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Short communication

Ultrafiltration studies on solutions of pectin, glucose and their mixtures in a pilot scale crossflow membrane unit

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Abstract

Ultrafiltration experiments on solutions of glucose, pectin, and their mixtures have been performed in a 500 l/h pilot scale crossflow membrane unit. A 25,000 MWCO polyethersulfone membrane with a total flow area of 0.9 m^2 was used in the process. Unlike the permeate flux profiles for glucose solutions, which showed linear relationship with transmembrane pressure (TMP), the flux for solutions of pectin showed a rapid increase with increasing TMP before leveling-off. Similar behavior was observed by adding different amounts of glucose to these pectin solutions, but with much lower permeate flows. The formation of gel layers on the membrane surface is mainly responsible for the lower permeate fluxes in the latter two cases. In addition, it was found that particle interactions due to electrostatic forces were also important for the development of stable gel layers. Due to differences in the experimental technique used in this work, no maximum permeate flux for the pectin solutions was observed at intermediate TMP as opposed to many results reported in the literature.

Keywords: Crossflow ultrafiltration; Tubular ultrafiltration; Pectin; Glucose

1. Introduction

Pectins are polysaccharides consisting of copolymers of partially esterified α-D-galacturonic acid and L-rhamnose as the main backbone structure with other neutral sugars that are present as side chains. They are grouped into two main categories depending on the degree of esterification, namely high methoxyl pectin (HMP) and low methoxyl pectin (LMP). Pectins have an average molecular weight of 70,000 Da, and are normally obtained from natural plants and fruits such as citrus and apple pomace. They are widely used in food formulations, and in the presence of sugars under suitable conditions, pectins would form gel. For this reason, the use of pectin in the food industry is mainly as gelling agents for the production of jams, jellies, and other foods. The appropriate conditions for the gelation of pectin differ, depending on the type of pectin used. HMP with a degree of esterification higher than 70% would form satisfactory gel with sugars at low pH of 3–3.4 and relatively high temperature, while those with ester levels slightly less than that require a more acidic condition at lower temperature [1]. For LMP, gel can form even without sugar. In addition to pH and temperature, the gelation behavior of pectins is also affected by the ionic strength of the solutions [2].

The concentration of pectin in fruits may be as high as 1 wt.%, and for tropical fruits such as guava and starfruit, it varies from 0.01 to 0.15% [3]. In addition, fruits also contain sugar in the form of glucose, which is typically in the range of 2–4%. A number of investigations evaluating the membrane-filtration behavior of fruit juices have related the observed data to their pectin contents. Kirk et al. [4] clarified pear juice using hollow fiber ultrafiltration and observed maximum fluxes at intermediate transmembrane pressure for the entire range of crossflow velocities investigated. This pattern is unlike that of protein, where limiting fluxes are normally observed. The investigators attributed their findings to the elastic nature of the polymeric pectin structure. To some extent, these results are in agreement with the recent work conducted by the authors [3] who clarified untreated starfruit juice in a batch-stirred cell membrane unit. The general trend of having maximum permeate flux at intermediate pressure was also noted for different feed concentrations, and this was likely due to the amount of pectin in the sample. A clearer picture on the

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role of pectin in membrane filtration is evident from the work of Szaniawski and Spencer [5]. Using solutions of pure pectin, they observed that for each crossflow velocity, the permeate flux increased to a maximum value at intermediate pressure before decreasing to a constant limiting value on further increase in pressure. The observed effect is more significant at higher velocities. In addition, they also reported that the pectin in the solutions irreversibly fouled the membrane, as evident from the measured water flux.

