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Interactions between Chlorolignin and Polysulfone Ultrafiltration Membranes

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Abstract

Interactions between chlorolignin and polysulfone ultrafiltration membranes have been studied by means of direct adsorption measurements and ultrafiltration experiments. The electrical properties of the membrane (zeta potential) and the chemical and physical properties of aqueous chlorolignin have been determined. Phenomena and parameters affecting separation of chlorolignin from aqueous solutions at various pH levels are discussed.

INTRODUCTION

Chlorolignin (CL) is one of the by-products in the pulp and paper industry for which no economically feasible recovery process has yet been developed. Chlorolignin is formed from lignin in the bleaching process of kraft pulp with chlorine or chlorine compounds (*1*, *2*). Its concentration in the bleach effluents, which in addition contain small ions (Na^+, Cl^-, and OH^-/H^+), may rise to a level of 0.5 wt%. The total amount of chlorolignin varies but can rise to several kg/ton of bleached pulp produced (*3*). Today most of the chlorolignin is disposed of with other effluents of the mill and its destination is to sediment along with the other macromolecules and solids. Some debate concerning the environmental hazards of chlorinated organic compounds, including chloro-

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lignin, has been going on for several years. It is also unquestionable that this substance is one of the principal COD-forming components in pulp mill effluents. Moreover, it constitutes about 50% of the total effluent color of an ordinary pulp and paper mill.

So far several separation methods have been tested besides the conventional biological activated sludge treatment and lagooning to reduce the environmental inconvenience of chlorolignin. In Sweden a method based on ion-exchange adsorption of chlorolignin has been successfully used on a pilot scale at the Skoghall Kraft mill (*4*). Reverse osmosis (RO) has also been tried for the removal of chlorolignin, and the concentrate has been further treated by freeze-drying. By using RO the electrolytes can also be removed and the permeate can be reused in the mill (*5*, *6*). The only severe disadvantage is that the method is very expensive.

One of the most promising methods for large-scale chlorolignin removal from bleach effluents seems to be ultrafiltration (UF). The technique of ultrafiltration of alkaline bleach effluents is well known from several studies, and long-term test runs have been carried out in Sweden (*7*, *8*), Canada (*9*), the United States (*10*), and France (*11*). The first commercial installations on a mill scale have already been made in Japan, where effluent regulations are very strict (*12*, *13*). The recovered chlorolignin is disposed of by incineration after evaporation along with black liquor in the recovery cycle.

In this study we concentrate on the surface phenomena related to the chlorolignin adsorption on polysulfone UF membranes. The effect of adsorption on water flux and retention of chlorolignin is measured by conventional methods. The final aim of this study is to clarify under what conditions fouling of membranes takes place and which are the parameters that govern water flux and retention of chlorolignin at various pH.

EXPERIMENTAL

Materials

The chlorolignin fraction used as test sample was recovered from pine kraft pulp bleach effluent, which was obtained from the first alkaline extraction stage, E1, of Kymmene Co. Kaukas Mills, Lappeenranta. An effluent sample of 270 dm^3 which contained about 0.18 wt% chlorolignin and other solids was first purified and fractionated by ultrafiltration. The first stage of UF fractionation was carried out with FP 10 membranes (PVDF, cut off 100,000, Paterson Candy International). The permeate (260 dm^3, 0.082 wt% chlorolignin), free from fibers and suspended particles, was then concentrated by UF using T4 membranes (polysulfone, cut off 8000, Paterson Candy International). The remaining concentrate (10 dm^3, 2.1 wt% chlorolignin), free from most of the low molecular weight organic compounds and most of the electrolytes, was further purified for analytical purposes by electrodialysis until the conductivity (κ) of the sample remained constant (κ = 4.1 mS/cm). The sample was then dried by evaporation.

Commercial synthetic asymmetric UF membranes made of polysulfone (GR 61 PP) were used in all experiments. The membranes were supplied by De Danske Sukkerfabrikker (DDS) and have a nominal cut off value of 20,000. All membranes used were from the same batch.

For the adsorption measurements with polysulfone surface, the quartz crystals were dipcoated with a dichloromethane solution containing 12 wt% polysulfone (Udel P-1700, Union Carbide).

