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Study of Fouling Phenomena in Apple Juice Clarification by Enzyme Membrane Reactor

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ABSTRACT

Membrane separation processes have great potential in the food industry due to their ability to operate in mild conditions and to involve no phase change or chemical agents. The present work is part of a project which investigates the use of integrated membrane processes to produce fruit juices that are additive-free and have a natural,

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fresh taste. A study to optimize the depectinization and clarification of apple juice by enzyme membrane reactors has been carried out by using laboratory and semipilot scale equipments. The performance of the membrane systems has been investigated in terms of permeate flux and degree of depectinization. The effects of various parameters (transmenbrane pressure, axial flow rate, feed mixture, etc.) on membrane fouling have been evaluated, and the fouling mechanism has been interpreted in terms of complete pore blocking or cake filtration. The permeate flux improved with an increasing enzyme percentage in the feed mixture.

Key Words. Pectins; Enzyme membrane reactor; Permeate flux; Fouling

INTRODUCTION

The possibility of improving the organolectic properties of concentrated apple juice and reduce its costs by introducing integrated membrane operations in its production is the goal of a multinational research project sponsored by the European Union in the framework of the AIR3 CT94 - 1931.

A flow sheet of the proposed overall process is shown in Fig. 1. The refined raw juice is treated in an enzyme membrane reactor which combines the hydrolysis of pectins and the separation of depectinized juice by ultrafiltration. The clarified juice is then preconcentrated by reverse osmosis or membrane distillation. In this way the excess water can be reused and the preconcentrated juice can be concentrated again by pervaporation. This operation allows recoverery of the aroma compounds and preserves them from the evaporation process (60–80°C). After evaporation, the concentrated juice is enriched with the aroma compounds.

The experimental results discussed in this work refer to the first step of the project. In particular, to a study of the enzyme membrane reactor for hydrolysis of pectins and clarification of apple juice.

Micro- and ultrafiltration have already been used in the clarification and stabilization of raw juices, following the depectinization process carried out in a traditional batch mode (1–3). The possibility of integrating these two operations is currently under investigation due to progress in the modeling of catalytic membrane reactors (4), which, in principle, permits the operating parameters to be optimized for minimizing the fouling phenomena which reduces transmembrane permeate fluxes.

Pectins are linear polymer essentially composed of α-1,4-linked D-galacturonic acid units characterized to a certain extent by methylation of their carboxylic group (5, 6). By accounting for the presence of other sugar units, such as galactose, arabinose, and rhamnose as side groups along the galacturonic acid chain, the thickening properties of pectins have been understood. Because