Gelation of pectin in the presence of glucose is expected to bear additional influence on its membrane-filtration behavior. The addition of glucose into a solution of pectin would affect its pH. For some systems, particularly those involving colloids, solution pH and particle interactions are extremely important in membrane filtration [6]. It is likely that these phenomena are also important in the membrane filtration of glucose and pectin-containing materials, such as in the processing of natural fruit juices by ultrafiltration. Reports on the membrane-filtration behavior of solutions having both pectin and glucose are still lacking in the literature. Furthermore, most of the work which has been conducted in the related areas used only small-scale membrane units with filtration area less than 0.025 m^2. To test the reliability of the process for commercial operation, data obtained from a bigger scale unit will be of interest. The work to be discussed in this paper will evaluate the ultrafiltration behavior of solutions of pectin, glucose, and their mixtures using a pilot scale unit. It is part of an ongoing investigation to evaluate the viability of membrane filtration to clarify tropical fruit juices.

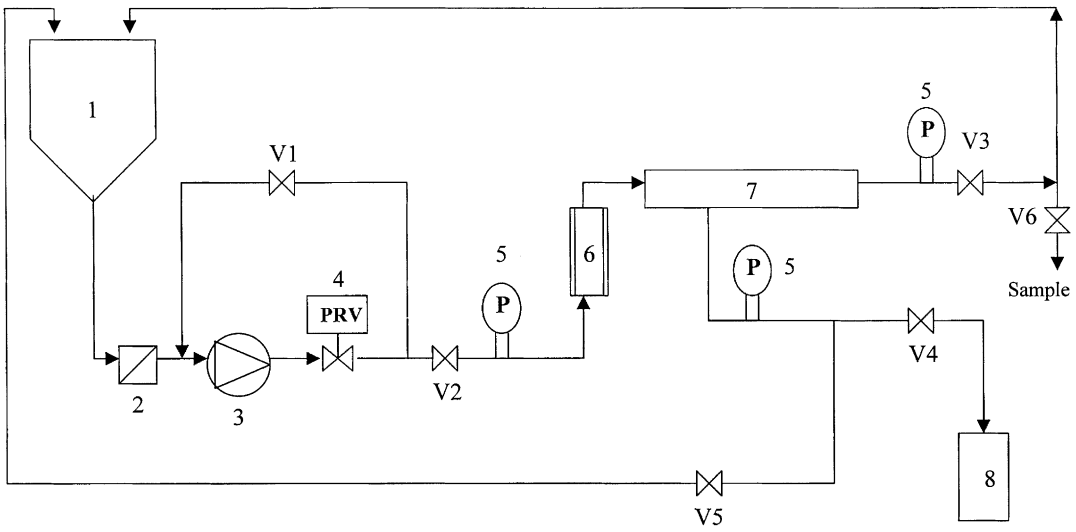
2. Experimental

2.1. Experimental set-up

The schematic diagram of the experimental set-up is shown in Fig. 1. The process material from a 50 l feed tank is fed to the membrane unit via a 3/4 HP Hydra-cell-pump (Hydra-cell, USA) and a magnetic float flowmeter (King USA Model 7700). The pump has a maximum delivery capacity of 500 l/h. A strainer is fitted upstream of the feed pump to trap any particles larger than 250 μm that may be present in the feed stream. To minimize pressure fluctuations, a damping tank is provided in the process line. The membrane module consists of 18 tubes of 12.7 mm diameter polyethersulfone membrane (25,000 MWCO) enclosed in a stainless steel casing (PCI, UK Model B1-ES625). The effective flow area of the membrane is 0.9 m^2. The permeate line is passed through valve V5 before being returned into the feed tank. Similarly, the retentate line is also recycled back into the feed tank. Sampling points (V4 and V6) are provided to collect permeate and retentate samples during experiments.

