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Separation of Humic Substances by Porous Ion-Exchange Membranes from Sulfonated Polysulfone

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ABSTRACT

Ultrafiltration involving sulfonated polysulfone membranes provides high efficiency for humic matter removal from water. The increase in ion-exchange capacity of the polymer matrix from 0.24 to 0.96 mmol SO_3H groups per 1 g of dry membrane increases the membrane pore diameter and its hydrophilicity, and thus the permeate flux from 0.05 to 3.69 $m^3/m^2 \cdot d$. In order to decrease the manufacturing cost, membranes from polysulfone and sulfonated polysulfone blends were investigated. It was shown that a one-to-one blend resulted in a membrane having similar antifouling properties to pure sulfonated polysulfone. Both membranes reject humic matter in the 91–98% range and show a flux decline of 5–30% as a result of surface fouling.

INTRODUCTION

Ultrafiltration of solutions containing a macromolecular solute is very often limited by membrane fouling which results in a decrease in process efficiency and a permeate flux decline. Experiments dealing with fouling indicate that flux reduction depends heavily on four phenomena (1, 2):

Pore diameter reduction due to solute sorption on the pore walls

Formation of a dense, low-permeability solute layer directly on the membrane surface
Formation of a hydrogel layer of concentrated solute which can behave as a compressible filter cake
Presence of a diffuse polarization layer of declining solute concentration

The two first phenomena are caused by sorption of a solute on/in the membrane. The two others are brought about by the solute concentration near the membrane and occur independently of the membrane nature. The above classification implies that membrane performance should depend heavily on the properties of both the feed solution (solute concentration, pH, and ionic strength) and the nature of the membrane (3). In the case of a nonsorptive membrane, fouling can be entirely attributed to the gel and polarization layers. These layers are easily removed with a suitable cleaning procedure. Thus, the search for nonadsorptive materials is an urgent challenge to research.

Having reviewed the papers dealing with the improvement of UF membrane performance (3–7), we focused our attention on membranes with ionogenic groups (8–10). These materials, which we call "porous ion-exchange membranes" (PIEM), exhibit two interesting features. They are not as susceptible to fouling as similar membranes which are not charged, and they give more solute rejection. This statement is true provided that the charge of both PIEM and solute is the same.

Particles of humic acids (HA) are the largest fraction of organic matter present in ground or surface water (11). They are composed of acidic and hydrophilic, partly aromatic, polymerlike bodies which are formed during biodegradation of plant matter. Their molecular weights range from several hundred to several million daltons. In drinking water, humic matter is a harmful pollutant and should be removed to obtain water of high quality. During the last decade, the attention of many investigators has focused on ultrafiltration. Lahoussine-Turcand et al. (12) investigated filtration of humic acids using a polysulfone membrane. They found a flux decline of 25% as a result of irreversible membrane fouling.

Polysulfone is an attractive material for the preparation of UF membranes because of its high thermal, chemical, and biological stability. Another major advantage is the potential for introducing ionic groups to the polymer chain.

The purpose of this study was to evaluate the effect of sulfonic groups bound with the membrane on both HA separation and membrane fouling. Because of the pH-dependent character of the humic acid molecules (13), we also examined the effect of pH value on the UF process when using

PIEM. We also wanted to show the possibility for removing humic acids from water in an ultrafiltration process.

EXPERIMENTAL METHODS

Membrane Preparation

Polysulfone UDEL P-1700 (Union Carbide) was subjected to chlorosulfonation in a solution of chlorosulfonic acid in 1,2-dichloroethane using the procedure described by Brousse et al. (14). The reaction proceeded for 1.5 h at room temperature with a molar ratio of acid to polymer of 1:0.7. The chlorosulfonation was followed by hydrolysis in a methanol solution of NaOH to yield a product in the form of a sodium salt. The UF membranes were formed by the phase inversion of sulfonated polysulfone (SPS) or its blend with neat polysulfone (SPSB). The *N*,*N*-dimethylformamide solutions of SPS or SPSB were cast on a glass plate, formed into 0.15 mm films by a doctor-blade technique, and immediately immersed in water. The ion-exchange capacity of the membranes were determined according to a standard method (15). The membrane porosity and average pore diameter were determined gravimetrically and calculated from the Elford–Ferry equation as described by Bodzek (16).