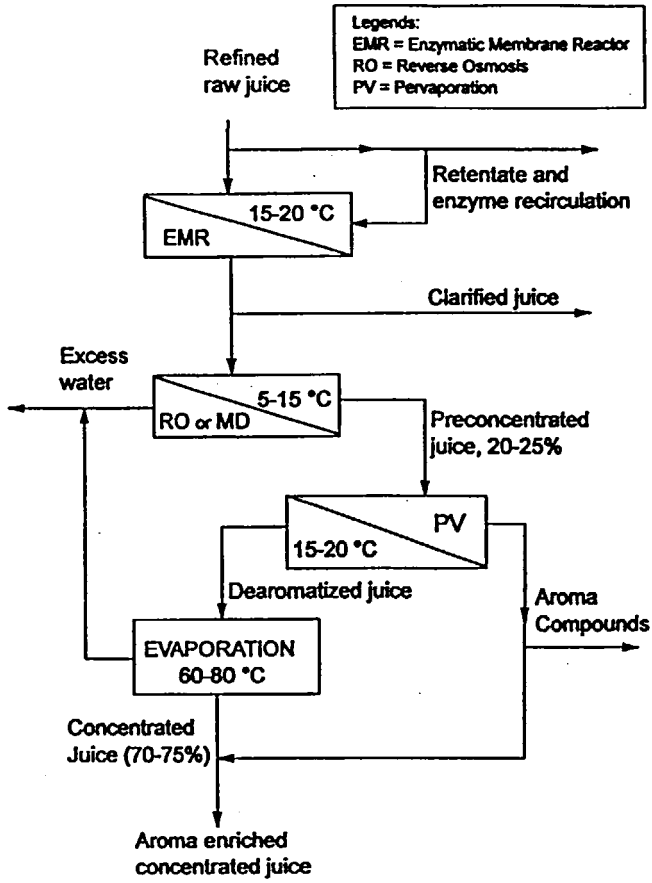

FIG. 1 Schematic diagram of apple juice and aroma compounds production by integrated membrane processes.

of these properties, pectins are responsible for the turbidity and high viscosity of fruit juices. In particular, it has been observed that at the same level of pulp, the viscosity increases as the concentration of pectins is increased, whereas at the same level of pectin the viscosity level remains unchanged even if the pulp content is increased by a factor of 6 (4). These results suggest that the pectin–sugars interactions are responsible for the high viscosity of a juice.

The effect of transmembrane pressure, axial flow rate, and feed mixture (refined raw juice with and without enzyme) on membrane fouling has been evaluated on the basis of permeate flux decline.

Membrane fouling in crossflow membrane separation processes is a key factor affecting the economic and commercial viability of a membrane system which essentially depends on the permeate fluxes obtained and their stability with time (7). Much work has been directed to studying the possibility of controlling fouling (8, 9). The advantage of membrane operation is that the separation process is athermal and involves no phase change or chemical agents. These features are very important factors in the production of new fruit juices with natural fresh tasting and additive-free (10–12). Fluxes are a function of time, and thus strongly depend on the operating conditions, membrane material, and feed solution (7). Provided the temperature is constant, the operating conditions in crossflow microfiltration are governed by the fluid dynamics variables crossflow velocity and transmembrane-pressure difference (TMP). Although the TMP is the driving force for permeation, the flux increases with pressure up to a limiting value TMP_{lim}, which depends on the physical properties of the suspension to be filtered and crossflow velocity. The latter is the second important parameter in the performance of a filtration system. The crossflow velocity affects the shear stress at the membrane wall, and consequently the rate of removal of the deposited particles responsible for flux decay. This consideration is consistent with the experimental evidence reported by several researchers who have found that by increasing the axial velocity, the permeate flux, J, increases according to a relationship generally expressed in terms of a power law (13). As far as the effects of the membrane type and the nature of the feed solutions on flux decline are concerned, much experimental data have proven that for a given separation, membranes with a larger pore size appear to offer no advantage in terms of flux performance (14). In the presence of large pores, the particles can penetrate the internal structure of the membrane and cause irreversible fouling. On the other hand, a membrane whose representative pore size is smaller than the size of all particles suspended in the feed stream merely acts as a support. In this case the layer of particles accumulated during the early filtration period to form a secondary membrane or cake whose thickness, responsible for an additional mass transport resistance, can be effectively controlled by an appropriate choice of the fluid dynamic conditions.

In this work the effect of the operating conditions on the permeate flux during crossflow filtration of refined apple juice during enzymatic treatment or without enzyme has been investigated.

A mathematical model able to describe the permeate flux decline in CFMF has recently been presented (15). The model is based on the classical constant pressure dead-end filtration Eq. (16) which have been unified in the following general differential equation:

$$-dJ/dt = k(J - J_{lim})J^{2-n} \quad (1)$$

where J_{lim} is the limiting value of the permeate flux attained in steady-state conditions; k and n are a phenomenological coefficient and a general index, respectively, both depending on the fouling mechanism. According to an analysis reported in the cited literature (15), the exponent n can assume the values 0, 1, 1.5, and 2. Depending on the value that n assumes, Eq. (1) degenerates into four different equations representative of possible fouling mechanisms. The phenomenology and the effect on mass transport related to each value of n are described in Table 1.