2.2. Experimental procedure

A typical run began by charging the feed material, which was a solution of either pectin, glucose, or their mixtures in water, into the feed tank and circulating it through the system for about 5 min. Any bubbles of air trapped in the system were removed through the venting valve. The feed flowrate was then adjusted to the required corresponding crossflow



1. Feed tank
2. Strainer
3. Feed pump
4. Pressure relief valve
5. Pressure gauge
6. Flowmeter
7. Membrane module
8. Measuring cylinder

Fig. 1. Schematic diagram of the experimental set-up.

velocity using valve V1. Another variable, which must also be set, is the transmembrane pressure, TMP, and this was accomplished by adjusting valves V2 and V3. The system was allowed to stabilize and to reach steady state, as indicated by stable and constant readings on the pressure gauges and flowmeters. This process may take between 20–40 min. Once a steady-state condition is attained, the retentate and permeate flowrates were recorded at 10 min interval for a period of 60 min. To ensure that recorded readings are correct, the time taken to collect 50 ml of permeate was also taken. Samples of permeate and retentate were also collected for further analysis. Each run was concluded by flushing and cleaning the membrane with a 250 ppm solution of sodium hypochlorite at 50°C. Freshly prepared feed material was used for each experiment using the precleaned membrane. All the experiments were conducted at room temperature (≈30°C). However, a temperature rise of about 5°C was observed at the end of the experiment mainly due to the re-circulation of the feed material in the system.

2.3. Materials and the preparation of feed solutions

Throughout this investigation, a high methoxyl citrus pectin with 99% of the particles less than 350 μm was used. It was purchased from Sbi, France. The glucose sample has a molecular weight of 180 and was obtained from Ajax Chemicals, Australia.

The different solutions were prepared by dissolving predetermined amounts of pectin and/or glucose in known volumes of distilled water using a hand-held blender. The final pH of the solution was also recorded.

2.4. Analysis

The feed material as well as the permeate and retentate samples were subjected to a series of analyses. The concentration of pectin and glucose in these samples was determined using a UV spectrophotometer (Varian Model Cary 1E). For pectin concentration, the analysis was performed at a wavelength of 300 nm using distilled water as the blank. In the case of solutions containing both pectin and glucose, the blank samples were pectin-free solutions containing equal amounts of glucose. For glucose determination, the enzymatic method [6] was used in the sample preparation, and the resulting sample was analyzed at a wavelength of 340 nm.

In addition to the above analyses, the feed materials were also analyzed for other parameters. These include the zeta potential using a Malvern Zeta Potential Meter and viscosity measurement using a Mettler RM 180 Viscometer. For each of these measurements, several readings were taken to compute the average value for each parameter.

3. Results and discussions

The present investigation only focused on the steady-state behavior of the system, which was attained in about 20–40 min from the start of the experiment. As an initial assessment of the system, with respect to both the operating procedure that was established as well as the consistency of the analytical techniques which were employed, a steady-state pectin balance was made for a number of runs. In all the cases, at least 97% of the pectin fed to the system could be accounted for. Indirectly, the results suggest that a reliable and consistent experimental technique has been adopted in this work.

In order to understand the ultrafiltration behavior of a mixture of pectin and glucose solution, it is firstly necessary to study the variation of permeate flux with TMP, as shown individually by pectin and glucose. The behavior of glucose was studied using solutions with glucose concentration of 3.4 and 10 wt.% at a crossflow velocity of 1.13 m/s. The measured zeta potentials at these two concentrations were relatively constant at −23.9 mV. These results are consistent with the solution pH, which was constant at 5.6 at room temperature. The plot of permeate flux, J, versus TMP for these solutions is shown in Fig. 2. Also included in the figure is the pure water flux. From the slope of the water flux, the hydraulic membrane permeability, L_p, was estimated to be 72.66 (l/m^2 bar h). Similarly, its hydraulic resistance, R_m, given by the relationship

$$L_p = \frac{1}{\mu R_m} \quad (1)$$

is estimated to be 47.8 h m^2/l. In Eq. (1), μ is the viscosity of water with a value of 2.88 kg/h m at the experimental temperature of 30°C.