Ultrafiltration Process

Ultrafiltration was carried out in a laboratory unit schematically shown in Fig. 1. The system consisted of a vessel of 1000 cm^3 volume and an ultrafiltration membrane with a surface area of 19.6 cm^2. The retentate

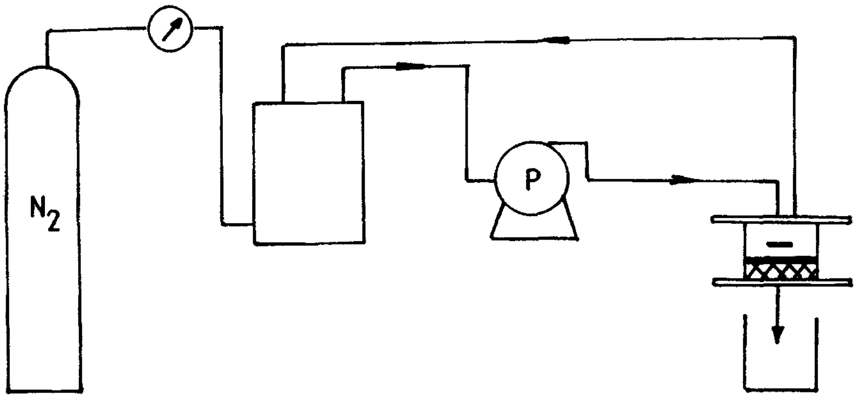

FIG. 1 Schematic setup of ultrafiltration unit.

was recirculated at a flow rate of 30 mL/min. Two transmembrane pressures (0.05 and 0.10 MPa) were employed using compressed nitrogen. A new membrane was used in each experiment. Before the UF measurements, 3 hours of filtration of redistilled water was conducted to establish the initial permeate flux. The UF process was started after the addition of 1000 cm^3 of HA solution to the system. The permeate flux was monitored over 2 hours. For each run, a relative permeability (α) and a rejection factor (R) were calculated according to the following equations:

$$\alpha = J_{HA}/J_w \tag{1}$$

$$R = \left(1 - \frac{C_P}{C_0}\right) \tag{2}$$

where J_{HA} and J_w are the fluxes of the HA permeate and water, respectively, and C_P and C_0 are the concentrations of HA in the permeate and in the feed, respectively.

Feed Solution

In all experiments, solutions of Aldrich HA in redistilled water were used as a feed. The solutions were prepared by dissolving 1 g of HA per 1 dm^3 of water at pH 11. Thereafter, the mixture was left for 24 hours and filtered through a dense filter paper. The filtrate was used to prepare feed solutions containing 10 to 50 mg of HA per 1 dm^3. Adjustments of the feed pH value was made either by NaOH or by HCl additions.

Determination of HA Concentration

The concentrations of HA in the feed, permeate, and retentate were determined spectrophotometrically at 254 nm (Carl Zeiss Jena, M-40 SPECORD).

RESULTS AND DISCUSSION

Porous ion-exchange membranes prove to be very useful in the ultrafiltration of charge-bearing solutes (6–9). The improvement in solute rejection and the decrease in the membrane fouling ability are the main advantages of such membranes. The PIEM in our investigations were prepared from sulfonated polysulfone which allowed us to compare the results obtained to those reported by other researchers (12, 17–21) and to continue our studies (22) with polysulfone membranes. The properties of the PIEM investigated are listed in Tables 1 and 2.

TABLE 1
Properties of PIEM Prepared from Sulfonated Polysulfone

Membrane	SPS concentration in casting solution (wt%)	Porosity (%)	Ion-exchange capacity[a] (mmol/g)	Average pore diameter[b] (nm)
SPS 15	15	89	0.96	19
SPS 20	20	85	0.96	14
SPS 25	25	83	0.96	9

[a] Ion-exchange capacity was expressed as the amount of SO_3H groups per 1 g dry membrane.

[b] Pore diameter was calculated by taking account of the thickness of the membrane skin (SEM photographs).