In all experiments p.a. grade chemicals and water purified by ion exchange and UF with a tight membrane were used for the preparation of the solutions.

Methods

Analytical Methods

The extinction coefficients of the chlorolignin solutions at various pH levels were determined in the region 340–440 nm with a spectrophotometer (Hitachi Model 100-60).

The ionic nature of chlorolignin was studied by simultaneous potentiometric and conductometric titrations.

The densities of the aqueous chlorolignin were measured with a densitometer (Anton Paar, DMA 55) and the viscosities with capillary viscometers (Ubbelohde Viscometer, Schott Geräte 52503 and 52510).

Zeta Potential Measurements

In order to get an idea of the net electric surface charge of the membrane material, streaming potentials (ΔE) caused by the driving pressure difference (ΔP) across the membrane were measured with the experimental setup depicted in Fig. 1. The measured signals of the streaming potential (ΔE) and the pressure difference (ΔP), conductivity (κ), and pH of the solution were electronically interfaced to a computer, which also performed the necessary calculations out of the collected data.

The zeta potential (ζ) of the membrane was calculated from

$$\zeta = \frac{\eta\kappa}{\varepsilon_0\varepsilon_r}\left(\frac{\Delta E}{\Delta P}\right) \tag{1}$$

where ε_0 and ε_r are the permittivity of vacuum and the dielectric constant of water, respectively, and η is the viscosity of the solution (*14*).

The zeta potentials at different pH values were first determined using an aqueous KCl solution (5×10^{-4} to 1×10^{-3} *M*) adjusted to the pH in question with HCl or KOH. Then similar experiments at each pH value with solutions of chlorolignin in 5×10^{-4} *M* KCl starting with the least concentrated one were carried out. Measurements made at pH < 3 and pH > 7.5 were rejected because of the limitations met in the measurement system. All the measurements were carried out at 298 K, with the same piece of membrane.

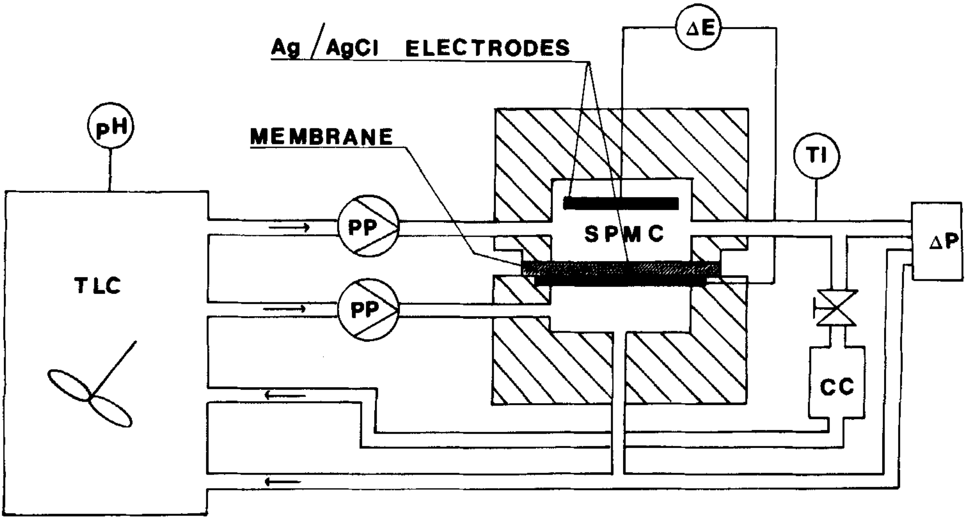

FIG. 1. Experimental setup for streaming potential measurements. Streaming potential measurement cell (SPMC), thermostated liquid container (TLC), peristaltic pumps (PP), and conductivity cell (CC).

Adsorption Measurements with a Quartz Crystal Microbalance (QCM)

The QCM technique is based on the tendency of a piezoelectric crystal to change its oscillation frequency when mass is deposited on the crystal surface. The frequency shift is linearly related to the mass change, provided that the shift is small. The mass sensitivity of the AT-cut 4 MHz quartz crystal used in this study was 3.6 Hz/(mg/m^2), and with ordinary equipment a resolution of 0.1 Hz could be attained. If the crystal surface is in contact with a liquid, the frequency is also affected by the viscous dissipation taking place in the momentum boundary layer (*15*).