For the glucose solutions, the fluxes vary linearly with TMP but with different slopes. The linear relationship strongly suggests the absence of any significant fouling of the membrane and the development of any gel or polarized layer on the membrane surface. Polyethersulfone is a polymeric material, which consists of long chains of benzene rings connected in between by molecules of SO_2 and oxygen. Studies have indicated that these membranes have negative zeta potentials that are pH dependent [7]. The glucose used in this work has a molecular weight of 180 Da, which is much smaller than the average pore size of the membrane used in this work (25,000 MWCO). Under this condition, any possible interactions of glucose molecules with the membrane surface and the pore walls will be at a minimum level, and one would expect that no glucose molecules would be rejected. Analyses on the amount of glucose in both permeate and retentate streams have confirmed that separation of glucose was not observed. This measurement further supports the above argument that membrane fouling has not occurred to any significant extent during the run. Furthermore, it was observed that the water fluxes obtained at the end of each run without cleaning the membrane were similar to the original water flux for the fresh membrane. A maximum deviation of less than 5% at the highest operating pressure of 10 bar was observed. The decrease in the apparent membrane permeability at higher glucose concentration

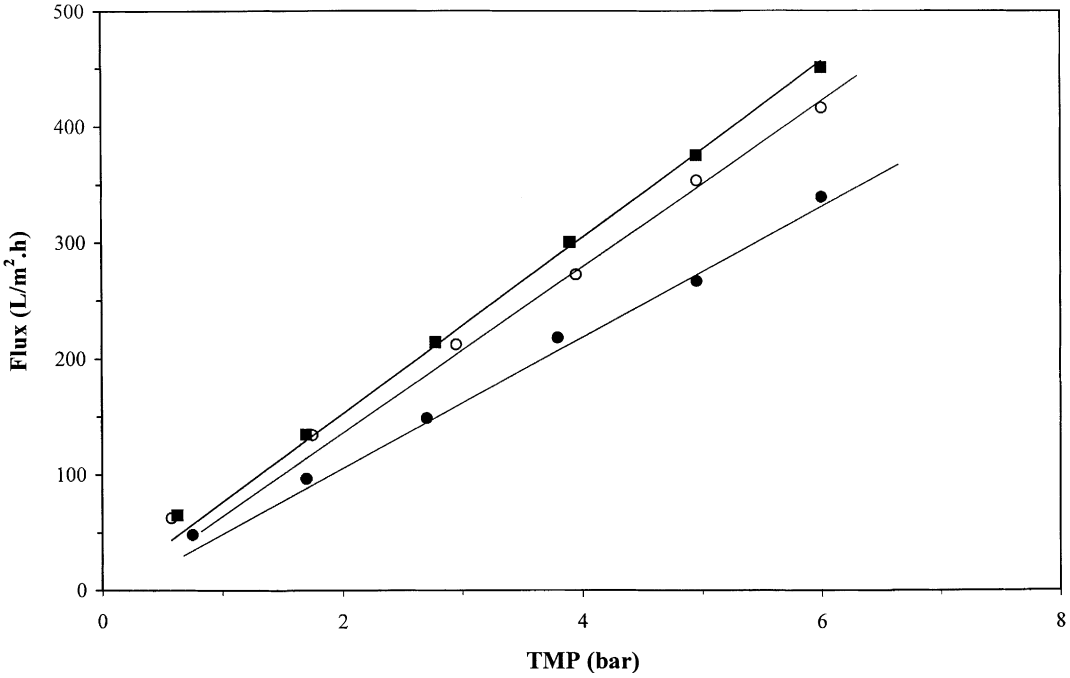


Fig. 2. Variations of permeate flux with TMP for pure water and glucose solutions: pure water (■); 3.4% glucose (○); 10% glucose (●).

is likely to be attributed to the higher viscosity of the solution. For the 3.4 and 10% solutions, the measured viscosity fluctuated around 3.6 and 7.2 kg/h m, respectively. Fluctuation in the readings was mainly due to the accuracy of the instrument used, which has a resolution of 3.6 kg/h m (1 cP). Although, the readings are not accurate, they do indicate the point that the viscosity changes with the amount glucose in the solution. The higher viscosity of the 10% solution results in a lower apparent value of the permeability of the membrane. From the slope of the line, the viscosity of the solution was estimated to be 5.0 kg/h m, which is within the measured range of measured values given above.

