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Ultrafiltration behaviors of pectin-containing solution extracted from citrus peel on a ZrO_2 ceramic membrane pilot unit

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Abstract−Ultrafiltration experiments on a solution of pectin, hesperidin, and other mixtures extracted from citrus peels have been performed on a 500 *l*/min pilot scale crossflow ceramic membrane unit. A 30,000 molecular weight cut-off (MWCO) zirconia (ZrO_2) ceramic membrane with a total effective flow area of 0.5 m^2 was used in the process. The permeate flux for pure water and hesperidin showed linear relationship with transmembrane pressure (ΔP), but the flux for pectin solutions showed a curvilinear relationship with ΔP and represented a rapid increase with increasing ΔP before leveling-off. Similar behavior was observed by adding different amounts of hesperidin 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 addition, the permeate flux decrease faster at higher ΔP, since higher ΔP brought bigger flux at lower pectin concentration. Compared with the more than 90% retention rate of macromolecular pectin, pigment and other component have less than 20% retention rate. So, the decolorization, the separation and purification of pectin preparations could be achieved simultaneously through ultrafiltration with a ceramic membrane.

Key words: Crossflow Ultrafiltration, ZrO_2 Ceramic Membrane, Pectin, Hesperidin, Pigment

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 as side chains [1]. Pectins have molecular weight 20,000 to 400,000 Da, with average molecular weight of 70,000 Da, and are normally obtained from natural plants and fruits such as citrus and apple pomace [2,3]. For their thickening and gelling properties in the presence of sugars under suitable conditions, they are widely used in many foods, as well as in industrial applications, e.g., ice cream, sauce, dairy desserts, flans, jams and jellies, meat preserves, confectionery, cosmetic etc. [4-6].

The content of pectin in fruits may be as high as 4 wt%, and the albedo of citrus fruits consists of nearly 50% pectin [7]. In addition, citrus peel also contains pigment, which is typically in the range of 1-6%. Commercial pectin is produced primarily from lemon and lime peel by hot aqueous acid extraction before filtration and separation [4]. A number of investigators including Kirk et al. [8,9] evaluated the membrane-filtration behavior of fruit juices related the observed data to their pectin contents. A clearer picture on the role of pectin in membrane filtration is evident from the work of Szaniawski and Spencer [10]. 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.

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The primary components of pigment in extract include hesperidin, naringin, narirutin, neohesperidin, tangeretin, and nobiletin [11]. The existence of pigment in pectin would affect the color and luster of commercial pectin product. Reports on the membrane-filtration behavior of solutions having both pectin and pigment are still lacking in the literature. Furthermore, most of the work which has been conducted in a related domain used only small-scale membrane units with effective 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 would be of interest. The work in this paper will evaluate the ultrafiltration behavior of solutions of pectin, hesperidin, their mixtures, and pectin extract mixtures from citrus peel using a pilot scale unit. It is part of an ongoing investigation to evaluate the viability of membrane filtration to purify and condense pectin from extract mixture containing pigment. The permeability of hesperidin on ceramic membrane was only discussed in this paper because it is the highest proportion among all components of pigment.

EXPERIMENTAL

1. Experimental Apparatus

Most ultrafiltration and microfiltration membranes are made from polymeric materials. However, porous inorganic membranes are better suited if high-temperature capability and resistance to corrosive chemicals are required [12]. Modules made from inorganic materials, especially ceramics, are generally superior to organic membranes in mechanical stability, microbiological resistance, extreme temperature tolerance and ease of cleaning.

A schematic diagram of the experimental apparatus is shown in Fig. 1. The process material from a 10 *l* feed tank is fed to the ceramic membrane unit via a press-steady pump (25QY-2, China)