TABLE 2
Properties of PIEM Prepared from Blends of Sulfonated Polysulfone and Neat Polysulfone. Concentration of Casting Solution: 20 Weight Percent of Polymers

Membrane	SPS concentration in casting solution (wt%)	Porosity (%)	Ion-exchange capacity[a] (mmol/g)	Average pore diameter[b] (nm)
SPSB/30	30	75	0.24	7
SPSB/50	50	82	0.52	13
SPS 20	100	85	0.96	14

[a] Ion-exchange capacity was expressed as the amount of SO_3H groups per 1 g dry membrane.

[b] Pore diameter was calculated by taking account of the thickness of the membrane skin (SEM photographs).

The effect of a polymer's concentration is a casting solution on membrane properties is well-established (23). Low polymer concentrations favor the formation of macroporous membrane structures, whereas high polymer concentrations contribute to the formation of spongy-like structures. These effects are clearly visible in photographs of a membrane cross-section taken under SEM (Fig. 2). The SPS 15 membrane has pores in the form of elongated droplets which cover a major part of the cross section. With an increase in the SPS concentration, the partition of the dropletlike pores decreases and ellipsoidal macropores are formed in the bottom part of the membrane (SPS 20 and SPS 25). Also, the increase of the hydrophilic component in the SPSB blend significantly affects the membrane structure. Pores become larger and fingerlike in shape (SPSB/30 and SPSB/50).

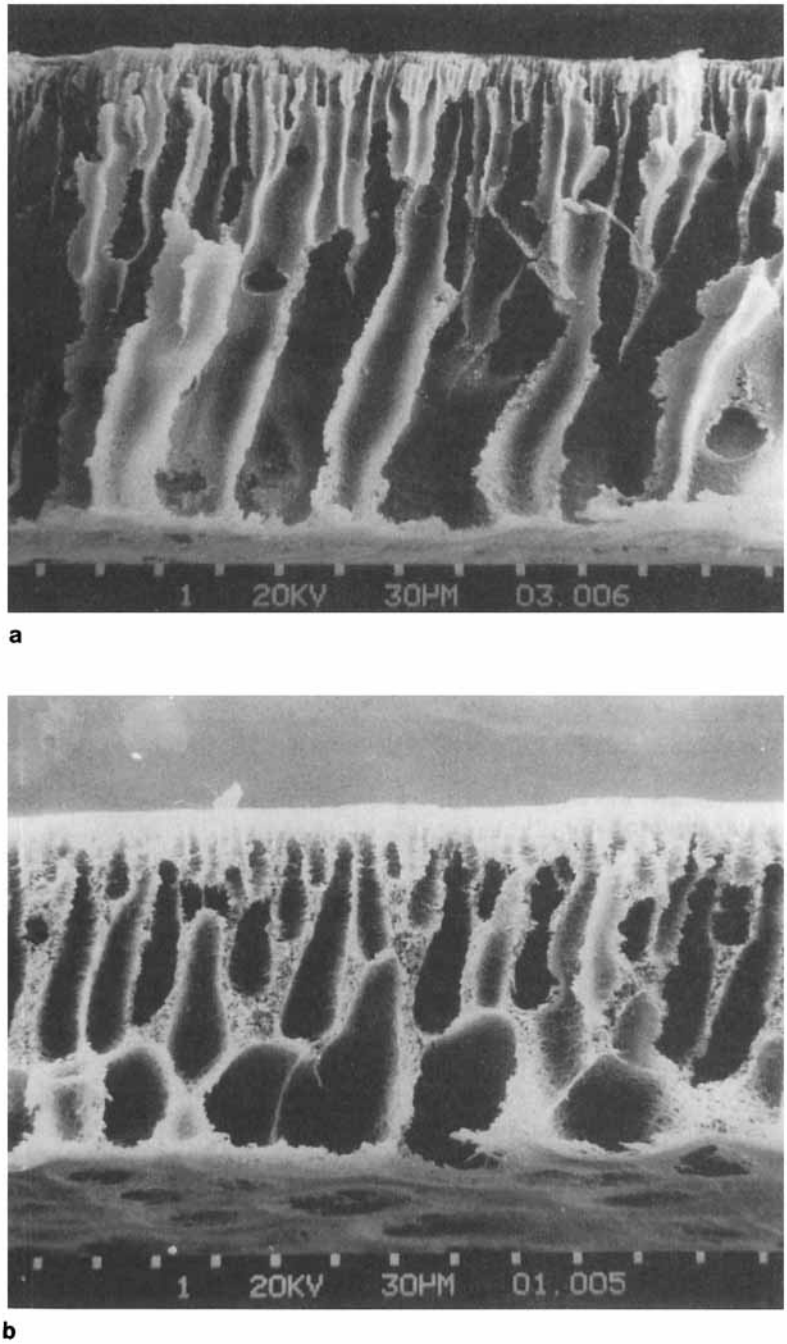

FIG. 2 SEM of membrane cross-section: (a) SPS 15, (b) SPS 20, (c) SPS 25, (d) SPSB/30, (e) SPSB/50.

