Interactions Responsible for Fouling Layer Formation during Apple Juice Microfiltration

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Microfiltration of model solutions was conducted to identify the principal interacting species in foulant produced during membrane clarification of apple juice. Tannin and gelatin solutions did not foul microfiltration membranes, whereas both low-methoxy (LMP) and high-methoxy pectin (HMP) produced a fouling layer with only modest resistance. However, solutions containing high concentrations of both tannin and gelatin had very low fluxes, indicating that the interaction of these two species is key to fouling layer formation. With unclarified apple juice, tannin addition did not increase flux resistance because these compounds were in excess. On the other hand, LMP or HMP addition significantly enhanced flux resistance, probably by stabilizing colloidal particles. At low concentrations, gelatin-induced flocculation produced large aggregated particles with lower fouling layer resistances, but at elevated concentrations, gelatin addition stabilized colloidal particles, increasing flux resistance. A direct correlation between particle flocculation behavior and fouling layer resistance was observed.

Keywords: *Apple; juice; clarification; microfiltration; fouling*

INTRODUCTION

Membrane filtration is commonly used to clarify apple juice (Drake and Nelson, 1987). Nevertheless, system productivity is often limited because the colloidal material present in the juice tends to foul the membrane surface, leading to reduced transmembrane flux (Heatherbell et al., 1977). Our previous research has shown that the manner by which colloidal material aggregates on the membrane surface strongly influences the flux resistance of the fouling layer (Riedl et al., 1997). The goal of this work is to determine what specific molecular forces and colloidal functional groups are responsible for aggregate formation.

It is well-known that the fouling behavior of a particular juice strongly depends on the age and varieties of apple used, as well as the method of juice extraction. However, it is not simply the amount of each component in the juice but the structure and interactive behavior of a wide variety of compounds that control filterability (Wucherpfennig et al., 1987; Flores et al., 1988, 1990; Spanos and Wrolstad, 1992). Still, it is not well understood which types of molecular interactions lead to fouling layer formation.

The principal components of apple juice are listed in Table 1. Specific classes of compounds shown to be involved include tannins (Heatherbell et al., 1977; Smock and Neubert, 1950), macromolecules including protein (Smock and Neubert, 1950; Yamasaki et al., 1964), and pectin and fiber (Smock and Neubert, 1950; Yamasaki et al., 1964). Pectin, phenolics, protein, and fiber can be present in both the soluble and suspended solid fractions. The major component of the suspended solids fraction is cell wall debris (Smock and Neubert, 1950; Yamasaki et al., 1964), which consists principally of cellulose and pectin, with small amounts of hemicellulose and hydroxyproline-rich protein (Knee and Bartley, 1981).

Table 1. Apple Juice Components and Their Presence in Filtration Foulant

component	contributes to foulant resistance?
water	N
sugars (fructose, sucrose, glucose)	N
organic acids (malic, quinic, galacturonic)	indirect effect
pectic materials[a]	Y
tannins[b]	Y
proteins[c]	Y
starch[d]	N
fiber (cellulose, hemicellulose)[a]	Y
minerals	Ca has indirect effect
other low molecular weight substances	N

[a] Smock and Neubert (1950); Yamasaki et al. (1967). [b] Heatherbell et al. (1977); Smock and Neubert (1950). [c] Smock and Neubert (1950); Yamasaki et al. (1964). [d] Wucherpfennig et al. (1987).

Of all the compounds found in apple juice, pectin is most often identified as the major hindrance to filtration performance (Pilnik and Voragen, 1970; Kilara, 1982; Wucherpfennig et al., 1987). Apple pectin typically has a high degree of esterification (DE)—between 60 and 65% after harvest (Plaschina et al., 1978). The apparent p*K* of 65% DE pectin is 3.55, which means roughly half of the carboxyl groups are ionized (negative) at the pH of apple juice (BeMiller, 1986). Consequently, changes in acid concentration can alter juice pH, thereby modifying component interactions by influencing pectin surface charge.