The behavior of pectin during ultrafiltration was investigated using solutions of 0.05, 0.15, and 0.25 wt.% at a crossflow velocity of 0.13 m/s, which is in the laminar flow regime. Low crossflow velocity was chosen so as not to destroy any layer of gel that may form on the membrane surface. The pH of these solutions reduced from 3.9 for the 0.05% solution to 3.4 for the 0.25% solution. Similarly, the measured zeta potential varied, respectively, from −38.4 to −17.7 mV. The plot of permeate flux versus TMP is given in Fig. 3. The results clearly indicate the significant effects of pectin concentration on the permeate flux. Solutions with the highest pectin content (0.25%) exhibited the lowest permeate flux. Throughout the TMP investigated, the flux obtained from this solution was about 50% that of the 0.05% solution. Experiments for the 0.25% solution were repeated twice to ascertain the reproducibility of the results obtained. The leveling-off of flux at higher TMP is possibly due to several factors, such as concentration polarization and gel-layer formation on the membrane surface. To ascertain the prevailing mechanism that is responsible for the observed phenomenon, a section of the used membrane was cut open to expose its internal surface. A layer of pectin was clearly observed on the membrane surface suggesting that it is likely to be the main resistant responsible for the nonlinear relationship of permeate flux with pressure given in Fig. 3. In line with this conclusion, it is expected that the extent of gel-layer formation is more significant for the 0.25% solution, resulting in a much lower permeate flux. For all the experiments, more than 90% rejection of pectin was obtained. As explained earlier, pectins are long-chain polymeric macromolecules, which are more difficult to push through the pores of the membrane. Based on this reason, most of the pectin materials were likely to be trapped within the membrane structure and retained on the membrane surface. However, it is still possible that some of the macromolecules are adsorbed on the pore walls of the membrane that leads to fouling. This is evident from the measurement of water flux performed after the experiment on the membrane, which was cleaned with 5% sodium hydroxide solution. A nonlinear relationship of flux with TMP was observed, indicating that the membrane was not completely cleaned. Some of the adsorbed pectin could have diffused back into the flowing water to give the nonlinear behavior. Szaniawski and Spencer have also reported this nonlinear water flux [5] in their work on the microfiltration of pectin solutions. However, fouling of the membrane by pectin is reversible, since the original water flux was obtained by employing sodium hyperclorite instead of sodium hydroxide as the cleaning agent. The possible interaction between the pectin molecules and the membrane played no role in the observed profiles.