Although the model expressed by Eq. (1) is not a predictive one, on the basis of experimental data it permits the fouling mechanisms involved dur-

TABLE 1
Mechanisms of Fouling and Their Effect on Mass Transport

Fouling mechanism	n	Phenomenology	Effect on mass transport
Complete pore blocking	2	When the particles are larger than the pore size, the membrane area reached by particles is blocked as a consequence of a complete pore obstruction.	Reduction of the membrane surface. Depending on the crossflow velocity, permeate flux may be increased by increasing the applied transmembrane pressure.
Partial pore blocking	1	Solid particles or macromolecules that at any time reach an open pore might seal it. Also, particles may bridge a pore by obstructing the entrance but not completely blocking it.	
Cake filtration	0	Particles or macromolecules which do not enter the pores form a cake on the membrane surface. The overall resistance is composed of a cake resistance and a membrane resistance, which is assumed to remain unchanged.	The overall transport resistance through the membrane is composed of cake resistance and membrane resistance, which is assumed to remain unchanged.
Internal pore blocking	1.5	Particles enter the pores and either get deposited or adsorbed, reducing pore volume. The irregularity of pore passages causes the particle to become tightly fixed, blinding the pore.	In this case membrane resistance increases as a consequence of pore size reduction. Besides, if internal pore blocking occurs, the fouling becomes independent of the crossflow velocity and no limiting value for the flux may be attained, that is, $J_{lim} = 0$.

ing the filtration process to be determined according to the estimated value for n.

MATERIALS AND METHODS

Refined raw apple juice (apple juice without pulp) was provided by Valle Ballina y Fernandez from Spain. The enzymes were commercial liquid solutions of Cytolase 219 (Genencor) or Rapidase Liq. plus (Gist Brocades) with protein concentrations of 1.0 and 1.18 g/mL, respectively. The major enzymatic activities in Cytolase 219 are pectinase, cellullase, and hemicellulase. It has an activity with apple pomace pectin of 3700 U/g (as provided by the source). Rapidase Liq. plus is an enzymatic preparation obtained from selected strains of *Aspergillus niger* and *Tricoderma longibrachiatum*. It is composed of pectinases, hemicellulase, and cellulase activities. Experiments have been carried out at pH 4.00, room temperature, and 40°C (the latter temperature was recommended for the highest enzyme activity, but room temperature has also been used to preserve fruit juice from heat degradation). The enzyme solutions were directly added to the juice. The chemical reactions were initially carried out in a stirred tank reactor for 2 hours. After this time the reaction mixture was recirculated through the lumen circuit (inner circuit) of asymmetric ultrafiltration (UF) membrane modules in order to separate the fractions of hydrolyzed pectins. The concentration of pectins was measured by the meta-hydroxybiphenyl method (17).

In some specific cases the enzyme was immobilized by crossflow filtration: the enzyme in aqueous solution was ultrafiltered through the membrane from lumen to the shell side. Protein concentration was measured by the BCA test (from Pierce). The amount of immobilized enzyme was obtained by mass balance between the initial and final solution. After immobilization was completed, the juice was added and the reaction was started.

Experiments were carried out with equipment on both the laboratory and semipilot scales.

Asymmetric capillary membranes made of polyamide (PA) with nominal molecular weight cut-offs (NMWCO) of 50, 10, and 2 kDa were used on a laboratory scale. The modules were made of four capillary membranes encased in parallel in a Pyrex cylinder 200 mm long. Capillary membranes made of PA with 50 kDa cut-off had $d_i = 1.1$ mm and an inner membrane surface of 25×10^{-4} m^2. Capillary membranes made of PA with cut-offs of 10 and 2 kDa had $d_i = 1.5$ mm and an inner membrane surface area of 34×10^{-4} m^2.