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Pectin that contains a large proportion of de-esterified galacturonic acid monomers (<55% DE) is referred to as low-methoxy pectin (LMP) (Pilnik and Voragen, 1970). Both high-methoxy pectin (HMP) and LMP have gel-forming abilities. However, sucrose concentrations much higher than those typically found in apple juice (~65%) are required to gel HMP (Whistler and Daniel, 1986). On the other hand, LMP is particularly sensitive to the presence of calcium, which can cross-link two demethylated areas of the pectin polymer to induce gel formation (Pilnik and Voragen, 1970). Thus, calcium is listed as indirectly affecting foulant structure in Table 1.

Phenolics are another important class of compounds present in apple juice, with two types dominating: cinnamics and catechins/procyanidins (Spanos and Wrolstad, 1992). Cinnamics such as chlorogenic acid can bind to protein but do not cause haze. Catechins or procyanidins can cause haze since they contain multiple phenolic groups that can cross-link proteins (Siebert et al., 1996a,b). Phenolics are also substrates for enzymatic browning reactions that produce the typical amber color and some of the flavor of apple juice. The resulting oxidatively cross-linked phenolics have a higher binding affinity for proteins than simple phenolics (Hagerman, 1992; Haslam et al., 1992), and the reactive quinones produced by enzymatic browning can also covalently attach to other macromolecules such as pectin (McManus et al., 1985; Haslam and Lilley, 1988; Ozawa et al., 1987).

Protein accounts for <0.5% of the total weight of apples (Gebhardt et al., 1982). However, after juice extraction, protein makes up a substantial fraction of the suspended solids. In 1964, Yamasaki et al. determined that protein accounted for 36% of the ultracentrifuged material from cloudy apple juice. Thus, the importance of the protein fraction cannot be overlooked.

When examined under a polarized light microscope, starch granules are observed in early season juices, but these granules quickly degraded during storage (Knee, 1993). Since starch granules are typically several orders of magnitude larger than the pores of microfiltration membranes (Whistler and Daniel, 1986), their influence on the resistance of the surface fouling layer is minimal. In addition, Wucherpfennig et al. (1987) have previously shown that soluble starch does not foul filtration membranes. Thus, starch is unlikely to play an important role in membrane fouling no matter what form is present in the juice. In contrast, the cellulose contained in the fiber fraction of the cell wall debris is known to add structure to the fouling layer (Yamasaki et al., 1967). However, in the native cell wall, cellulose microfibrils are embedded in a matrix of noncellulosic polysaccharides and protein (Fisher and Bennett, 1991). Therefore, it is more likely the protein or polysaccharide components, and not the cellulosic microfibrils, are responsible for mediating cell wall debris interactions.

Because of the highly heterogeneous nature of apple juice colloidal material, a wide variety of interactions could potentially be responsible for fouling layer formation. This work focused on the behavior of the three most prevalent and reactive soluble compounds in apple juice: pectin, tannin, and protein. Model solutions were used to determine which of these compounds, or combinations of compounds, were capable of associating on the membrane surface to form a fouling layer. Solutions of HMP extracted from apples as well as an LMP were used to examine pectin aggregation behavior. Because calcium can strongly influence pectin interactions (Fisher and Bennett, 1991), this compound was also added to some model solutions. For the phenolic component, Quebracho tannin was chosen because it is easily extracted and purified and has a structure similar to those found in apples (Spanos and Wrolstad, 1992). Type A gelatin served as the model protein because it is used in juice treatment as a flocculating agent (Kilara and VanBuren, 1989) and its high hydroxyproline content makes it structurally similar to apple extensin (Knee, 1993). It is the high proline content of gelatin (12−14%) that endows it with flocculating activity, but hydroxyproline may affect tannin−protein interactions through the structure breaking properties of the proline side chain. This indirect effect may increase access to the peptide backbone, proposed to be the important site for tannin−protein interactions (Hagerman and Butler, 1981).

The compounds used to make model solutions were also added to fresh apple juice to see how they influenced the aggregation behavior of the juice soluble and suspended solids. Filtration experiments were performed using smooth (polysulfone) and rough (polyethersulfone) microfiltration membranes since previous work has shown that surface roughness can affect fouling behavior (Riedl et al., 1997).