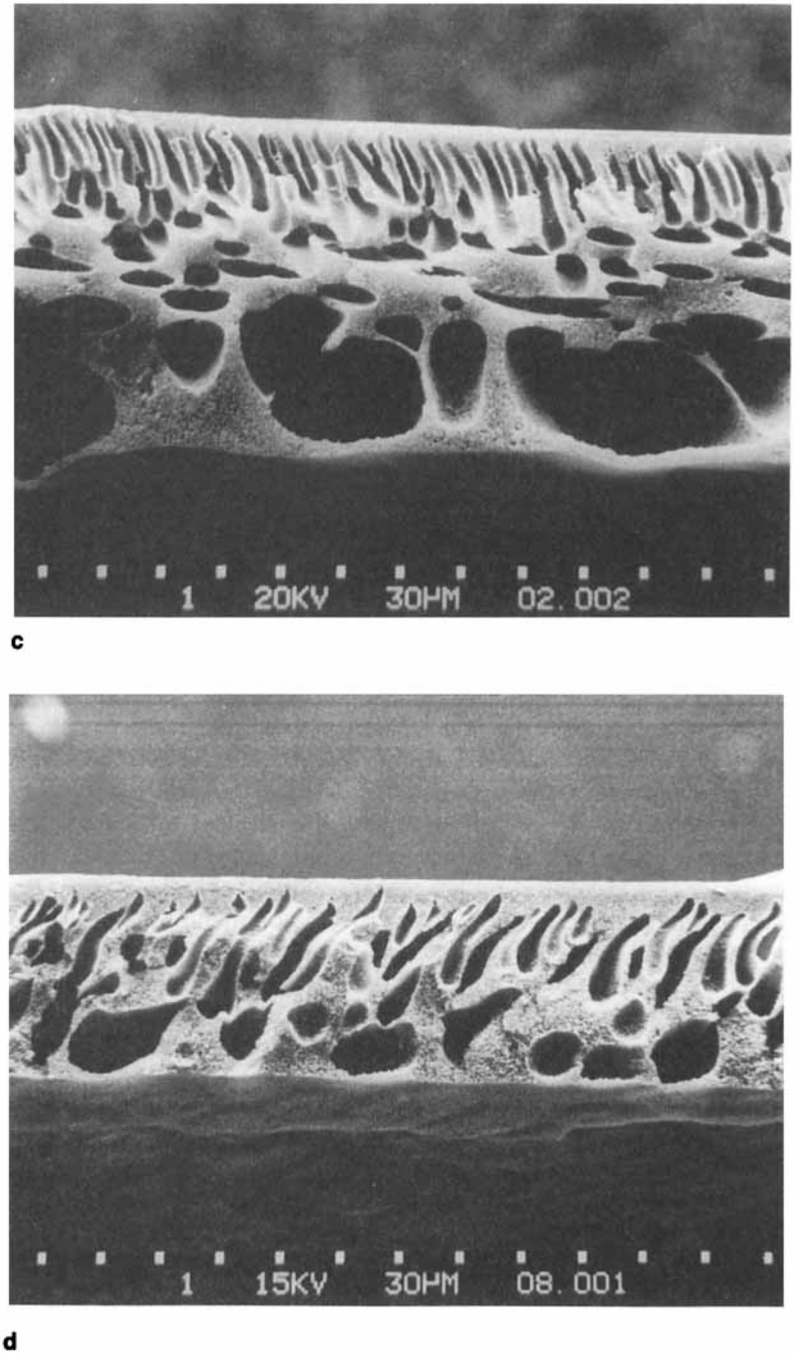

FIG. 2 *Continued*

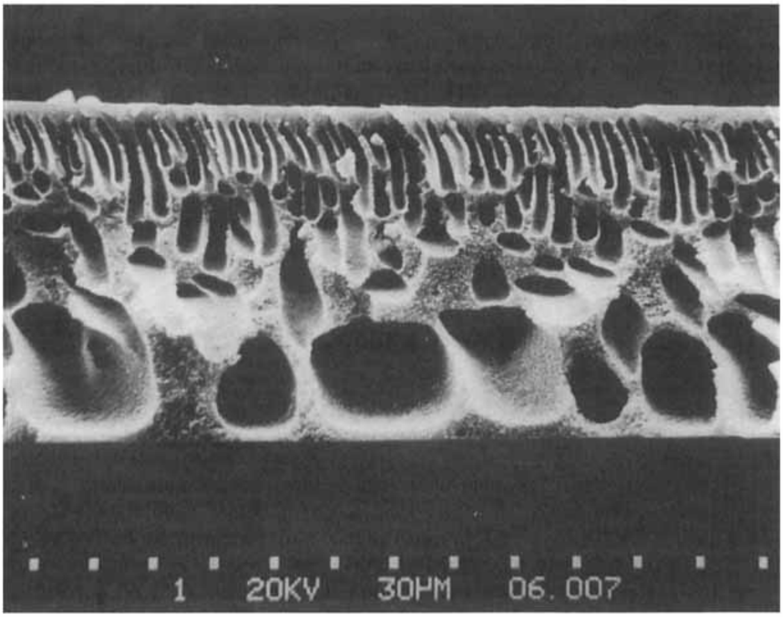

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FIG. 2 *Continued*

For the purpose of this work, SPS 20 and SPSB/50 membranes were selected. Their porosities and average pore diameters are comparable, but they differ significantly in their sulfonic group content (expressed as ion-exchange capacity). The relative permeabilities and the retention factors characteristic of HA filtration are juxtaposed in Table 3.

In analyzing the effect of HA concentration on membrane performance it should be noted that the retention factor increases with an increase of HA concentration up to 30 g/m^3 and then decreases. Relative permeabilities decrease during all concentrations of HA, which implies that electrostatic repulsion is essential in membrane performance at HA concentrations up to 30 g/m^3. When HA concentration exceeds this threshold value, the formation of ultrafiltration cake at the membrane surface becomes possible. Comparison of the SPS 20 and SPSB/50 membranes allows us to state that retention factor values for blended membranes are slightly