In the present study the QCM principle was applied to adsorption measurements in the liquid phase. The sample crystal (4.0 MHz, International Crystal Mfg.) was coated with polysulfone and inserted in a flow system. The adsorption of chlorolignin was measured by a sequential addition method, and between each addition the equilibrium frequency shift due to the adsorbed mass was recorded. The shift was measured with a pulse counter (Philips, PM 6670) relative to an uncoated reference crystal. The stability of the frequency reading before chlorolignin additions was typically better than ±0.5 Hz/h.

Chlorolignin was adsorbed from a 0.015 *M* NaCl solution, and the pH was adjusted with HCl or NaOH. Between measurements of each isotherm the system was washed extensively with 0.01 *M* NaOH solution and water.

UF Experiments with a Crossflow Flat Module

The experimental setup for the UF experiments is depicted in Fig. 2. The crossflow flat module (CFFM) used was an ordinary small-scale test module with no entrance region. The active membrane area of the module was 19.3 cm^2 and the height of the slit-shaped flow channel was 1 mm. The volumetric flow rate ($\dot{V}$) used in the experiments was 3 dm^3/min, which corresponds to an average linear flow velocity of 2.5 m/s over the membrane and a Reynolds number of 5300.

The sample volume in the sample container (SCO) was 2 dm^3, and it was kept constant by recirculating the permeate after analyses. The thermostated solution was circulated by a seal-less sliding vane pump (XP) (Pompe Caster, MPA 314 316). The pressure (P) and the volumetric flow rate were regulated manually and measured by a pressure gauge and a rotameter. The permeate mass flow rate ($\dot{m}$) was measured by a digital balance (Mettler, PE 600). Temperature (T) was recorded with electronic

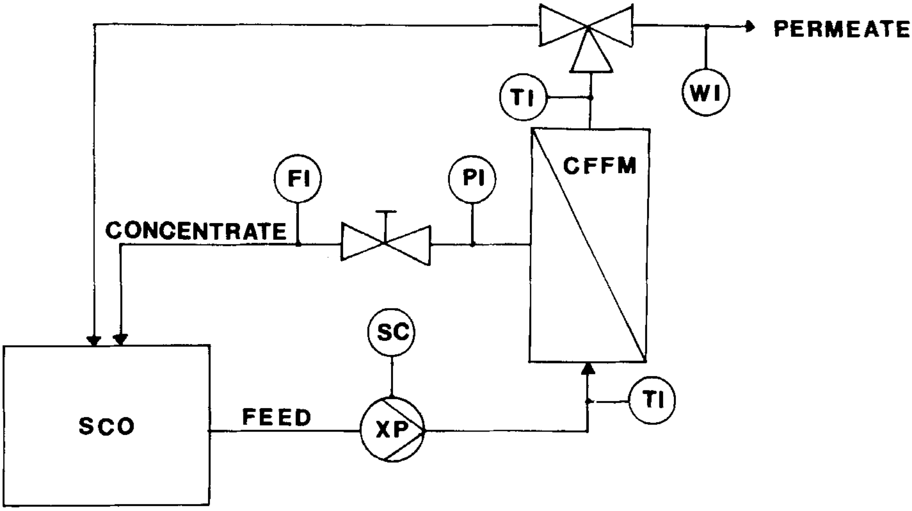

FIG. 2. Experimental setup for ultrafiltration with a crossflow flat module (CFFM).

sensors. The concentration of chlorolignin (in wt%) in the permeate (z_p) was determined from absorbance measurements at 340 nm. Retention (R) was calculated according to

$$R = 1 - \frac{z_p}{z_b} \tag{2}$$

where z_b = the bulk concentration of chlorolignin (in wt%).

Before the UF experiments the membranes were stabilized by UF with pure water at $P = 5$ bar until a constant volume flux (J_v^0) was obtained. The chlorolignin solutions were then adjusted to the pH in question and the permeate volume flux (J_v^p) was measured at different pressures starting with the lowest one. Flux reduction was calculated from

$$\text{Flux reduction} = 1 - \frac{J_v^p}{J_v^0} \tag{3}$$

UF experiments at two pressures, $P = 5$ and 3 bar, and two concentrations, $z_b = 0.3$ and 1.0 wt%, were carried out in the whole pH range of interest.