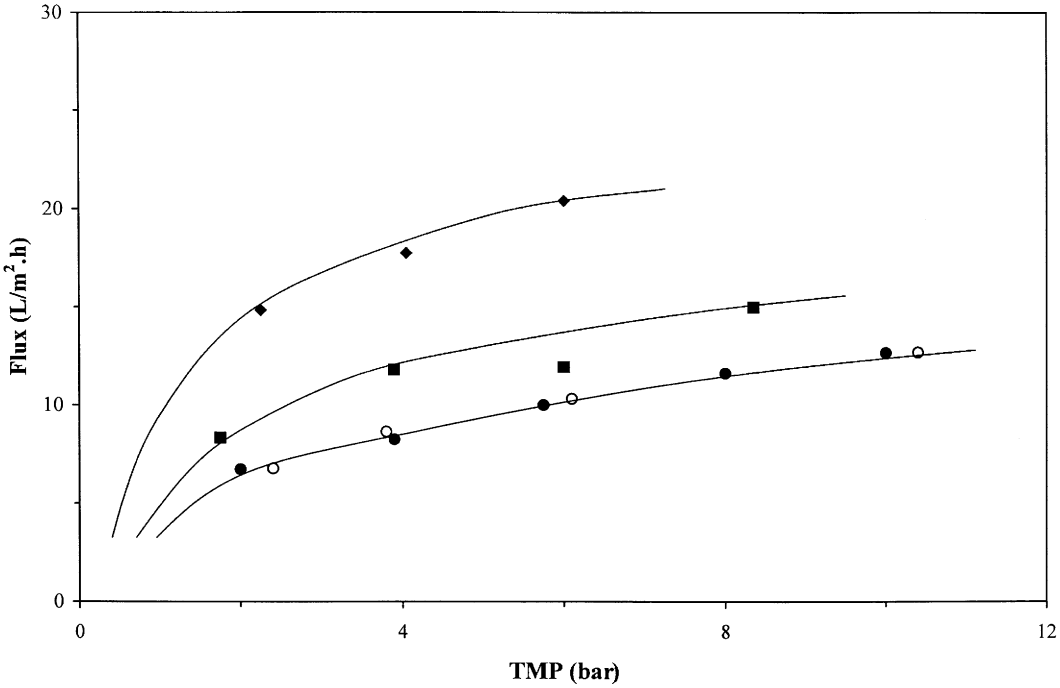


Fig. 3. Variations of permeate flux with TMP for different pectin solutions: 0.05% pectin (◆); 0.15% pectin (■); 0.25% pectin (●, ○).

The profiles of permeate flux versus TMP observed in this work are slightly different from those reported in the literature. Kirk et al. [4] who studied the ultrafiltration of pear juice observed a bell-shaped profile, where the flux showed a maximum value at intermediate pressure. The authors in their recent work also reported relatively similar profile on the clarification of untreated starfruit juice. Similarly, Szaniawski and Spencer [5] reported the same profiles in their study on the crossflow microfiltration of pectin solutions. In the present work, fresh feed material and cleaned membrane were used to obtain flux data at each TMP. This approach is different from that of the others, where the same sample and membrane were used throughout each set of experiments over the entire range of TMP investigated. In the latter case, an increase in pressure in the system would cause the macromolecules, which were already on the membrane as well as inside the membrane porous structure, to pack more tightly. At moderate pressures, there are still possibilities for the permeate to pass through. However, as higher pressures are applied, the densely packed pectin molecules form a barrier across the membrane and prevent the flow of permeate flux, thus displaying a decreasing trend with increasing pressure. It is important to highlight that within the range investigated, the permeate fluxes observed in this work did not actually reach the limiting values but appeared to increase continuously. From this comparison, it appears that the permeate flux profiles would also depend on the experimental procedure used in collecting the data.

Experiments to study the variations of permeate flux with TMP were also conducted on solutions containing different ratios of pectin to glucose under similar conditions for that of pectin solutions. Results for the 0, 2, and 8 wt.% glucose in 0.25 wt.% pectin as well as 2% glucose in 0.15% pectin are shown in Fig. 4. For all the TMP and pectin concentrations investigated, the permeate fluxes for solutions with higher glucose concentration is always lower than that of lower glucose content. For a given glucose concentration, similar conclusion also applies to solutions with varying pectin content as evident when comparing the 2% glucose solutions having different proportions of pectin. In general, it can be concluded that rapid decay in the flux is expected for solutions containing high concentrations of glucose and pectin. From the analysis of glucose and pectin in the permeate and retentate streams, more than 90% pectin rejection but none for glucose were observed for all feed concentrations. These results are similar to the values obtained for the individual pure solutions, indicating that similar separation efficiency with respect to both components was maintained.