MATERIALS AND METHODS

Materials. Model solutions were prepared using the following compounds: low-methoxy pectin (7.8% DE, Sigma Chemical Co., St. Louis, MO), $CaCl_2$ (anhydrous, Fisher Scientific, Fair Lawn, NJ), high-methoxy pectin (74% DE, Classic AF 201, Herbstreith & Fox KG, Germany), gelatin type A (100 bloom, ICN Biochemicals, Cleveland, OH), and Quebracho tannin (a gift from Dr. Ann Hagerman, Miami University, Oxford, OH). All compounds were solubilized at 40 °C in a pH 3.5 phosphate buffer. Model solutions were equilibrated to 25 °C before filtration.

The unclarified apple juice used in the supplementation experiments was produced by Apple Valley Juices (Collingwood, ON) from locally grown McIntosh and Red Delicious apples. No pectinase enzymes were used during its production, but the juice was lightly pasteurized and potassium sorbate was added to the final product to improve stability. Filtration experiments were performed within the first few days of the juice's 2 week shelf life to minimize changes due to spoilage organisms.

With the juice supplementation experiments, additive solubilization was performed at 40 °C. For experiments in which calcium and pectin were combined, the pectin was first solubilized and then the calcium was dissolved into the juice. Disodium ethylenediaminetetraacetate (EDTA; certified ACS grade, Fisher Scientific) was added in the same manner as $CaCl_2$. Supplemented juices were also equilibrated to 25 °C before filtration.

Analytical Methods. The following analyses were performed on the commercial juice: total juice solids by freezing samples at −20 °C followed by overnight freeze-drying; soluble juice solids by Abbe refractometry (Pomeranz and Meloan, 1978); suspended juice solids by centrifugation of 50 mL of juice at 90000*g* for 30 min followed by air-drying in a 100 °C oven overnight; juice pectin by the MHDP method (Kintner and Van Buren, 1982); juice phenolics using the Folin−Ciocalteu assay (Singleton and Rossi, 1965); total protein via Kjeldahl analysis of suspended solids samples; starch analysis via solubilization with perchloric acid followed by reaction with Lugol's reagent (Hovenkamp-Hermelink et al., 1988). All percentages were reported with respect to initial juice mass.

Membranes, Apparatus, and Procedures. Flux experiments using 0.2 μm pore size, 43 mm diameter polysulfone

Table 2. Comparison of Commercial Unclarified Apple Juice Composition with Typical Literature Values

component	method	juice blend	McIntosh[a]	Red Delicious[a]
total solids, %	freeze-drying	12	10.5−13.1	13.7−15.0
soluble solids, %	Abbe refractometer	11.5	9−12	13.2−14.4
suspended solids, %	centrifugation at 90000*g* for 30 min	0.37	0.50−1.1	0.50−1.30
pH	pH meter	3.45	3.3−3.5	3.6−4.1
total pectin, %	MHDP method[b]	0.14		
total phenolics, %	Folin−Ciocalteu[c]	0.07	0.30−1.0	0.40−0.95
protein, %	Kjeldahl[d]	0.09		
starch, %	perchloric acid and Lugol's reagent[e]	0.07		

[a] Cliff et al. (1991). [b] Kinter and Van Buren (1982). [c] Singleton and Rossi (1965). [d] Woodman (1915). [e] Hovenkamp-Hermelink et al. (1988).

(HT Tuffryn) and polyethersulfone (Supor) microfiltation membranes (Gelman Sciences, Ann Arbor, MI) were performed in a 50 mL capacity Amicon (Beverly, MA) model 8050 filtration cell operating in dead-end mode (i.e., without stirring). All experiments were conducted at room temperature (25 °C). A transmembrane pressure of 50 psi (344.6 kPa) was supplied by a compressed nitrogen cylinder. Flux data were obtained by collecting the permeate on a Mettler model BB3000 scale (Mettler, Switzerland) interfaced to a computer executing the data collection program Labtech Notebook Pro version 8.1 (Laboratory Technologies, Wilmington, MA).