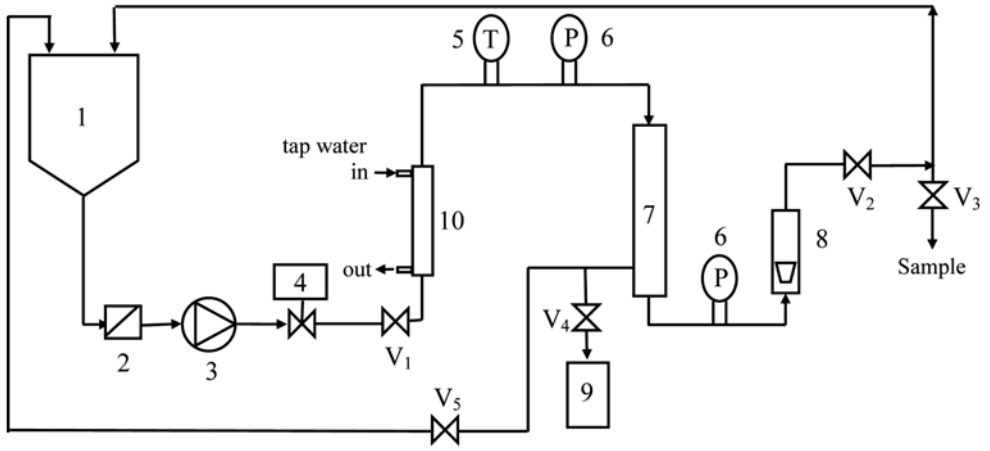

Fig. 1. Schematic diagram of the experimental apparatus.

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

and a float flowmeter (MBLD Instrument Company Model 60L). The pump has a maximum delivery capacity of 500 *l*/h. A strainer is fixed upstream of the feed pump to trap any particles larger than 250 μm that may be present in the feed stream. To eliminate temperature rising of the solution, a heat exchanger is installed on the stream prior to the membrane module. The membrane module consists of four tubes of 25.0 mm diameter ceramic membrane (30,000 MWCO). The total effective flow area of the membrane is 0.5 m^2. The permeate line is passed through valve V_5 before being returned into the feed tank. Similarly, the retentate line is also recycled back into the feed tank. Sampling points (V_3 and V_4) are provided to collect permeate and retentate samples during experiments.

2. Materials and the Preparation of Feed Solutions

Throughout investigation, a high-methoxyl pectin from citrus (Sigma) with 99% of the particles less than 250 μm was used. The hesperidin (>95%) sample was obtained from Fluka. The pectin extract mixture was extracted from fresh peel of mandarin orange, one of the main Chinese citrus, with 0.01 mol/*l* hydrochloric acid for 2 h at 90 ℃. Its content of pectin and several pigments were determined according to the following analysis before runs. The different solutions were prepared by dissolving predetermined amounts of pectin in known volumes of distilled water.

3. Experimental Procedure

A typical run began with charging the feed material, which was a solution of pectin and other mixtures in distilled water, into the feed tank and circulating it through the system for about 10 min. The feed flowrate was then adjusted to the required corresponding crossflow velocity by using a pressure relief valve. Another variable, the transmembrane pressure, ΔP, also had to be set, which was accomplished by adjusting valves V_1 and V_2. The system was allowed to stabilize, as indicated by stable and constant readings on the pressure gauges and flowmeter. This process may take between 10-15 min. Once a steady-state condition was attained, the retentate and permeate flowrates were recorded at 10 min interval for a period of 60 min. Samples of permeate and retentate were also collected for further analysis. Each run was concluded by flushing and cleaning the membrane with a 1.5×10^{-4} mol/*l* solution of hydrochloric acid at 30 ℃. Freshly prepared feed material was used for each experiment by using the pre-cleaned membrane. All the experiments were conducted at ambient temperature (30 ℃). In addition, a temperature rise of about 1 ℃ was observed at the end of the experiment, mainly because of a heat exchanger in the system.

4. Analysis Methods

The feed material, permeate and retentate samples were subjected to a series of analyses. The concentration of pectin in these samples was determined with a UV spectrophotometer (Varian Model Cary 4000). For pectin concentration, at first a chromogenic reaction between pectin solution and carbazole dye was conducted, then the analysis was performed at a wavelength of 530 nm using distilled water as the blank. In the case of solutions containing both pectin and hesperidin, the blank samples were pectin-free solutions containing equal amounts of hesperidin.

In addition to the above analyses, the contents of hesperidin, naringin, neohesperidin, tangeretin, narirutin and nobiletin in feed materials, permeate and retentate samples were also analyzed according to the method proposed by Bronner and Reecher [13].