The presence of glucose in a pectin solution leads to the formation of stable gel layers through gelation phenomenon, as reported in the literature [1]. In addition, its presence would also affect some of the physical properties of the bulk solution that eventually influences the ultrafiltration behavior. In order to assess these changes, a series of measurements were performed to determine variations in solution viscosity and zeta potential of the glucose–pectin agglomerates as a function of different ratios of glucose to pectin and the pH of the solutions. The pH of each solution was adjusted to the required value by adding the appropriate amount of sodium hydroxide. Some variations in the viscosity of the solutions were noticed. For a solution of 0.1% pectin and 3.4% glucose, the recorded viscosity was 7.2 kg/h m as

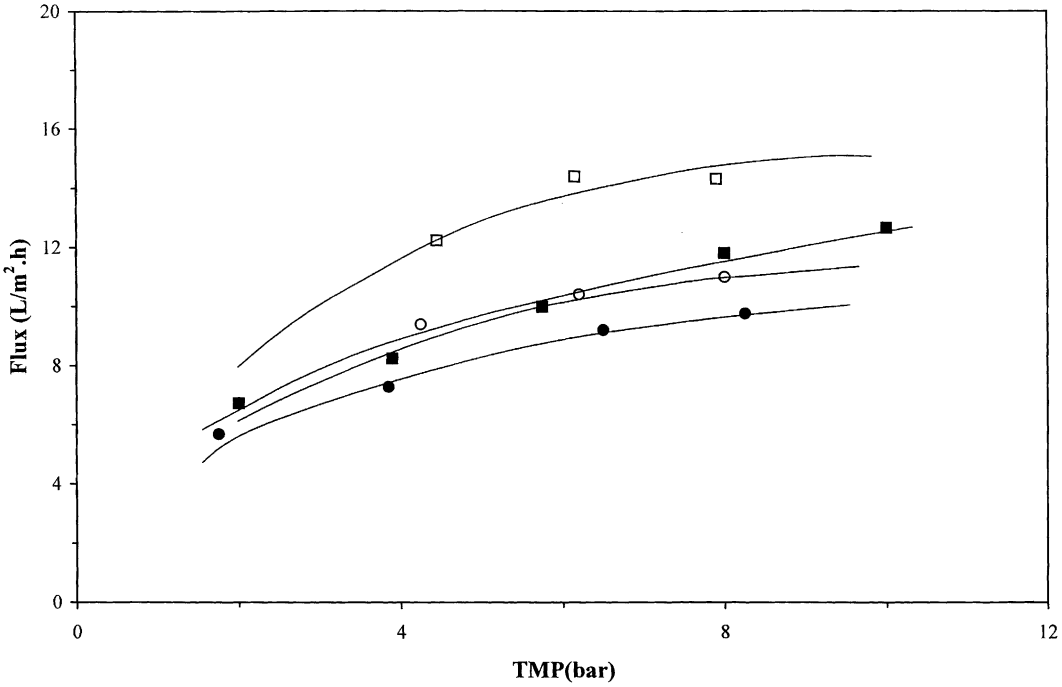


Fig. 4. Variations of permeate flux with TMP for solutions with different pectin and glucose concentrations: 0% glucose + 0.25% pectin (■); 2% glucose + 0.15% pectin (□); 2% glucose + 0.25% pectin (○); 8% glucose + 0.25% pectin (●).

compared to 10.8 kg/h m for the 0.4% pectin and 10% glucose solution. Variations in solution viscosity would affect the mass transfer coefficient, and hence the resulting flux. The effect of solution composition on zeta potential is shown in Fig. 5 at two different solution pH of 5 and 7. At all glucose concentrations and solution pH, the pectin–glucose agglomerates become more positive as the pectin concentration is increased. Similarly, for a fixed pectin concentration, these