RESULTS AND DISCUSSION

Chemical and Physical Properties of Aqueous Chlorolignin

As the analyses of chlorolignin were carried out spectrophotometrically, the extinction coefficient (ε) of the aqueous solutions of the sample substance was determined as a function of pH and wavelength (λ). These data are collected in Table 1 and indicate the strong increase of ε with rising pH. From time to time the whole range of wavelengths studied was used in the determinations of chlorolignin concentration in the permeate. This was done to ensure that possible differences in the absorption spectra of the bulk solution and the permeate did not interfere in the analyses. Such differences were, however, not detected, and most of the analyses were carried out at $\lambda = 340$ nm.

The results from the simultaneous potentiometric and conductometric titrations of chlorolignin are depicted in Fig. 3. It can be seen that below pH ≈ 3.5 the chlorolignin is in undissociated neutral form. The total amount of acidic groups, carboxylic or phenolic in nature, in the material is 1.7 mmol/g chlorolignin. Dissociation of these groups takes place in the range $3.5 < \text{pH} < 9.1$, and chlorolignin can be considered completely dissociated above the higher limit. The degree of dissociation (α) of chlorolignin at various pH values is given in Table 2.

The density (ρ) of aqueous chlorolignin at 298 K depends almost linearly on the concentration and can be calculated from

$$\rho(\text{g/cm}^3) = 0.997 + 0.00372z \tag{4}$$

TABLE 1
Extinction Coefficients (ε) ($\text{m}^3/\text{g} \cdot \text{m}$) for Aqueous Chlorolignin at Different pH Values and Wavelengths

	pH							
λ (nm)	3	4	5	6	7	8	9	10
340	0.571	0.591	0.607	0.618	0.631	0.648	0.670	0.695
360	0.448	0.466	0.479	0.491	0.505	0.521	0.542	0.564
380	0.350	0.364	0.376	0.387	0.400	0.416	0.435	0.456
400	0.268	0.280	0.291	0.302	0.314	0.330	0.347	0.367
440	0.166	0.174	0.182	0.191	0.202	0.213	0.228	0.247

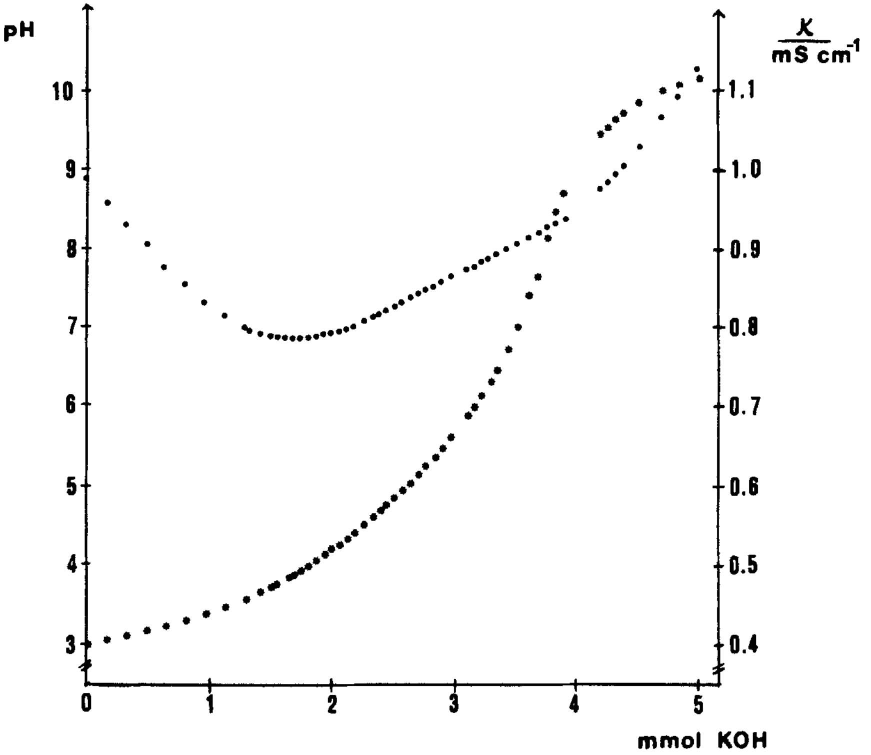

FIG. 3. Potentiometric (*) and conductometric (●) titration curves of an aqueous solution of chlorolignin (CL) (1.16 g CL + 3.226 mmol HCl)/(dm^3 H_2O). Titration with 0.1 *M* KOH.