Fouling layer resistance was measured using conventional filtration theory (Suki et al., 1984). The volumetric flux through a membrane can be characterized by

$$\frac{1}{A_m}\frac{dV}{dt} = \frac{\Delta P}{\mu(R_m + R_f)} \quad (1)$$

where A_m is membrane surface area, V is permeate volume, t is time, ΔP is transmembrane pressure, μ is permeate viscosity, R_m is resistance of the bare membrane, and R_f is the fouling layer resistance. If all solids are retained on the membrane surface, then

$$R_f = \alpha_p C_B (V/A_m) \quad (2)$$

where α_p is the specific resistance and C_B is the bulk solids concentration. Substituting eq 2 into eq 1 and rearranging gives

$$\frac{t}{V} = \frac{R_m \mu}{\Delta P A_m} + \left(\frac{\alpha_p C_B \mu}{2A_m^2 \Delta P}\right) V \quad (3)$$

Thus, the slope of the linear region of a t/V versus V plot can be used to determine the fouling layer specific resistance ($\alpha_p C_B$). Unless otherwise noted, all measurements were made in triplicate.

RESULTS AND DISCUSSION

Table 2 compares the analysis of the juice blend used in our experiments with literature values for McIntosh and Red Delicious apple juice (Cliff et al., 1991). Most of the values obtained for the juice blend were within the expected range. The suspended solids concentration was lower than typically observed, most likely because pectinases were not used during juice production. Even though the protein concentration in the juice was low (0.09%), it represented 24% of the suspended solids—a percentage similar to the 36% of suspended solids value previously obtained by Yamasaki et al. (1967). The measured phenolic concentration was also low, a consequence of the phenolics assay used. Phenolics were first extracted with ethanol before being analyzed with

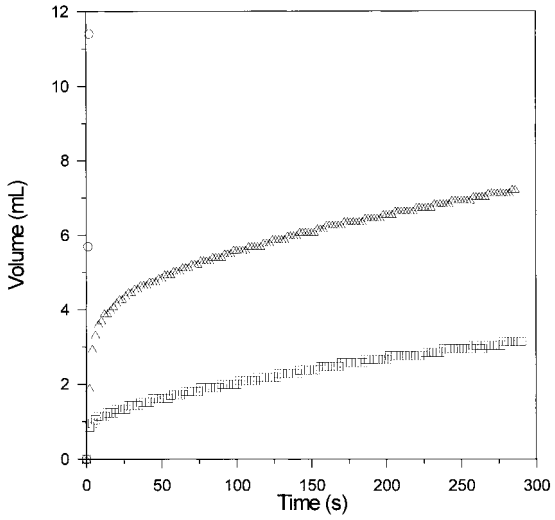

Figure 1. Typical permeate volume versus time curves for dead-end microfiltration of 0.10% tannin (○), 0.20% HMP (△), and 0.10% tannin + 0.20% HMP (□) model solutions on polysulfone membranes.

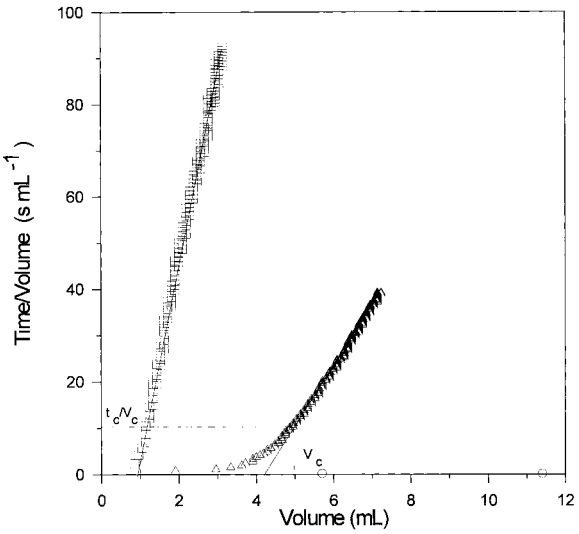

Figure 2. Typical time/volume versus volume curves for dead-end microfiltration of 0.10% tannin (○), 0.20% HMP (△), and 0.10% tannin + 0.20% HMP (□) model solutions on polysulfone membranes.

Folin−Ciocalteu reagent (Singleton and Rossi, 1965). However, not all of the tannin was soluble because the alcohol insoluble fraction was still distinctly brown after repeated extractions. This indicates that strong interactions exist between tannin and other colloidal compounds in apple juice.