RESULTS AND DISCUSSIONS

In recent years, ultrafiltration performance has been mostly described in three models: the gel model [14], the osmotic pressure model [15], and the resistance model [16]. The flux of pectin-containing solution can be represented by a resistance model

$$J = \frac{\Delta P}{\mu \bullet (R_m + R_f)} \quad (1)$$

where ΔP is the transmembrane pressure, μ is the solvent viscosity, R_m is the resistance of the clean membrane, and R_f is the resistance of any fouling layer on the membrane surface or within the membrane. It is reported that membrane modules whose channel diameter or height are greater than 1 mm will probably operate under turbulent flow conditions, otherwise under laminar flow conditions [17]. Ceramic membrane falls into the turbulent flow category.

In order to understand the ultrafiltration behavior of pectin solu-

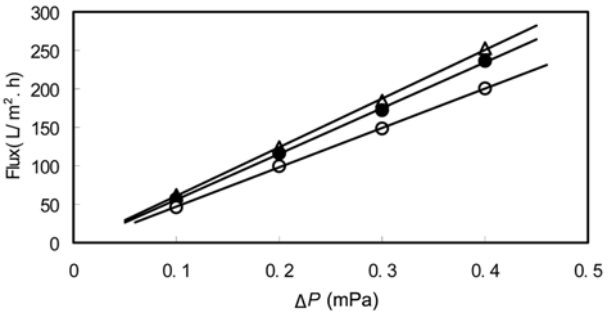

Fig. 2. Variations of permeate flux with ΔP for pure water and hesperidin solutions: pure water (△); 0.1 g/*l* hesperidin (●); 0.5 g/*l* hesperidin (○).

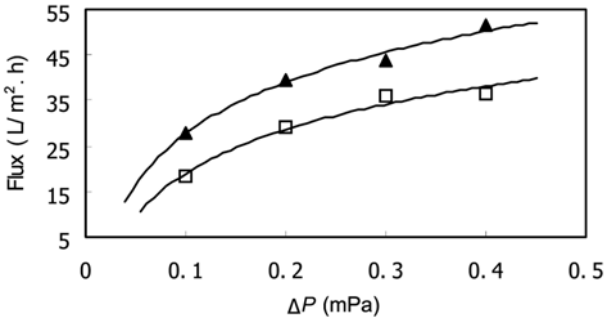

Fig. 3. Variations of permeate flux with ΔP for different pectin solutions: 2.0 g/*l* pectin (▲); 6.0 g/*l* pectin (□).

tion, it is first necessary to study the variation of permeate flux with ΔP, as shown by pure water and hesperidin, respectively. Fig. 2 shows the plot of pure water and hesperidin flux versus ΔP. There is no fouling layer on the membrane surface or within the membrane, the R_f is null, so Eq. (1) becomes

$$J = \frac{\Delta P}{\mu R_m} = \Delta P L_p \tag{2}$$

From the slope of the water flux, the hydraulic membrane permeability, L_p, was estimated to be 632.79 $lm^{-2}h^{-1}mPa^{-1}$. Looking through Eq. (2), its resistance of the clean membrane, R_m, given by the relationship

$$L_p = \frac{1}{\mu R_m} \tag{3}$$

is estimated to be 54.8 $m^2\ l^{-1}$. In Eq. (2) and Eq. (3), μ is the viscosity of water with a value of 2.88×10^{-5} mPa·h at 30 °C.

For the hesperidin solutions, the fluxes vary linearly with ΔP 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. The hesperidin used in this work has a molecular weight of 610.56 Da, which is much smaller than the average pore size of the membrane used in this work. Under this condition, any possible interactions of hesperidin molecules with the membrane surface and the pore walls will be at a minimum level, and one would expect that no hesperidin molecules would be rejected. Analyses on the amount of hesperidin in both permeate and retentate streams have confirmed that separation of hesperidin 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 1% at the highest operating pressure of 0.4 mPa was observed. The decrease in the apparent membrane permeability at higher hesperidin concentration is likely to be attributed to the higher viscosity of the solution. For the 0.1 g/*l* and 0.5 g/*l* solutions, the measured viscosity fluctuated around 3.2×10^{-5} mPa·h and 3.7×10^{-5} mPa·h, respectively, which indicates the point that the viscosity changes with the amount of hesperidin in the solution. The higher viscosity of the 0.5 g/*l* solution results in a lower apparent value of the permeability of the membrane. From the slope of the line, the viscosity of 0.1 g/*l* and 0.5 g/*l* hesperidin solution was estimated to be 3.1×10^{-5} mPa·h and 3.5×10^{-5} mPa·h, respectively, which is within the measured range of measured values.