higher. Nevertheless, the SPS 20 membrane was less susceptible to fouling, and thus the decrease in permeate flux was smaller for the HA concentrations under investigations. The difference between the expected and measured properties proves that a subtle variation in both membrane structures exists. The microphotographs (Fig. 2) show higher skin porosity

TABLE 3
Effect of HA Concentration on Relative Permeability (α) and Retention Factor (*R*) for the SPS 20 and SPSB/50 Membranes (the pH value of the solution was adjusted to 6.5)

HA concentration (g/m^3)	Transmembrane pressure (MPa)							
	SPS 20				SPSB/50			
	0.05		0.1		0.05		0.1	
	α	*R* (%)	α	*R* (%)	α	*R* (%)	α	*R* (%)
10	0.99	92.7	0.97	84.4	0.95	94.0	0.94	90.7
20	0.91	94.8	0.92	89.6	0.90	96.7	0.85	92.0
30	0.89	97.7	0.85	92.7	0.86	98.4	0.79	92.5
40	0.81	95.1	0.79	91.4	0.79	97.8	0.75	92.0
50	0.79	93.5	0.78	89.5	0.73	95.1	0.70	91.9

for SPS 20 than for SPSB/50 membrane. However, speculations based on the microphotographs may lead to some mistakes; e.g., the area of investigation is limited to several hundred square micrometers and its selection is arbitrarily dependent on the investigator's choice.