Tubular membranes made of polyvinylidene fluoride (PVDF) with a NMWCO of 18 kDA have been used on a semipilot scale (Koch, Dusseldorf, Germany). The module consisted of three tubular membranes connected in

series in a plastic cartridge (HF-180) 0.5 m long. The inner diameter of fiber was 12.5 mm, and the inner membrane surface area was 5×10^{-2} m^2. The juice was recirculated continuously along the lumen by a 0.75 HP gear pump by varying the axial velocity and transmembrane pressure (TMP). A tube-and-shell heat exchanger, placed after the membrane module, was used to maintain the juice temperature at approximately 20°C.

RESULTS AND DISCUSSION

Experiments with Capillary Membranes on the Laboratory Scale

Enzyme membrane reactors have been created by integrating UF membrane modules with a stirred tank reactor or using UF membranes alone as a reaction and separation unit (18). In the first configuration the enzyme is suspended in bulk solution where the chemical reaction takes place; the membrane acts as a selective barrier, rejecting macromolecules (enzyme, pectins, etc.) which, on the basis of their respective sizes, cannot pass through the pores of the membrane.

In the other case the enzyme is immobilized on the inner surface of the membrane; the membrane module is continuously fed with juice, and both reaction and separation occur at the membrane level.

UF Membranes Combined in a Stirred Tank Reactor (free enzyme)

Experiments with the enzyme suspended (using the first type of configuration) were carried out using 500 mL of apple juice at 40°C. The amounts of cytolase enzyme solution used were 0.05 and 0.5% v/v. Cytolase was added to the juice and the reaction was carried out in the stirred tank reactor for 2 hours before the start of the crossflow ultrafiltration process.

Experiments were carried out by the following procedure. The reaction mixture was initially ultrafiltered through a membrane module with a NMWCO of 50 kDa; the permeate collected from this module (named PERM 50 kDa) was then ultrafiltered through a membrane module with a NMWCO of 10 kDa, and again the permeate obtained (PERM 10 kDa) was ultrafiltered through a membrane module with a NMWCO of 2 kDa (PERM 2 kDa). In other words, the permeate from each module constituted the feed of the subsequent step (discontinuous cascade ultrafiltration mode) (19). During crossflow filtration the axial flow rate was 1.56 L/h and the transmembrane pressure (TMP) was 0.7 bar. The concentration of pectins in each permeate solution was measured. In this way it was possible to identify the molecular

TABLE 2
Recovery of Pectins by Discontinuous Cascade Ultrafiltration through Capillary Membrane Modules Using Different Amounts of Enzyme Solution

Sample	Volume (mL)	Concentration of pectins (mg/mL)	Mass of pectins (mg)	% of recovered fraction
		(a) 0.05% of Enzyme		
Initial feed	500	0.771	385	
Permeate: 50 kDa	80	0.518	41.6	10.6
Permeate: 10 kDa	65	0.631	40.9	10.3
Permeate: 2 kDa	32	0.199	6.8	6.0
		(b) 0.5% of Enzyme		
Initial feed	500	0.199	189.5	
Permeate: 50 kDa	330	0.286	65.67	34.7
Permeate: 10 kDa	224	0.106	64.06	34
Permeate: 2 kDa	130	0.379	13.78	8.4

weight range values of the hydrolyzed pectins. The results of typical runs with 0.05 and 0.5% v/v of cytolase 219 enzyme mixture are reported in Table 2. In both series of experiments the enzyme produced fractions of pectins with molecular weights between 10 and 2 kDA and lower than 2 kDA. A 10% enzyme increase improved the percentage of recovered pectins to 24%.

