the membrane formed in the acidic solution (F-9) retained high BSA rejection at high ionic strength. It also exhibited the lowest permeability to the BSA solution, as shown in Figure 4. Apparently the alginate membrane formed at pH 3.3 developed a gel that was more stable to increasing ionic strength at pH 6.5 than the membranes formed at pH 6.5 and 10.5, possibly because the alginic acid was uncharged and the hydrogen bonding occurring at pH 3.3 contributed to the formation of a more

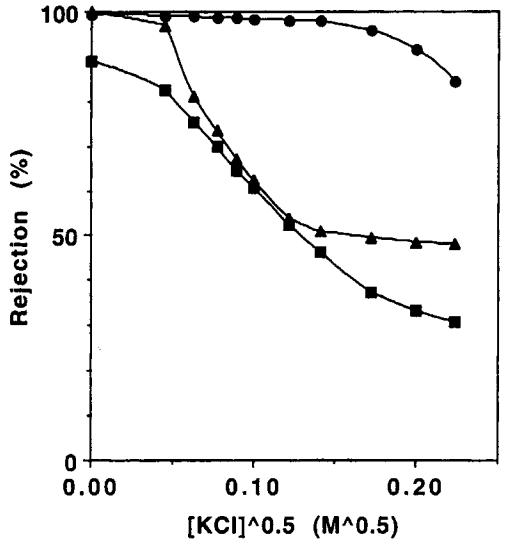

Figure 3 Rejection of BSA vs. $[KCl]^{1/2}$ for the retentive microfiltration experiments at pH 6.5 for sodium alginate membranes formed at pH 3.3 (circles), 6.5 (triangles), and 10.5 (squares).

stable membrane gel than was formed at higher pH where less hydrogen bonding occurs in the alginate polyion.

To evaluate the membrane stability, the volume fluxes of water were determined before and after selected steps in the experimental sequences. The symbols for the various flux and experimental resistance determinations are summarized in Table III.

The experimental resistances, $P/\eta J_i$, are related to the characteristic resistances, R_i, and normalized resistances, $N(R_i)$, by resistance to water before formation,[12]

$$\frac{P}{\eta J_{\text{wbf}}} = R_s \tag{1}$$

where R_s is the substrate resistance; resistance at the end of the formation,

$$\frac{P}{\eta J_f} = \frac{R_s + R_m}{(1 - \pi'_f)} \tag{2}$$

where R_m is the alginate membrane resistance and π'_f is the relative osmotic pressure difference, $\pi'_f = \pi_f/P$, during formation; resistance to water after formation and two crossflow rinses,

$$\frac{P}{\eta J_{\text{wa f}}} = (R_s + R_m) \tag{3}$$

resistance at the end of the BSA microfiltration experiment,

$$\frac{P}{\eta J} = \frac{(R_s + R_m) + R_a}{(1 - \pi'_f)} \tag{4}$$

where R_a is the resistance of the foulant adsorbed from the BSA solution; resistance to water after the BSA microfiltration experiment and two crossflow water rinses,

$$\frac{P}{\eta J_{\text{wa}}} = R_s + R_m + R_a \tag{5}$$

normalized resistance before crossflow rinses,

$$N(R) = \frac{R_m + R_s}{R_s(1 - \pi'_f)} = \frac{\dfrac{P}{\eta J_f}}{\dfrac{P}{\eta J_{\text{wb f}}}} \tag{6}$$

normalized membrane resistance,

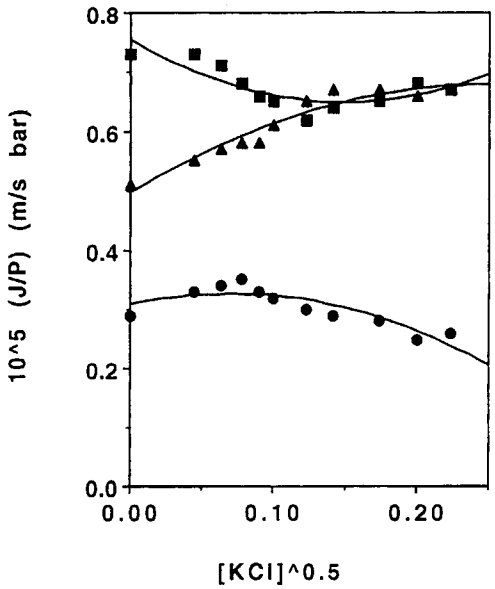

Figure 4 Steady-state permeability vs. $[KCl]^{1/2}$ for the retentive microfiltration experiments at pH 6.5 for sodium alginate membranes formed at pH 3.3 (circles), 6.5 (triangles), and 10.5 (squares).