In order to characterize better the effect of membrane structure on properties, HA ultrafiltration was carried out using various membranes (Table 4). In the case of sulfonated polysulfone membranes (SPS-bunch), humic acid does not affect membrane permeability. The repulsive force between the charged membrane and the solute limits the ability of HA to be deposited. When a membrane structure becomes more compact (decrease in pore diameter), humic matter is retained more efficiently. Such behavior is not surprising. But this clear picture darkens when we deal with blended membranes (SPSB-bunch). The retention factor and relative permeability depend first of all on the contribution of sulfonated polysulfone to the membrane. This relationship proves that a saturation effect is produced. SPSB/50 membranes which reject a solute to the same extent as SPS 20 membranes are only slightly fouled (2–5%). In the same time, permeate flux continuously increases when more sulfonated polysulfones are involved in the SPSB membranes. Subtle change in membrane structure may elucidate this phenomenon. Pore diameter (Table 2) does not change for SPS 20 and SPSB/50 membranes. The porosity presented in Table 2 is the total porosity, i.e., the sum of structural (water in pores) and gel (water integrally bound to sulfonic groups) porosities. Thus, the total porosity cannot be considered an accurate assessment of the active porosity of a membrane as a sieving structure. Thus, active transport through membranes being compared may be different. Differences in the

TABLE 4
Transport and Separation Properties of the SPS and SPSB Membranes (HA concentration and solution pH adjusted to 10 g/m^3 and 6.5, respectively)

Membrane[a]	Pressure (MPa)	Permeate flux (m^3/m^2·d)	Retention factor (%)	Relative permeability
SPS 15	0.05	5.42	95.7	0.99
SPS 20	0.05	3.69	92.7	0.99
SPS 25	0.05	2.74	98.8	0.98
SPS 15	0.10	7.63	92.7	0.96
SPS 20	0.10	4.90	84.4	0.97
SPS 25	0.10	3.10	97.1	0.95
SPSB/30	0.05	0.05	95.2	0.62
SPSB/50	0.05	2.23	94.0	0.95
SPS 20	0.05	3.69	96.5	0.99
SPSB/30	0.10	0.55	94.3	0.54
SPSB/50	0.10	2.54	90.7	0.94
SPS 20	0.10	4.90	95.0	0.97

[a] The SPS 20 membrane is equivalent to SPSB/100.

fine structures of membranes can be explained by the discrepancy between flux and retention. Sulfonic groups make the pore walls of SPS 20 membranes easily wettable. Water enters them, and a high permeate flux is generated. In the case of the SPSB/50 membrane, which is a blend of polysulfone and sulfonated polysulfone in a 1 : 1 ratio, the number of small pores is not as large as for SPS 20 and their wettability should not be as extensive as that of the sulfonated membrane. Consequently, the flux was not as high. However, comparison of the membrane susceptibilities to fouling (relative permeability) revealed their similar sorption levels (see also Table 3). This behavior can be explained by the immiscibility of both polymers. Thus, it is conceivable that sulfonated polysulfone is shifted toward the membrane (pore) surface, forming hydrophilic patches. The HA molecules passing through the membrane interact with the wall material. Therefore, sorption is reduced and the membrane properties are similar to those expected if the membrane were made from pure sulfonated polysulfone. Relative permeability reaches the value characteristic of the SPS 20 membrane. This hypothesis can be strengthen by making the HA molecules capable of entering the pores of the membranes under investigation. In the case of Aldrich humic acid, this is quite easy. Cornel et al. (24) reported that 40% of carbon is involved in macromolecules with dimensions smaller than 5000 daltons. Moreover, the molecular weight distribution depends upon the pH of the solution (13). Wilson (13) states that the degree of aggregation of the humic acid molecules decreases with increases in pH due to increased ionic repulsion forces between humic acid molecules. Consequently, more humic molecules pass through the membrane, and the retention factor slowly decreases (Fig. 3). The SPSB/50 membrane appears to be more effective than SPS 20 at low pH values. When the alkalinity of the solution increases, the SPS 20 membrane becomes more active. At pH > 10, which corresponds to maximal HA poly-

