Effects on Membrane Processing of Pretreatments of Whey

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Alteration or control of the chemical and physical characteristics of the various types of whey has been shown to have a marked influence on the operating characteristics of ultrafiltration and reverse osmosis plants. Whey treatments which have improved performance during ultrafiltration include clarification, centrifugation (sometimes preceded by calcium addition), heating under conditions determined by type of whey and pH, demineralization, pH control, and preconcentration. With reverse osmosis, only demineralization and pH adjustment have been reported to be effective. While the data on plant performance as related to pretreatment are fairly comprehensive, the understanding of how the changes in the whey influence the interactions at the membrane surface is far from complete. There is some evidence, especially with minerals, of binding to the membrane being influenced by both type of membrane and components of the whey system.

The last decade has seen the initial stages of commercial application of ultrafiltration and reverse osmosis. The basic principles of these processes have been well documented by such authors as Sourirajan (1970), Lacey and Loeb (1972), and Madsen (1977). There is also a growing literature reporting on commercial applications to whey processing.

The implementation of the commercial applications to whey are limited to some extent by the need to find useful outlets for all the whey solids. However, there is a further limitation imposed by the cost of processing as related to efficiency of performance.

Lim et al. (1971) expressed flux (J) for reverse osmosis as

$$J = [K(\Delta P - \Delta\pi)/(R_m + R_p + R_f)] \quad (1)$$

where K is a constant, ΔP is the transmembrane hydraulic pressure drop, $\Delta\pi$ is the osmotic pressure difference across the membrane, and R_m, R_p, and R_f are resistances due to the membrane, concentration polarization, and fouling, respectively.

The osmotic pressure difference is a significant factor in reverse osmosis (RO) of whey. MacBean and Smith (1977) estimate the osmotic pressure of whey to be about 0.65–0.70 MPa— a fairly large fraction of the 4–6 MPa which is the usual operating ΔP for RO. As the whey is concentrated, the increasing osmotic pressure at the membrane surface, which may be aggravated by concentration polarization, leads to such a low driving force that operating becomes impracticable over about 25% soluble solids.

Equation 1 can also describe ultrafiltration (UF) but in this case, as the membrane is permeable to compounds of low molecular weight, the factor for osmotic pressure can be ignored. With the range of membranes available, the factor R_m has an influence in both RO (e.g., Short and Doughty, 1976) and UF (e.g., Muller et al., 1973). However, there is no doubt from numerous reports that the combined effect of R_p and R_f is the major force governing the efficiency of both processes. The research effort to reduce these sources of resistance is discussed below.

FACTORS INFLUENCING R_F AND R_P IN ULTRAFILTRATION

pH. The chemical and physical state of whey components and their environment are significant factors affecting R_f and R_p.

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The pH of the whey is an important variable (Forbes, 1972; Muller et al., 1973). Flux rates are high below pH 3.0 and low at about pH 4.0–5.0. As the pH is increased further, permeation rates improve with sweet cheese wheys but not usually with acid wheys. These differences in performance with type of whey and pH are obviously related to changes in the nature of the deposit which formed on the membrane surface during UF. At the present tme it is difficult to determine exactly the reasons for the difference. Obvious differenes in acid and sweet wheys are the higher calcium, phosphorus, and lactic acid content in acid whey and the higher lipid content of sweet whey. Lee and Harper (1977), using P-33 phosphate in the form of sodium phosphate, found that the binding of phosphate at low concentration was maximal at pH 6 on cellulose acetate, polyamide, and polysulfone UF membranes. An increase in concentration tended to shift the pH of maximum binding to a higher level, but this shift was insufficient to explain the differences in performance of UF systems for sweet and acid wheys. Harper and Patel (1977) found an increasing retention of lactic acid as pH was increased above 3.5. At the same time, there have been a number of observations that have indicated an increase in fat level can be related to a decrease in the initial flux rates (J) and increased fouling. A better understanding is needed of complex interactions that may involve lipid, lactate, calcium phosphate, and proteins and which vary as a function both of pH and relative concentrations.

Proteins. The effects on flux rate of the components of whey have been examined (e.g., Peri and Dunkley, 1971). Proteins and other macromolecules in whey had a greater influence on performance than smaller solute molecules. However, there is a lack of agreement on the roles of specific proteins. The most extensive work has been by Lee and Merson (1976a) who showed that the fouling layer was a complex network of several proteins. From scanning electron microscope studies, these authors postulated that fouling occurs when the larger whey constituents, including microorganisms, settle on the membrane in a lattice network which fills in and is coated over with small, sheet-forming proteins such as β-lactoglobulin.