Table III Identification of Flux and Operational Resistance Symbols

Sequence	Feed	Flux	Resistance
Before membrane formation	Water	J_{wbf}	$P/\eta J_{wbf}$
End of formation	Formation solution	J_f	$P/\eta J_f$
After two crossflow rinses	Water	J_{waf}	$P/\eta J_{waf}$
End of BSA rejection test	BSA/KCl solution	J	$P/\eta J$
After two crossflow rinses	Water	J_{wa}	$P/\eta J_{wa}$

$$N(R_m) = \frac{R_m}{R_s} = \frac{\dfrac{P}{\eta J_{waf}}}{\dfrac{P}{\eta J_{wbf}}} - 1 \qquad (7)$$

normalized resistance of adsorbed foulant in the protein microfiltration experiment,

$$N(R_a) = \frac{R_a}{R_s} = \frac{\dfrac{P}{\eta J_{wa}}}{\dfrac{P}{\eta J_{wbf}}} - 1 - N(R_m) \qquad (8)$$

The experimental resistance and the normalized characteristic resistance results calculated from eqs. (6) through (8) are given in Table IV. Values of $P/\eta J_{wbf}$ indicate that the resistances of the substrate upon which the various membranes were formed were similar. Comparison of the membrane normalized resistance $N(R_m)$ measured after the crossflow rinses with water and normalized resistance after formation but before the crossflow rinses $N(R)$, showed that, with the exception of formation F-9, the crossflow rinsing after formation decreased the resistance significantly. This result indicates a high retention of the sodium alginate for formations at pH 3.3 but not for the formations at pH 6.5 and 10.5. The resistances to water after the BSA experiment and water rinse ($P/\eta J_{wa}$) were smaller than before the microfiltration of the protein solution ($P/\eta J_{waf}$), resulting in negative values for $N(R_a)$. These results imply that the sodium alginate membranes were damaged by the retentive microfiltration experiments carried out to high ionic strength, about $0.05M$ added KCl, and the following crossflow wash.

CONCLUSIONS

The sodium alginate membranes were formed by the deposition of a continuous layer or cake on a TiO_2 substrate in neutral or basic conditions, whereas the membrane formed at a lower pH was initially deposited as a layer followed by a more complex mechanism. Only the membrane formed in the acidic solution retained its resistance after the water crossflow rinses following formation. Its permeability in the retentive microfiltration experiments was about 50% of the permeabilities obtained with the membranes formed at higher pH and it retained a high rejection of the BSA at high ionic strength while the others did not. These results are consistent with the formation of a continuous layer of sodium alginate at each pH, but with subsequent loss or rearrangement of the sodium alginate for the membranes formed at pH 6.5 and 10.5 during the rinsing after formation to leave macroporous membranes. All three membranes were damaged by the retentive microfiltration of BSA solutions carried out at neutral pH to high ionic strength, about $0.05M$ KCl, and the following water rinse. However, steady-state

Table IV Experimental and Normalized Characteristic Resistances for the Membrane Formation and BSA Microfiltration

Membrane	$\frac{10^{-12}P}{\eta J_{wbf}}$	$\frac{10^{-12}P}{\eta J_f}$	$\frac{10^{-12}P}{\eta J_{waf}}$	$\frac{10^{-12}P}{\eta J_{wa}}$	$N(R)$	$N(R_m)$	$N(R_a)$
F-1	1.4	14.6	5.2	3.2	10.0	2.8	−1.42
F-7	1.4	22.1	4.2	3.1	15.2	1.5	−0.19
F-9	0.94	21.6	18.5	4.8	21.3	18.7	−14.6

Units: (1/m).

performance was obtained at each ionic strength in the BSA filtration experiments and the membranes were suitable for concentrating BSA solutions under these conditions. Subsequent removal of the fouled membranes by rinsing with water at high pH and reformation of clean membranes was readily accomplished.

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