Model solutions were produced using pectin, tannin, and protein concentrations within the ranges given in Table 2. Some typical volume versus time curves are shown in Figure 1. A solution of 0.10% tannin did not foul the membrane, with the observed flux being similar to what was observed with pure water. With some solutions such as 0.20% HMP, a large burst of liquid was observed within the first 10 s of filtration, which was followed by a rapid decline in the rate of liquid production. However, with most solutions (e.g., 0.10% tannin + 0.20% HMP), the fouling layer rapidly formed on the membrane surface, leading to a low liquid flux. Figure 2 provides t/V versus V curves for the examples given in Figure 1. At extended filtration times, all plots were linear, and from the slopes of these lines, $\alpha_p C_B$

Table 3. Consolidation Time (t_c, s) and Specific Resistance ($\alpha_p C_B$, $m^{-2} \times 10^{-14}$) of Fouling Layers Formed during the Filtration of Buffered (pH 3.5) Model Solutions Using Polysulfone and Polyethersulfone Membranes

	polysulfone		polyethersulfone	
solute (s)	t_c[a]	$\alpha_p C_B$[a]	t_c[a]	$\alpha_p C_B$[a]
apple juice control	9.10 ± 1.10	249 ± 4.72	37.9 ± 1.95	201 ± 4.55
0.05% LMP	81.5 ± 4.40	2.20 ± 0.035	>300	0
0.20% LMP	89.3 ± 4.90	29.3 ± 2.77	>300	0
0.05% LMP + 0.10% $CaCl_2$	8.85 ± 0.55	237 ± 1.57	26.4 ± 4.45	226 ± 6.29
0.05% HMP	91.7 ± 3.10	11.8 ± 0.57	>300	0
0.20% HMP	39.4 ± 11.2	83.3 ± 0.94	85.9 ± 1.55	31.4 ± 2.14
0.10% tannin	>300	0	>300	0
0.10% gelatin	>300	0	>300	0
0.10% tannin + 0.01% gelatin	>300	0	>300	0
0.10% tannin + 0.10% gelatin	2.70 ± 0.21	729 ± 12.6	80.9 ± 0.95	842 ± 69.3
0.20% LMP + 0.10% tannin	47.9 ± 1.45	110 ± 5.03	109 ± 10.7	29.3 ± 0.94
0.20% LMP + 0.10% gelatin	6.00 ± 0.10	379 ± 34.9	41.8 ± 1.35	197 ± 22.4
0.20% LMP + 0.10% tannin + 0.10% gelatin	2.65 ± 0.15	600 ± 3.15	80.9 ± 0.15	712 ± 157
0.20% HMP + 0.10% tannin	22.8 ± 8.85	93.4 ± 6.61	68.5 ± 2.10	36.5 ± 8.19
0.20% HMP + 0.10% gelatin	3.70 ± 2.10	259 ± 7.87	24.4 ± 1.50	163 ± 32.7
0.20% HMP + 0.10% tannin + 0.10% gelatin	0	255 ± 4.40	44.9 ± 16.8	138 ± 40.3

[a] Average ± SD, $n = 3$.

values were calculated. The fouling layer consolidation time (t_c) was also estimated from the V_c and t_c/V_c values at the point where linear behavior began.

Table 3 lists t_c and $\alpha_p C_B$ values for the apple juice control and all model solutions filtered with PS and PES membranes. Apple juice foulant consolidated on PS ≈4 times faster than on PES. Also, once the fouling layer formed on PS, its resistance was significantly higher than that observed with PES. These differences in fouling behavior between PS and PES have been observed previously (Riedl et al., 1997) and were attributed to differences in membrane surface roughness. As compared to the rough PES membranes, the smoother PS membrane surface creates a much thinner, denser fouling layer that forms more rapidly and has a higher flux resistance (Riedl et al., 1997).

Both low and high concentrations of LMP did not foul PES membranes within a 5 min filtration run. These same concentrations fouled PS only to a limited extent. However, if 0.10% $CaCl_2$ was added to the 0.05% LMP solution, results similar to those observed with apple juice were obtained. Thus, LMP will significantly foul membranes only if high concentrations of Ca^{2+} ions are present to form ionic cross-links. HMP was a somewhat more effective fouling agent than pure LMP but was able to foul PES membranes only when high concentrations were used. At low concentrations, pectin molecules are unassociated in solution and would not be large enough to foul a 0.2 μm pore (Bartolini and Jen, 1990). However, since these solutions did foul microfiltration membranes, pectin aggregation must be occurring at the high concentrations found in the concentration polarization layer on the membrane surface (Bartonini and Jen, 1990). Nevertheless, it is unlikely that juice filtration resistance is solely due to this pectin surface aggregation phenomenon as the HMP resistance was at best only 33% of the value observed with commercial juice.