TABLE 2
The Degree of Dissociation (α) of Chlorolignin as a Function of pH

pH	3	4	5	6	7	8	9	10
α	0.00	0.06	0.34	0.62	0.79	0.91	0.98	1.00

where z is the concentration of chlorolignin (wt%).

The viscosity (η) of chlorolignin solutions prepared from the dry sample (pH 5.5–6) is not linearly dependent on concentration above 5 wt%. In this pH range the viscosity of aqueous chlorolignin can be calculated from Eq. (5) at 298 K:

$$\eta(\mathrm{cP}) = 0.90594 + 0.05049z + 0.000178z^3 \tag{5}$$

However, the viscosity of the solutions depends on pH (Fig. 4). At pH > 6 the viscosities are somewhat higher than the values calculated from Eq. (5). This phenomenon can be explained by the opening of the molecules caused by dissociation. At lower pH the behavior of viscosity indicates gel formation. This phenomenon is clearly shown in Fig. 4.

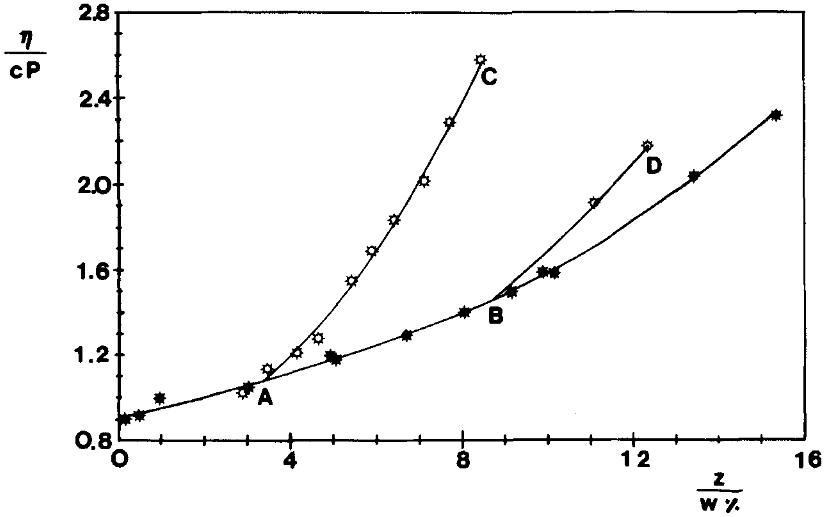

FIG. 4. Viscosity of aqueous chlorolignin as a function of concentration (wt%) at different pH levels. pH 5.5–6.0 (●), pH 3 (O), and pH 4 (O). Points A and B indicate the lowest concentration of gel formation at pH = 3 and pH = 4. Points C and D indicate precipitation, respectively.

Interaction between Chlorolignin and the UF Membranes

Zeta potential measurements indicate that the polysulfone membrane (GR 61, DDS) studied has a negative surface charge in the pH range of interest, which can be deduced from Fig. 5.

Although both the virgin surface of the membrane and the polyelectrolytic chlorolignin carry a negative net charge at pH > 3.5, there seems at first, according to the zeta potential measurements, to exist a certain amount of chlorolignin attachment on the surface and possibly in the pores of the membrane. The amount of this attachment and the rise of the negative zeta potential of the membrane are approximately proportional to the concentration of chlorolignin in solution, as indicated in Fig. 5.

To verify the role of adsorption phenomena, adsorption isotherms of chlorolignin on a homogenous polysulfone surface were determined at different pH values with a quartz crystal microbalance. The measured frequency shifts ($-\delta f$) are given in Fig. 6. The effect of bulk solution properties is evidently negligible, and these values can be considered to represent the adsorbed mass.