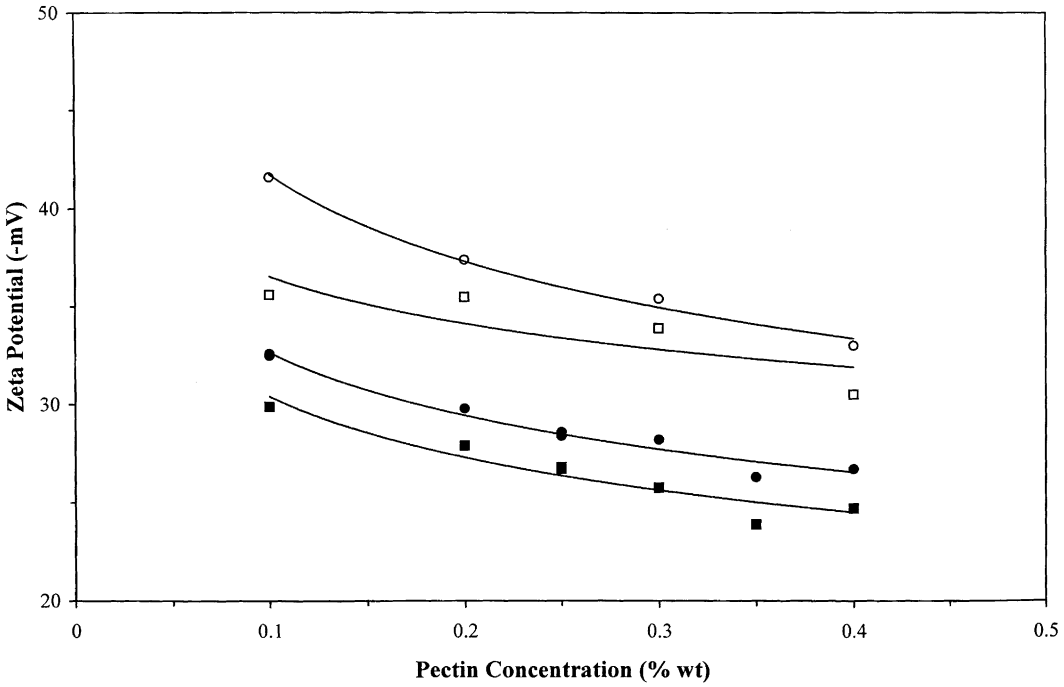


Fig. 5. Variations of zeta potential with pectin concentrations at different solution pH and glucose contents: 3.4% glucose, pH = 7 (○); 3.4% glucose, pH = 5 (□); 10% glucose, pH = 7 (●); 10% glucose, pH = 5 (■).

agglomerates become less negative by increasing the glucose concentration. However, within the range investigated, these agglomerates remained negatively charged. Electrostatic repulsion plays a major role in reducing chain aggregation of pectin [8]. As the charges become less negative for higher concentration solutions, the effect of repulsion is reduced. This will lead to a maximum elongation of chains, thus allowing a higher degree of chain aggregation and therefore a more stable gel layer on the membrane. This explanation is consistent with the result observed in this work, where the solution with the highest concentration of pectin and glucose showed a rapid decay in the flux with TMP. This evidence indicates the importance of particle interactions in the membrane processing of glucose–pectin solutions.

4. Conclusion

Solutions of glucose, pectin, and their mixtures showed some variations in their ultrafiltration characteristics. Using a 25,000 MWCO polyethersulfone membrane, a linear relationship of permeate flux with TMP was obtained for glucose solutions. Differences in the slope of the lines for solutions of different glucose concentrations were due to the variations in the viscosity of these solutions. In contrast, the permeate flux obtained from the filtration of a pectin solution initially increases with increasing TMP before leveling-off with further increase in pressure. The effects are more significant at high pectin concentrations. In this case, it was observed that the flow of permeate at high TMP is limited by the formation of a gel layer on the membrane surface. The addition of glucose to a solution of pectin further reduces the permeate flux at all TMPs investigated. The gelation of pectin in the presence of glucose is believed to have contributed to the observed behavior. From the measurement of zeta potentials, it is also evident that particle interactions due to electrostatic forces between the pectin–glucose agglomerates are also important and played a role in establishing stable gel layers. Unlike other results reported in the literature, the permeate flux profiles for pectin solutions obtained in this work do not show any maximum value at intermediate TMP.

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