The behavior of pectin during ultrafiltration was investigated by using solutions of 2.0 g/*l*, and 6.0 g/*l* at a crossflow velocity of 0.88 m/s, which is within the turbulent flow range. High crossflow velocity was chosen so as to probably destroy any layer of gel that may have formed on the membrane surface. The plot of permeate flux versus ΔP is given in Fig. 3. The results clearly indicate the significant effects of pectin concentration on the permeate flux. Solutions with a higher pectin content (6.0 g/*l*) exhibited lower permeate flux. Throughout the ΔP investigated, the flux obtained from this solution was about 66% to 82% that of the 2.0 g/*l* solution. The leveling-off of flux at higher ΔP is possibly due to several factors, such as concentration polarization and gel-layer formation on the membrane surface. It is expected that the extent of gel-layer formation is more significant for the 6.0 g/*l* solution, resulting in a much lower permeate flux. For all the experiments, more than 90% rejection of pectin was obtained. As explained before, pectin is long-chain polymeric macromolecule, which is 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. A linear relationship of flux with ΔP was not observed as before, indicating that the membrane was not completely cleaned. Szaniawski and Spencer [10] have also reported this phenomenon in their work on the microfiltration of pectin solutions. However, fouling of the ceramic membrane by pectin is reversible, since the original water flux was obtained by employing perchloric acid instead of hydrochloric acid as the cleaning agent.

In this work, the same sample and membrane were used throughout each set of experiments over the entire range of ΔP investigated. A plot of permeate flux versus concentration of pectin under 0.1 mPa and 0.2 mPa stream press (ΔP) is given in Fig. 4. The results indicate that the permeate flux decreases faster as higher ΔP, since higher ΔP brought bigger flux at lower pectin concentration. Perhaps due to an increase in pressure of the system, the macromolecules which were already on the membrane or inside the membrane porous structure would be packed more tightly. At moderate

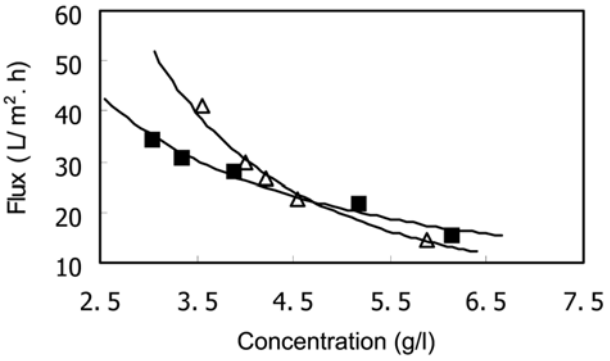

Fig. 4. Variations of permeate flux with concentration of pectin under different pressure in stream: ΔP=0.1 mPa (■); ΔP= 0.2 mPa (△).

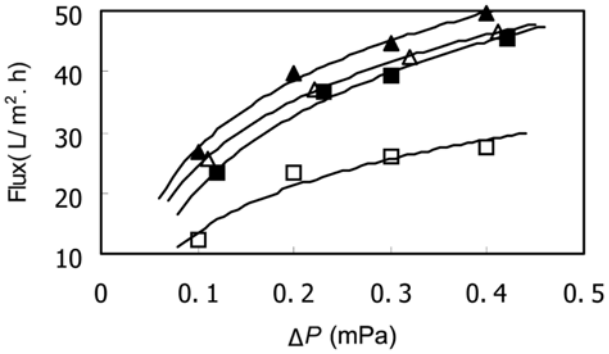

Fig. 5. Variations of permeate flux with ΔP for solutions with different pectin and hesperidin concentrations: 0.0 g/*l* hesperidin+2.0 g/*l* pectin (▲); 0.1 g/*l* hesperidin+2.0 g/*l* pectin (△); 0.5 g/*l* hesperidin+2.0 g/*l* pectin (■); 0.1 g/*l* hesperidin+5.0 g/*l* pectin (□).

pressures, there are still possibilities for the permeate to pass through. However, as higher pressures were applied, the densely packed pectin molecules formed a barrier across the membrane and prevented the flow of permeate flux, thus showing a decreasing trend with increasing pressure. It is important to highlight that within the range investigated, the permeate fluxes observed did not actually reach the limiting values but appeared to increase continuously. And it appears that the permeate flux profiles would depend on the experimental procedure used in collecting the data.