Lipids. Lipids have received attention only recently and there is considerable work in progress to reduce the lipid content of whey prior to UF or RO to improve performance and certain functional properties, such as foaming.

Role of Calcium Salts. The studies of Hayes et al. (1974) showed that the difference in behavior at pH values over 5 of Cheddar cheese whey and hydrochloric acid (HCl) casein whey was associated with their calcium content—the cheese whey contained less than half the calcium of HCl casein whey. Increasing the calcium content of the cheese whey to the level of the casein whey at pH values around

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6 increased the fouling of membranes during UF. The severity of the fouling was greatest if the method of pH adjustment favored precipitation of calcium phosphate in the gelatinous, apatite form. Results of Hickey (1976) indicated, however, that such gels do not reduce permeation rates unless the circumstances favor formation of the gel in the pores of the membrane.

Hayes et al. (1974) also noted that increasing the calcium content of HCl casein whey at room temperature and adjusting pH to 6.7–6.9 gave a precipitate of protein and calcium salts. After removing the precipitate by centrifuging, a small improvement in flux rate resulted. When the whey was similarly treated and heated (77 °C for 15 s) before centrifuging, the improvement during UF was more marked. Conversely, when sufficient EDTA to sequester about 80% of the calcium was added to HCl casein whey, the treated whey showed little fouling tendency even at pH 6.5.

The studies of Lee and Merson (1976b) resulted in similar findings and showed that the improved UF performance could be related to alteration in the nature of the deposits on the membrane.

Phosphate Interactions. Phosphate, the concentration of which is also higher in acid whey, can bind to membranes and serve as a locus for binding other species (Lee and Harper, 1977). The binding of phosphate was markedly affected by constituents in the media being treated and type of membrane used. Addition of calcium increased the binding of phosphate on polyamide membranes while decreasing the binding of phosphate to all three membranes and whey dialysate was more effective than whey in causing binding of phosphate to UF membrane surfaces. Thus the deposits on membranes may involve not only protein, but protein–protein, protein–mineral, and protein–lipid interactions.

PRETREATMENT FOR ULTRAFILTRATION

Clarification and Filtration. Flux rates during UF of lactic casein whey were shown (Marshall et al., 1974) to be improved by prefiltration and centrifuging of the whey. This observation was confirmed and would appear to be explained by the studies of Lee and Merson (1976a) on cottage cheese whey, which is very similar to lactic casein whey. Prefiltration with filter paper and with a series of membranes of decreasing molecular weight cut off progressively improved UF performance.

Centrifugation and filtration can remove some of the larger fat globules and thus improve performance as well as altering the final functional behavior of the whey protein concentrates obtained by UF. In addition, utilization of precipitating agents to remove lipids has been shown to have some beneficial effect on UF performance.

Heating and pH Adjustment. Their preliminary observations on the effects of pH and calcium content in relation to heating led Hayes et al. (1974) to study this aspect in more detail.

They found that, with HCl casein whey, heating to 80 °C/15 s and adjustment of pH resulted in minimum fouling at a pH optimum in the region of 5.9 (determined at the UF temperature of 50 °C). This treatment at least doubled flux rates as compared with those of the pasteurized whey at the normal pH of about 4.4. Cheese whey at its natural pH of 6 or above when heated at 85 °C/15 s gave flux rates at least 50% above those of pasteurized whey.

They ascribed the reduction of fouling mainly to the aggregation of a complex of casein-like components and β-lactoglobulin. Hickey (1976) found evidence that the interactions of the proteins involved bovine serum albumin and that the occurrence of the pH optimum is related to the solubility of the proteins involved and to the ionic strength of the whey. He considered that the smaller extent of the interactions in Cheddar cheese whey was because of the lower ionic strength and lower calcium level in this type of whey. Recent work at CSIRO has shown that these complexes can be dissociated with isopropyl alcohol, but not urea or mercaptoethanol.

Demineralization. As could be expected from the evidence above on the influence of calcium and ionic strength, demineralization of whey has a beneficial effect on flux rates during UF. Hayes et al. (1974), using ion exchange, showed that exchange of cations in HCl casein whey gave a marked improvement in flux, particularly outside the pH range of 4 to 5. Cation exchange and UF at low pH has been applied commercially in Germany (Kuipers, 1975). Demineralization (95%) was shown by Hayes et al. (1974) to improve flux rates even more than did cation exchange—probably, in view of Hickey's findings, a result of the lower ionic strength or a reduction in phosphate. Delaney and Donnelly (1975) showed that demineralization gave similar benefits with cheese whey.