By themselves, neither gelatin nor tannin fouled either membrane (Table 3). Therefore, unlike pectin, these macromolecules did not aggregate significantly on the membrane surface within the experimental time frame used in this study. To obtain a gel, gelatin must first be solubilized in the random coil form, which exists in solution above 40 °C, and then cooled to below 30 °C, at which it transforms to a more helical structure (Elysée-Collen and Lencki, 1996); the protein concentration must also be above a critical level of 0.5% (Hayashi and Oh, 1983; Slade and Levine, 1987). Because the highest gelatin concentration used in this study was 0.10% and these solutions were cooled to room temperature before filtration experiments were performed, the gelatin would be present in solution as unassociated helical structures that would not strongly interact on the membrane surface (Elysée-Collen and Lencki, 1997).

Table 4. Effect of Various Juice Additives and Supplements on the Consolidation Time (t_c, s) and Resistance ($\alpha_p C_B$, $m^{-2} \times 10^{-14}$) of Fouling Layers Formed during the Filtration of Unclarified Apple Juice Using Polysulfone and Polyethersulfone Membranes

	polysulfone		polyethersulfone	
additive or supplement	t_c[a]	$\alpha_p C_B$[a]	t_c[a]	$\alpha_p C_B$[a]
apple juice control	9.10 ± 1.10	249 ± 4.72	37.9 ± 1.95	201 ± 4.55
0.10% tannin	11.6 ± 0.88	235 ± 6.77	44.5 ± 2.66	189 ± 7.34
0.05% LMP	5.62 ± 0.38	305 ± 9.45	21.7 ± 3.10	251 ± 6.30
0.05% HMP	3.70 ± 1.90	292 ± 3.25	32.1 ± 5.00	256 ± 1.45
0.10% $CaCl_2$	4.15 ± 0.35	242 ± 3.15	28.4 ± 2.65	207 ± 1.57
0.10% EDTA	2.15 ± 0.35	265 ± 4.72	40.5 ± 0.55	231 ± 5.35

[a] Average ± SD, $n = 3$.

The mixing of 0.10% tannin with a low concentration of gelatin (0.01%) produced a clear reddish-brown nonfouling solution. However, this same combination but with a higher gelatin concentration (0.10%) created a solution that was a cloudy pink color. When filtered through PS membranes, this opaque solution formed a fouling layer with a $\alpha_p C_B$ value that was almost 3 times that observed with the apple juice control. Even though this solution consolidated relatively slowly on PES, the final $\alpha_p C_B$ was still >4 times the control value. It would thus appear that protein−tannin interactions play an important role in membrane fouling phenomena. Proteins are known to strongly bind to tannin compounds and can be precipitated by them, with the interaction forces being a combination of hydrogen bonding and hydrophobic effects (Hagerman, 1992; Haslam et al., 1992). In fact, until the exact structure of tannins was elucidated, these compounds were defined by their protein precipitating ability (Haslam et al., 1992).

Tannins also increased the fouling ability of both LMP and HMP (Table 3). However, since the resistances of these combinations were still rather low compared to the control, pectin−tannin interactions appear to be of lesser importance than those of protein−tannin. Phe-

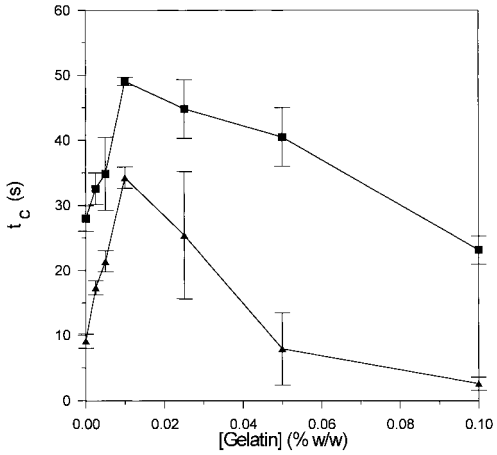

Figure 3. Effect of added type A gelatin on apple juice consolidation time (t_c) during dead-end microfiltration: (▲) polysulfone; (■) polyethersulfone.