The permeate flux at steady state with pure water and reaction mixtures is reported in Fig. 2, where it is shown that a higher permeate flux is obtained by increasing the amount of enzyme. The permeate flux is determined by the applied pressure, membrane permeability, and solution composition. Flux values for applied pressure in ultrafiltration processes are considered acceptable around 20 $L/h \cdot m^2 \cdot bar$. In our systems, when using 0.5% of enzyme, permeate fluxs (per applied pressure) of 28 $L/m^2 \cdot h \cdot bar$ through 10 kDa membranes and of 70 $L/m^2 \cdot h \cdot bar$ through 2 kDa membranes were obtained. These results indicate that from the economic point of view a 10% of increase in enzyme content can be balanced by an increase of flux. The reason for the higher flux through the membrane with lower pore dimensions is due to the solution composition. The solution fed to the 2 kDa membrane is the permeate coming from the 10 kDa membrane and thus is a clarified solution (which means a solution containing no protein but only pectins and others components with a molecular weight lower than 10 kDa).

Experiments were also carried out using rapidase enzyme 0.5% v/v added to 500 mL of refined raw juice thermostated at 40°C. The reaction was initially carried out in a stirred tank reactor for 2 hours. After this time the reaction mixture was ultrafiltered through PA membrane modules of 50 kDa. For 9

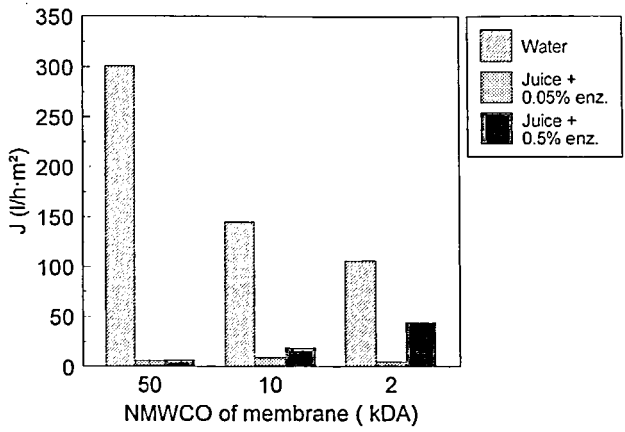

FIG. 2 Permeate flux through membrane with different molecular weight cutoff using water and juice containing 0.05 and 0.5% enzyme. (The system operated in the discontinuous cascade mode, where the permeate from each membrane was the feed of the subsequent membrane.)

hours the permeate and retentate streams were recirculated to the feed tank to maintain steady conditions throughout the runs. The experiments were carried out at TMP = 0.7 bar and feed flow rate = 2.7 L/h.

The same kinds of experiments were carried out using PA membrane modules of 10 and 2 kDa. The results, summarized in Table 3, show the rapidase produces a higher depectinization degree with respect to the cytolase.

A continuous flux decay in the permeate stream was observed in all the experiments, as described in Fig. 3.

TABLE 3
Recovery of Pectins by Single Ultrafiltration of Reaction Mixture through Different Membranes[a]

NMWCO (kDa)	Feed volume (mL)	Permeate volume (mL)	Concentration of pectins in the permeate (mg/mL)	Mass of pectins in the permeate (mg)	% of recovered fractions
50	500	440	0.219	96.36	49.2
10	500	310	0.359	111.29	56.78
2	500	25	0.252	6.3	3.2

[a] The concentration of pectins in each feed volume was 0.392 mg/mL and the mass was 196 mg.