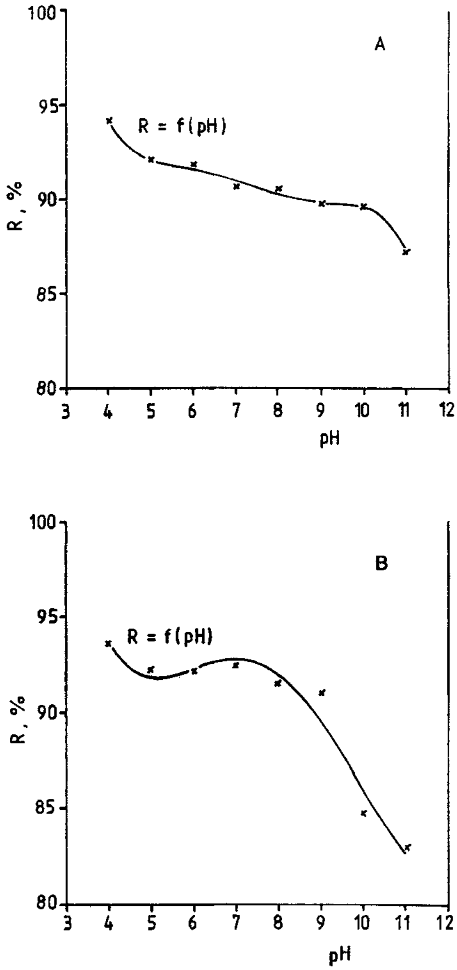

FIG. 3 Effect of pH on HA retention coefficient: (A) SPS 20, (B) SPSB/50. HA concentration, 20 g/m^3; Δp = 0.05 MPa.

dispersity (25), there is a dramatical decrease in the retention factor for both membranes.

More data are shown in Fig. 4. The relative value of permeability is very low, particularly for the SPSB/50 membrane, at low pH values. An accumulation of poorly dissociated organic particles on the membrane surface (hydrophobic interaction with surface polysulfone patches) governs this behavior. At higher pH values the SPSB/50 membrane is a little more vulnerable to fouling than is SPS 20 (again, there is a hydrophobic interaction phenomenon). However, when HA bodies become more hydrophilic (more groups are dissociated), this difference vanishes. At pH 11, the α-values for both membranes are similar. These pH values provide a large fraction of low-molecular-weight humic matter and the solute which was searched for because of its small size and ionic character. The values of the relative permeabilities for SPS 20 and SPSB/50 membranes confirm the hypothesis about the presence of sulfonated polysulfone protective patches; these patches fill the function of a continuous layer.

CONCLUSIONS

Evaluation of porous ion-exchange membranes enables the following generalizations to be made.

1. PIEMs prepared from sulfonated polysulfone provide high efficiency humic acid removal. Their porous and ionic structures guarantee both

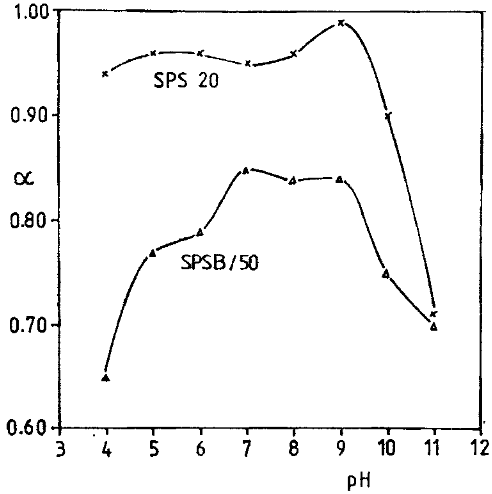

FIG. 4 pH versus relative permeability. HA concentration, 20 g/m^3; Δp = 0.05 MPa.

complete solute rejection and insignificant fouling. The highest value of their permeate flux allows us to classify these materials at the top of the list of interest to potential users.

2. The membranes prepared from a blend of polysulfone and sulfonated polysulfone can be considered as substitutes for the much more expensive sulfonated materials. Although such membranes are not as efficient as sulfonated materials, they can be applied successfully to ultrafiltration of humic acids. Their performances are affected mostly by material composition. Due to phase separation, the blended membrane prepared from polysulfone and sulfonated polysulfone mixed at a 1:1 ratio exhibits the same properties as a sulfonated polysulfone membrane. In the separation of humic acids, the function of the membrane surface is essential. This surface is responsible for solute sorption which occurs with two competing processes, i.e., ionic and hydrophobic interactions. Changes in the ratio of surface polymer and humic acid properties (size and dissociation capacity) allow for control of the important process parameters.

3. Humic acid is an excellent compound for testing. One can alter its hydrophilic/hydrophobic properties or size and the distribution of its macromolecule by changing the pH of the solution.

4. Removal of humic matter from water by ultrafiltration can supplement the techniques of water treatment used so far. However, the selection of PIEM is needed to prevent (or limit) membrane fouling.

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