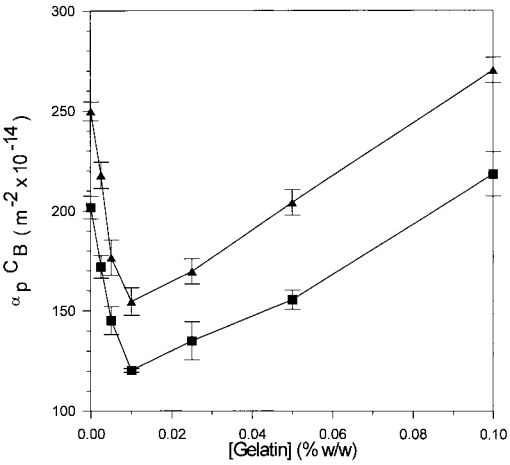

Figure 4. Effect of added type A gelatin on apple juice specific resistance ($\alpha_p C_B$) during dead-end microfiltration: (▲) polysulfone; (■) polyethersulfone.

nolics are known to complex reversibly with polysaccharides (McManus et al., 1985; Williamson et al., 1995). Whereas the exact mechanism of this interaction has not yet been determined, it appears to be driven by the hydrophobic effect and secured by hydrogen bonding.

Added protein had a stronger effect on pectin resistance than added tannin. The presence of proteins also greatly accelerated the rate of fouling layer consolidation. Since gelatin had a more significant effect on the $\alpha_p C_B$ value of LMP than HMP, electrostatic interactions are likely the principal protein−pectin interaction mechanism. LMP has a slightly negative charge at pH 3.5. whereas most proteins are below their p*I* at this pH and are, therefore, positively charged (Yamasaki et al., 1967; Kilara, 1982). Pectin has been shown to complex with whey (Serov et al., 1985) or blood plasma (Imeson et al., 1978) proteins. When pectin, gelatin, and tannin were combined, they had a moderating effect on protein−tannin interactions. This effect was particularly evident with HMP, for which the addition of this compound decreased the total $\alpha_p C_B$ value by approximately 65% with PS and 83.6% with PES. It would seem that pectin and tannin compete for the available gelatin in solution.

A better understanding of which of the many different interactions outlined above dominate in apple juice can be obtained by adding the various compounds used to prepare the model solutions to the commercial juice (Table 4). The addition of 0.10% tannin to the juice only increased t_c and decreased $\alpha_p C_B$ values by ≈5%. Therefore, tannins appeared to be in excess, a logical result because the apple juice used had a dark brown hue. However, a synergistic effect occurred with the addition of a low concentration of LMP or HMP as indicated by the resulting resistance increases being larger than those obtained by simply summing the resistances of the control and model solutions. The added pectin may have complexed with the excess tannin to produce a more resistant fouling layer. The presence of 0.10% $CaCl_2$ did increase the fouling layer consolidation rate, but its influence on the final resistance was minor.