Experiments to study the variations of permeate flux with ΔP were also conducted on solutions containing different ratios of pectin to hesperidin under similar conditions. Results for the 0.0 g/*l*, 0.1 g/*l* and 0.5 g/*l* hesperidin in 2.0 g/*l* pectin as well as 0.1 g/*l* hesperidin in 5.0 g/*l* pectin are shown in Fig. 5. For all the ΔP and pectin concentrations investigated, compared with solutions with lower hesperidin concentration, the permeate fluxes for solutions with higher hesperidin concentration are always lower. For a given hesperidin concentration, a similar conclusion also applies to solutions with varying pectin content as evident when comparing the 0.1 g/*l* hesperidin solutions having different proportions of pectin. In general, it can be concluded that rapid decrease in the flux is expected for solutions containing high concentrations of hesperidin and pectin. From the analysis of hesperidin and pectin in the permeate and retentate streams, more than 90% pectin rejection but none for hesperidin was 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, and the ultrafiltration behavior of pectin mixture with pigment extraction could be predicted correspondingly.

After the best ultrafiltration conditions of pectin were identified, the permeation process of 10 *l* pectin mixture solution extracted from citrus peel was conducted, 8.2 *l* permeate and 1.8 *l* retentate were collected. The concentration in permeate and retentate, retention rate of main components as well as molecular weight are shown in Table 1. From the analysis of pectin and other main pigment components in the permeate and retentate streams, more than 90% pectin rejection but almost no concentration changes for pigment were observed for all feed; however, the retention rates calculated according to total content of every kind of pigment were far lower than that of pectin and were close to each other. Compared with pectin, the molecular weight of each pigment is not more than 1,000 Da, and is far lower than the MWCO of membrane. So a great deal of (80% above) pigment was permeated, and at the same time 90% more of pectin was cut off. The retentate rate of pigment could decrease more again as long as some pure water was added to previous retentate before a second process was conducted. Therefore, the decolorization, separation and purification of pectin preparations are achieved simultaneously through ultrafiltration process with a

Table 1. The results of main pigment and pectin analysis in mixture solution extracted from citrus peel with 0.01 mol/*l* hydrochloric acid

Component	Molecular weight (Da)	Concentration in permeate (g/*l*)	Concentration in retentate (g/*l*)	Retention rate (%)
Hesperidin	610.56	0.463	0.459	17.9
Naringin	580.53	0.025	0.024	17.4
Neohesperidin	610.56	0.357	0.362	18.2
Narirutin	580.53	0.114	0.113	17.9
Tangeretin	372.34	0.087	0.088	18.2
Nobiletin	402.36	0.029	0.029	18.0
Beta-carotene	536.87	0.562	0.557	17.9
Friedelin	426.72	0.0036	0.0036	18.0
Beta-sitosterol	414.71	0.0085	0.0086	18.2
Pectin	70,000 (average)	0.23	10.41	90.9

ceramic membrane.

CONCLUSIONS

Solutions of pectin, hesperidin, and their mixtures showed some variations in their ultrafiltration performance. Using a 30,000 MWCO ceramic membrane, a linear relationship of permeate flux with ΔP was obtained for hesperidin solutions. Differences in the slope of the lines for solutions of different hesperidin 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 increased with increasing ΔP 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 ΔP is limited by the formation of a gel layer on the membrane surface. The gelation of pectin is believed to have contributed to the observed behavior. The permeate flux decreased faster as higher ΔP, since higher ΔP brought bigger flux at lower pectin concentration. Compared with the more 90% retentate rate of macromolecular pectin, pigment mostly (80% above) permeated. So, the decolorization, the separation and purification of pectin preparations could be achieved simultaneously through ultrafiltration with a ceramic membrane.

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