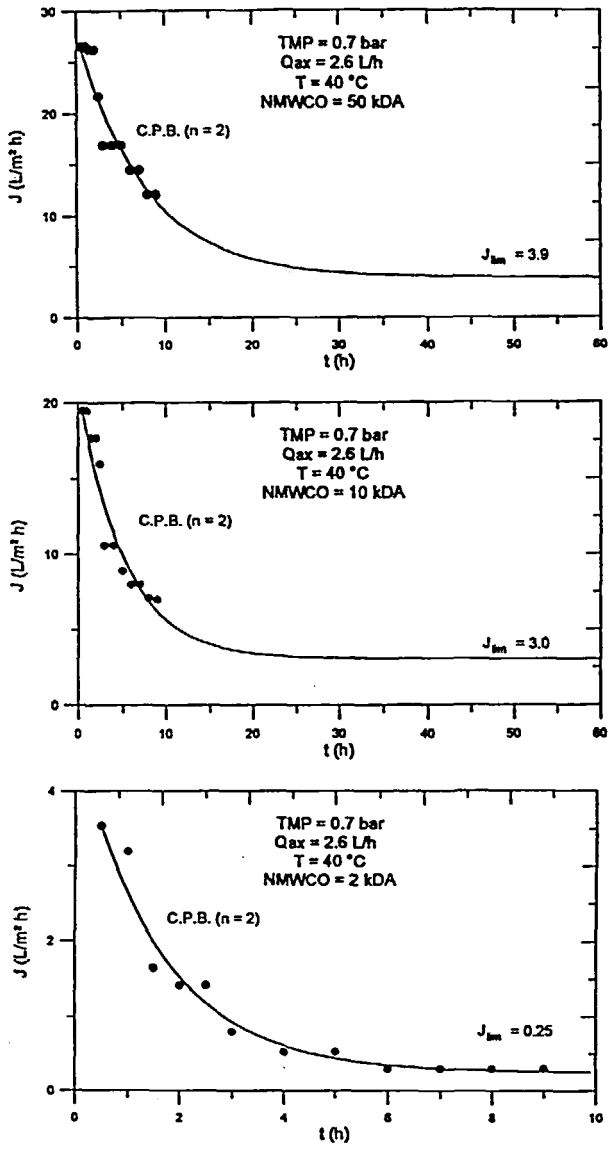

FIG. 3 Flux decay and fouling mechanism for UF membranes with different NMWCO. Comparison between experimental data (solid circles) and theoretical predictions (lines). The feed of each membrane was fresh refined raw juice.

TABLE 4
Fouling Index as a Function of NMWCO

Membrane NMWCO (kDa)	Fouling index
50	0.10
10	0.12
2	0.30

The lower the NMWCO of the membrane, the lower the limit value of the permeate flux. In particular, a near total flux reduction has been observed after 9 hours for the membrane with NMWCO = 2 kDa, whereas flux reductions of 64 and 54% were observed in the same operating conditions for membranes with NMWCO of 10 and 50 kDA, respectively.

Besides, by analyzing the fouling mechanism on the basis of Eq. (1), it appears that regardless the NMWCO of a membrane the prevailing mechanism is complete pore blocking with $n = 2$. Furthermore, the flux limit estimated by the model was in a good agreement with that experimentally observed for the membrane with a NMWCO of 2 kDa. In the other cases the theoretical predictions show that after 9 hours the system is very far from the steady-state condition.

A proper fouling index for each membrane module was also evaluated from the slope of the fitting straight line of the experimental (permeate flux)–(time) pairs represented on a semilogarithmic scale.

As summarized in Table 4, the fouling index increases as the NMWCO of the membrane is decreased in the order 50, 10, and 2 kDa.

This study on apple juice clarification by integrated processes of pectinolysis and ultrafiltration shows that ultrafiltration membranes with larger pores reduce the extent of the pore-blocking fouling phenomena. In particular it may be argued that a membrane with a NMWCO of 10 kDa could be the most appropriate in terms of depectinization degree and flux because it gives a higher recovery of hydrolyzed pectin, a very good clarification level, and the same approximately fouling level as a membrane with a NMWCO of 50 kDa.

This conclusion is strengthened when we consider that the membrane with a NMWCO of 50 kDa showed very poor selectivity toward pectinase from other sources.