Figure 6 reveals three interesting aspects. Adsorption of chlorolignin on polysulfone is evidently monolayer adsorption. At each pH studied the adsorption is virtually complete above the concentration $z = 0.05$

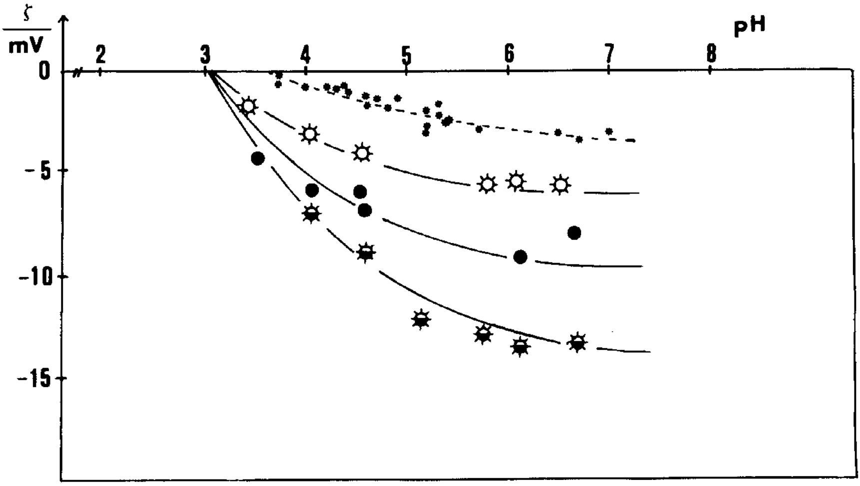

FIG. 5. Zeta potential dependence of pH. Polysulfone (GR 61, DDS) membrane. Chlorolignin concentration: 0.02 wt% (○), 0.04 wt% (●) and 0.07 wt% (○); (- - -) without chlorolignin.

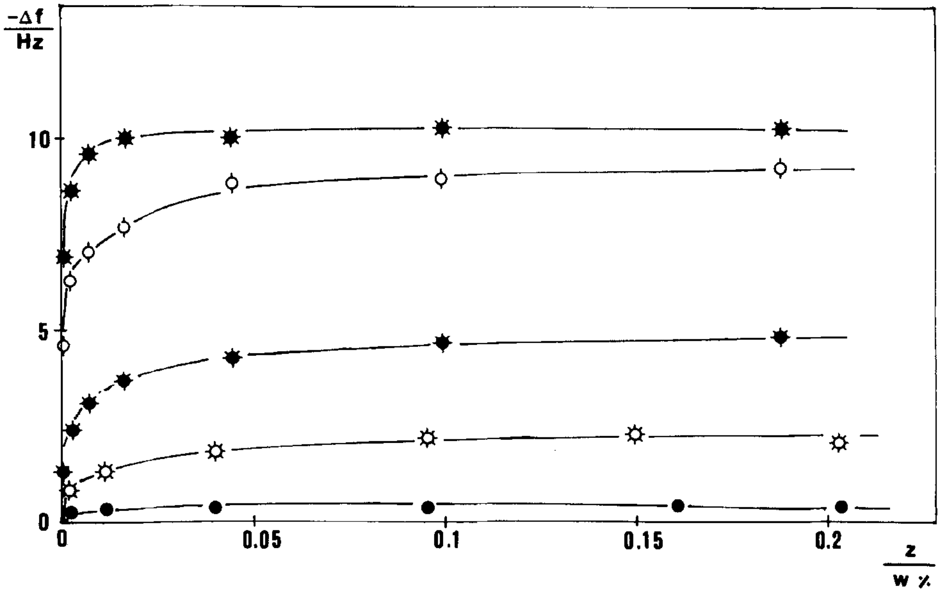

FIG. 6. Adsorption isotherms of chlorolignin at the surface of homogeneous polysulfone at various pH levels: pH 9.8 (●), pH 6.0 (○), pH 5.0 (●), pH 4.0 (○), and pH 3.0 (●). T = 298 K; I = 0.015 M.

wt%. Moreover, the amount of adsorption is highly pH-dependent. The last phenomenon can be explained by means of electrostatic repulsion between the negatively charged surface and the polyelectrolyte ions. This effect becomes strong at high pH values and results in a low level of adsorption. On the contrary, at low pH values the adsorption of chlorolignin on polysulfone is governed by purely noncoulombic interactions between chlorolignin and the surface, and appreciably higher mass deposition on the polysulfone surface is therefore observed. Comparison of the results given in Figs. 5 and 6 further reveals that the adsorption of chlorolignin on a polysulfone surface cannot alone explain the rise of the negative zeta potential along with the bulk concentration of adsorbate. It is more probable that this phenomenon is due to penetration of some of the low molecular weight chlorolignin molecules into the pores of the membrane, which is more pronounced at high bulk concentrations.