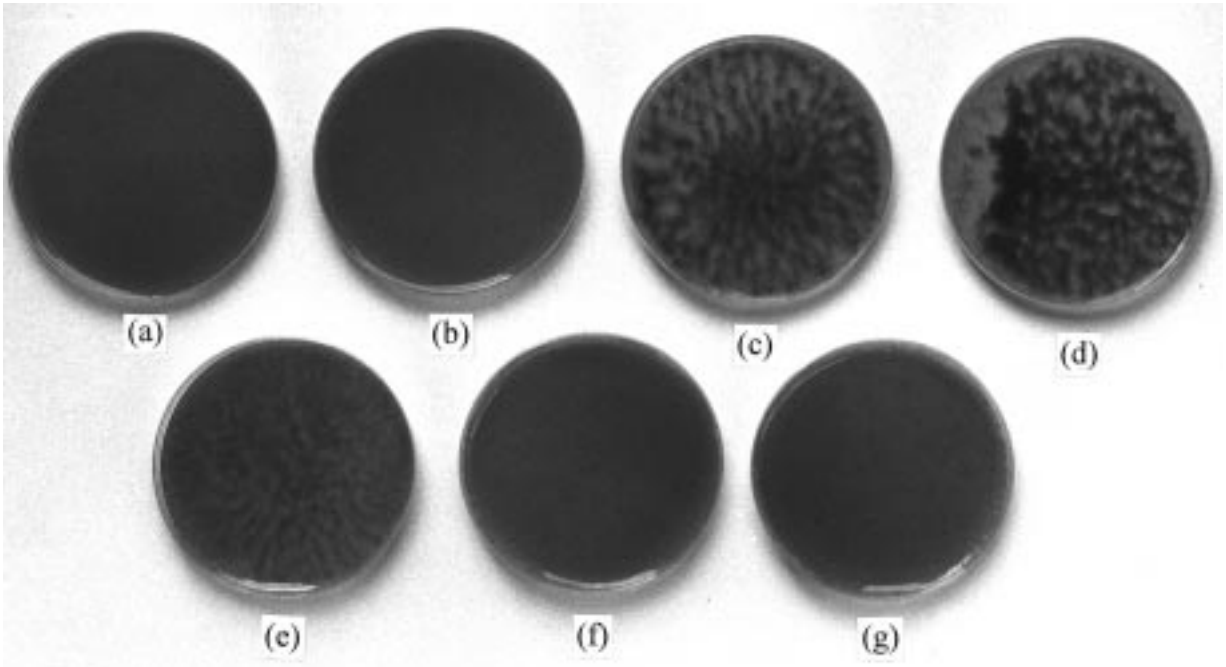

Figure 5. Aggregation patterns of unclarified apple juice with added gelatin: (a) control; (b) 0.0025%; (c) 0.0050%; (d) 0.010%; (e) 0.025%; (f) 0.05%; (g) 0.10%.

Thus, Ca^{2+} was also probably in excess in the apple juice. EDTA addition had more of a detrimental effect on flux resistance than $CaCl_2$, but its effect was still relatively small. Therefore, either charge effects played only a minor role or anionic binding sites were already occupied in fouling layer interactions.

By far the largest effects on consolidation time and $\alpha_p C_B$ were obtained with the addition of gelatin (Figures 3 and 4). With both membranes, t_c reached a maximum and $\alpha_p C_B$ a minimum at a concentration of 0.01% gelatin. At this optimum treatment level, resistances were ≈60% of their original values. However, as the gelatin concentration was further increased, these trends were reversed, with t_c decreasing and $\alpha_p C_B$ increasing. Gelatin may affect the fouling layer resistance by influencing the flocculation behavior of the apple juice solids. Initially, the solids in the apple juice control are very stable, showing no tendency to flocculate even over a period of several days. As the gelatin concentration was increased, flocculation became apparent, creating a very dense floc at the optimum gelatin concentration of 0.01% (Figure 5). However, further addition of gelatin decreased the degree of flocculation until a very stable solution was once again produced.

This destabilizing followed by stabilizing effect is often observed with flocculating agents (Gregory, 1993). At lower concentrations, each gelatin molecule can easily compete for more than one particle interaction site and cross-link particles. However, when in excess, the gelatin molecules can bind to only one site, being outcompeted for neighboring particle sites by other gelatin molecules. As a consequence, gelatin acts as a stabilizer at high concentrations.

Our results indicate a direct correlation between colloidal flocculation behavior in solution and fouling layer resistance. Our previous work has shown that the density of the surface fouling layer has a strong influence on flux resistance (Riedl et al., 1997). In the current study, the highest resistance was obtained with small colloidal particles that interact weakly at low concentration (i.e., tannin + gelatin) but strongly at the high concentrations found on the membrane surface. Since noncovalent forces are more important between small particles as compared to large ones (German, 1989), the tannin + gelatin solution probably forms a dense structure on the membrane surface that has a low porosity and high flux resistance. On the other hand, soluble compounds that interact less strongly (e.g., LMP + tannin, HMP + gelatin) have lower $\alpha_p C_B$ values. Larger particles are less likely to form tight associations than smaller particles, particularly if a great deal of their interaction potential has already been exploited during aggregation formation. Consequently, at the optimum gelatin concentration of 0.01%, a more open pore structure with the lowest filtration resistance was produced.

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