In a different series of experiments the permeate flux through a PA 10 kDa membrane was evaluated at 40°C, using refined raw juice with enzyme suspended or just refined raw juice (without enzyme). Membrane modules were initially used to ultrafilter 250 mL of refined raw juice containing rap-

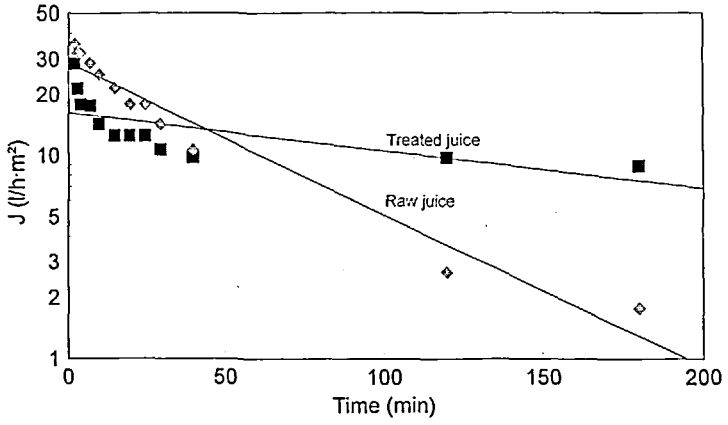

FIG. 4 Permeate flux through PA 10 kDA membrane using juice treated with enzyme and untreated juice. TMP = 0.7 bar; T = 40°C; axial flow rate = 2.8 L/h.

idase. After regeneration of the membrane with 0.05 N NaOH at 40°C, the modules were used to ultrafilter 250 mL of refined raw juice (without enzyme). As shown Fig. 4, the permeate flux at steady state is higher when the juice treated with enzyme is used. This accounts for the increase of flux because of the presence of enzyme more than to a decrease of viscosity at 40°C.

UF Membranes Acting as Reaction and Separation Unit (enzyme immobilized)

Experiments with the enzyme immobilized on the inner surface of membranes, wherein the membrane works as a catalytic interface and separation unit, were carried out using PA membranes of 50 and 10 kDa. The enzyme was immobilized by crossflow filtration at room temperature: 250 mL of cytolase 219 solution in water (0.5% v/v) were ultrafiltered from lumen to shell at an axial flow rate of 1.56 L/h and a TMP of 0.7 bar. The amount of gelified enzyme was determined by the mass balance between the enzyme present in the feed solution at the beginning and that present in the permeate and retentate at the end. The enzyme concentration was measured by the BCA protein assay test from Pierce.

The results indicated that the enzyme was only retained by the 10 kDa membrane. About 30 mg of enzyme were gelified on the inner surface of the membrane (34×10^{-4} m^2). After immobilization of the enzyme the module was fed with refined raw juice and the reaction was carried out in a batch

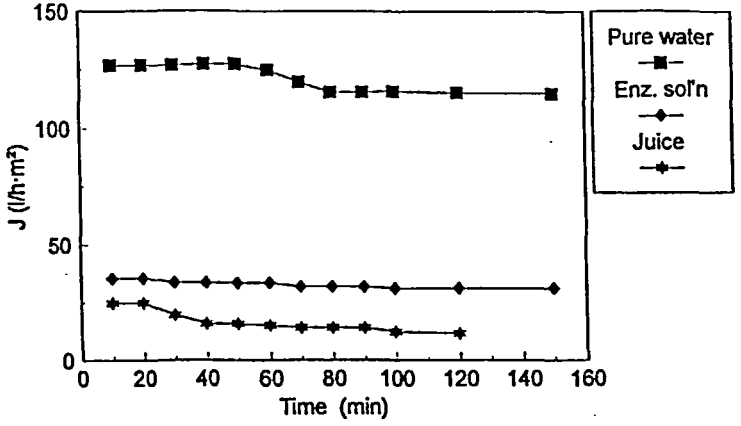

FIG. 5 Permeate flux with pure water, enzyme solution (during immobilization), and refined raw juice (after immobilization).

recycle mode. In other words the permeate was recycled back to the retentate stream and both were recirculated through the membrane for about 20 hours. In this way it was possible to operate at constant volume. After this time the permeate was collected in a separate tank. The amount of pectins present in the permeate was about the 50% of the total mass present in the feed solution at the beginning.