Although these molecules are not permanently adsorbed on the walls of the pores, steric factors slow down their motion which, combined with their rather high negative charge, is seen as a rise in the measured negative streaming potentials and the calculated zeta potentials at pH values > 4. This explanation of the origin of the high negative values of the zeta potentials is further confirmed as the zeta potentials of a membrane treated with chlorolignin return close to those of a virgin membrane as streaming potential measurements are carried out with pure KCl solution. This observation also indicates that no permanent fouling of a polysulfone membrane is caused by chlorolignin at pH > 4.

The results of the ultrafiltration experiments with the crossflow flat module (Figs. 7 and 8) indicate strong pH-dependence of both flux reduction and retention. At high pH values the retention of chlorolignin at both concentrations studied stays high according to the electrostatic repulsion between the polyelectrolyte ions and the surface of the membrane. This effect ceases gradually as both the degree of dissociation of chlorolignin and the surface charge of the membrane approach zero at pH = 3.0 and pH = 3.5, respectively. As a result, retention starts to fall rapidly at pH < 5. The penetration rate of a relatively small amount of chlorolignin molecules into the pores of the membrane, even at high pH values, which depends both on the bulk concentration of the substance in the solution and on volume flux, is clearly indicated by the decrease in retention as the bulk concentration increases. Because of the secondary effect of this phenomenon, rising friction in the pores of the membrane, the flux reduction is also somewhat higher at $z_p = 1$ wt% when pH > 5.

At pH values < 5 the flux reduction seems to be more pronounced at $z_p = 0.3$ wt% than at $z_p = 1.0$ wt%. The reason for this phenomenon can be speculated on by means of competitive adsorption of chlorolignin in the pores of the membrane and gel formation at the surface of the membrane. The former phenomenon is more probable at low bulk concentrations while the latter seems to prevail at high bulk concentrations. The gel layer formed on the membrane surface at the edge of the concentration polarization layer can obviously function as a secondary membrane in ultrafiltration of chlorolignin, which possibly prevents penetration of high molecular weight chlorolignin into the pores and their adsorption and also decreases fouling in the pores of the membrane.

CONCLUSIONS

Electrostatic repulsion between the negatively charged polyions and the surface of the membrane seems to govern ultrafiltration of chlorolignin at pH > 5, which is characterized by high retention and relatively low flux reduction. At these pH values, adsorption of chlorolignin on polysulfone surfaces is negligible and irreversible fouling of the mem-