Flow Velocity. As Forbes (1972) points out, during UF at a given set of conditions, the gel layer will increase until the rate of back-diffusion to the bulk is in equilibrium with the rate of arrival at the membrane surface. All UF plants aim for flow conditions designed to induce high shear rates at the gel interface to favor back-diffusion. Many authors (e.g., Peri and Setti, 1976) have examined the influence of flow velocity on flux rate but usually with whey which could be tending to foul the membrane so that the combined effects of R_f and R_p would be operating. Recent studies by Marshall and Muller (1978) using two UF plants have confirmed the benefits to flux rate of high flow velocity and have shown that the degree of flux improvement by the pretreatment involving heating is also a function of flow velocity. For example, with a UF plant of the plate and frame type with laminar flow, the increase in flux due to pretreatment of Cheddar cheese whey was 11% at 0.66 m/s and 48% at both 2.2 and 3.2 m/s. In a plant using 2.5-cm tubes, the increase was 7% at 1.5 m/s and 58% at 4.2 m/s.

With the combination of pretreatment of whey and the use of high flow velocities it now appears possible to achieve three- to fourfold increases in UF efficiency as compared with results on pasteurized whey in the earlier versions of UF equipment.

Effect of Preconcentration. Recent studies in France (Goudedranche et al., 1976) and Holland (Hiddink et al., 1976) highlighted another approach to increasing the efficiency of UF. Looked at from the viewpoint of the end products, the duty of a UF plant can be considered that of fractionation of the whey solids. The criterion for performance can then be expressed in terms of kg of solids/m^2h rather than, as is more usual, in terms of flux rates as 1/m^2h. By preconcentrating the whey, performance in terms of kilograms of solids can be more than doubled. A whey protein concentrate (WPC) of about 37% protein can be obtained with high UF efficiency from whey preconcentrated to about 20% solids. The viscosity of the retentate during the latter stages of UF is the limiting factor. Higher protein levels can be achieved directly if preconcentration is restricted to about 11% solids or if diafiltration (washing with water) is used when the viscosity of the retentate reaches a critical level. Indications of the reduction in costs, including the reduction by using RO instead of evaporation for the concentration step, were given by Hiddink et al. (1976).

Muller (1977) compared the cost of the alternative approaches using pretreatment or preconcentration of cheese whey and found that, assuming that both whey fractions required concentration at some stage of the overall process, preconcentration appeared to give lower UF costs than pretreatment. Both approaches gave considerably lower UF costs than applied to pasteurized cheese whey. The effects of combining pretreatment and preconcentration are currently being investigated in Australia. The ultimate choice of process will depend not only on economics, but also on the properties desired in the end products. As Muller (1977) points out, there are differences in properties in the WPC related to both the type of whey used and its pretreatment.

REVERSE OSMOSIS

In their studies on RO of cottage cheese whey, Lim et al. (1971) calculated values for R_p and R_f and showed the values decreased threefold for R_p and tenfold for R_f as the Reynold's number was increased from 1500 to 5900. Hence, flow velocity and turbulence are major factors influencing the efficiency of RO. Short and Doughty (1976) chose practical operating conditions for several types of RO modules based on considerations of flow velocity and pressure.

A further important operating variable is temperature. In this respect a recent paper by de Boer et al. (1977) is of interest. They showed that while there was the normal considerable increase in flux as processing temperature was raised from 10 to 30 °C, the benefit to efficiency applied only at low concentration ratios. The fouling of the membrane, probably accentuated by the high initial flux rates at 30 °C, reduced the average flux to concentration ratios over 2 to less than the average at 10 °C.

The effects of pretreatment of whey to overcome its fouling tendencies have been explored by Smith et al. (1977). Their findings were that most of the pretreatments of whey found useful for UF led to increased fouling in RO. Fouling during RO was less severe with Cheddar cheese whey than with HCl casein whey and could be reduced by lowering the pH or virtually eliminated by adding calcium sequestering agents. With HCl casein whey only demineralization by ion exchange was effective in reducing fouling. In cottage cheese whey, reduction of pH minimized fouling (Harper and Patel, 1977).

Adjusting the pH of both Swiss cheese whey and cottage cheese whey was found by Harper and Patel (1977) to markedly influence the COD of the permeate. On increasing the pH to 7.0, the COD of the permeate was reduced by a factor of 2 or more and the lactic acid content as percentage of permeate solids also decreased.

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