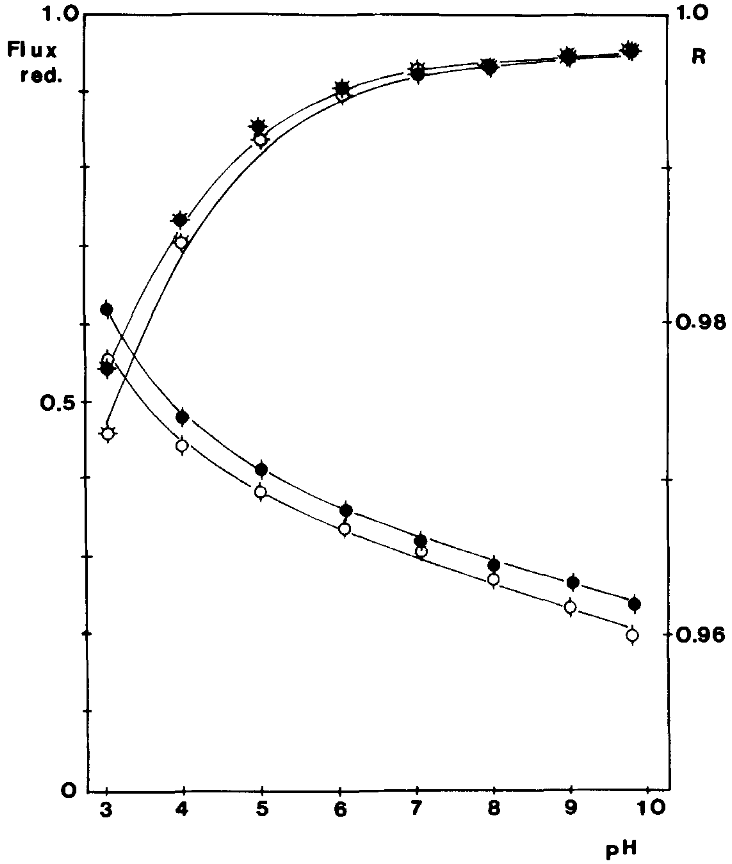

FIG. 7. Flux reduction ($P = 5$ bar (●), $P = 3$ bar (○)) and retention, R, ($P = 5$ bar (●), $P = 3$ bar (○)) as function of pH in ultrafiltration of a 0.3 wt% chlorolignin solution at 298 K and $V = 3$ L/min. Polysulfone membrane (GR 61, DDS).

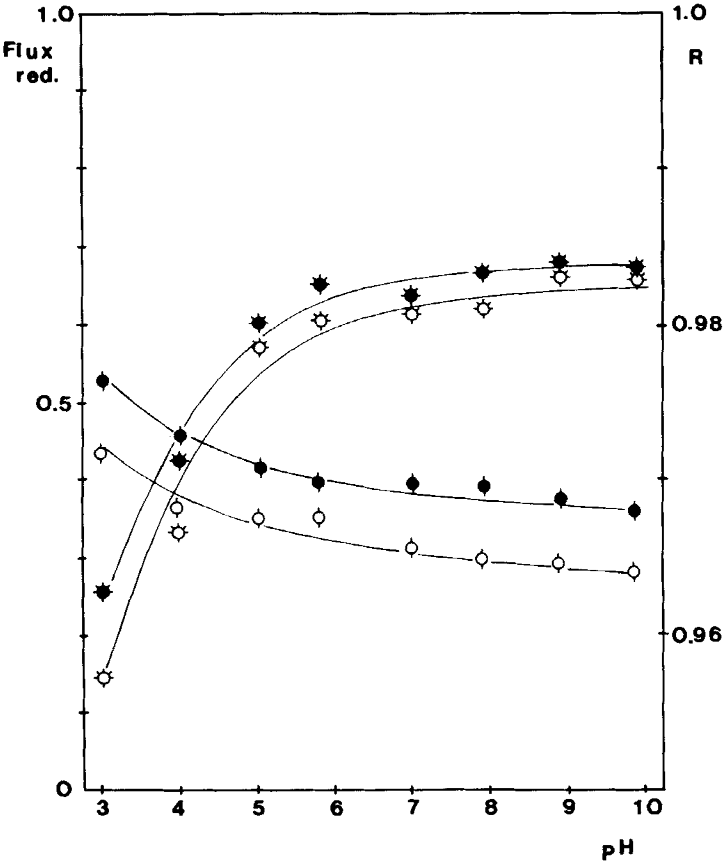

FIG. 8. Flux reduction (P = 5 bar (●), P = 3 bar (○)) and retention, R, (P = 5 bar (●), P = 3 bar (○)) as function of pH in ultrafiltration of a 1 wt% chlorolignin solution at 298 K and V = 3 L/min. Polysulfone membrane (GR 61, DDS).

brane does not occur. Flux reduction at high pH values is caused mainly by penetration of a small fraction of chlorolignin molecules into the pores of the membrane, which causes frictional flux reduction and lower retention. These phenomena are bound to the bulk concentration of chlorolignin in solution.

At low pH values, adsorption of chlorolignin in the pores of polysulfone membranes may cause fouling which, however, can be purged by washing with alkaline solutions. In addition, at low pH values the tendency of chlorolignin to gel can cause gel layer formation on the surface of the membrane. This gel layer may act as a secondary membrane which affects retention and flux in a way which is somewhat difficult to predict.

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