Figure 5 shows the permeate flux behavior through a 10 kDa membrane with three different solutions: pure water, enzyme solution (during immobilization), and refined raw juice (during ultrafiltration of juice, after immobilization). With this last solution the permeate flux decreased to about 20 $L/m^2 \cdot h \cdot bar$. From a comparison with the results shown in Fig. 4, it is possible to conclude that the permeate flux improves when the juice is treated with pectinase enzyme; in particular the permeate flux is resulted higher when the enzyme is immobilized on the membrane. This is probably due to the fact that the presence of gelified enzyme prevents fouling of the pectins which are hydrolyzed as they deposit on the membrane surface. This means that the high molecular weight pectins (probably in the presence of sugars) cause a permeate flux decline greater than do proteins.

Experiments with Tubular Membranes on Semipilot Scale

Experiments were carried out using semipilot plant equipment including a membrane module of PVDF 18 kDa with a membrane surface area of 5 ×

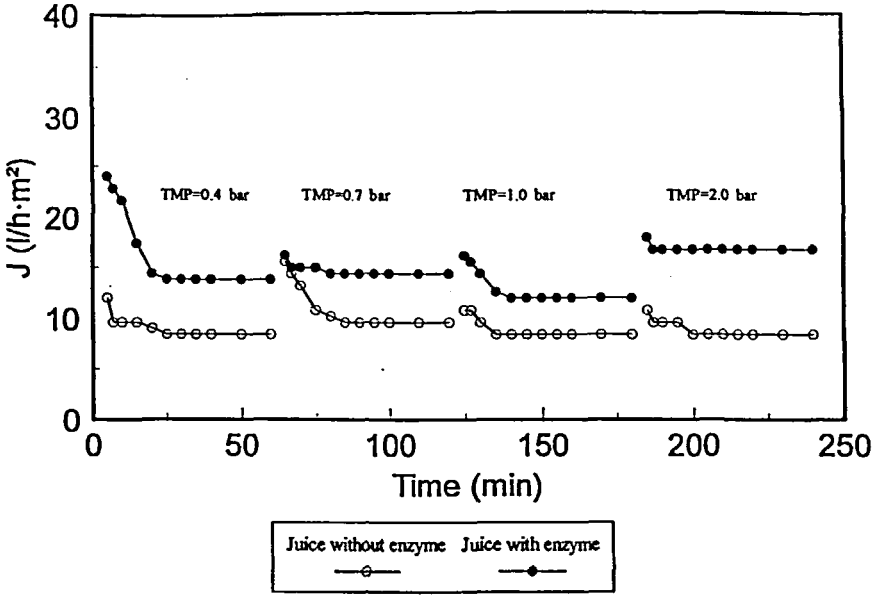

FIG. 6 Ultrafiltration of treated and untreated juice through 18 kDA membrane at an axial flow rate of 360 L/h and different TMPs.

10^{-2} m^2. The permeate flux was studied as a function of the TMP and the axial flow rate. In addition, analysis of flux performance when a certain amount of enzyme was added to the juice was carried out.

In Fig. 6 the time evolution of permeate flux of refined raw juice treated with enzyme is compared with that observed with only refined raw juice under the same operating conditions. The permeate flux achieves the same limiting value in all the experiments, regardless the applied TMP. However, due to the hydrolytic action of the enzyme toward the pectins, the limiting flux increases by about 50% with respect to ultrafiltration of refined raw juice.

In Fig. 7 the same comparison is reported at a higher feed flow rate, but in this case there was not the advantage of using higher pressure to obtain a higher permeate flux. On the contrary, the presence of the enzyme allows the limiting value of the flux to increase by about 30%.

In order to evaluate the effects of enzyme on the fouling mechanism involved during crossflow ultrafiltration of apple juice, estimations of a model parameters k and n in Eq. (1) were carried out according to a nonlinear regression optimization procedure based on Powell's method of conjugate directions

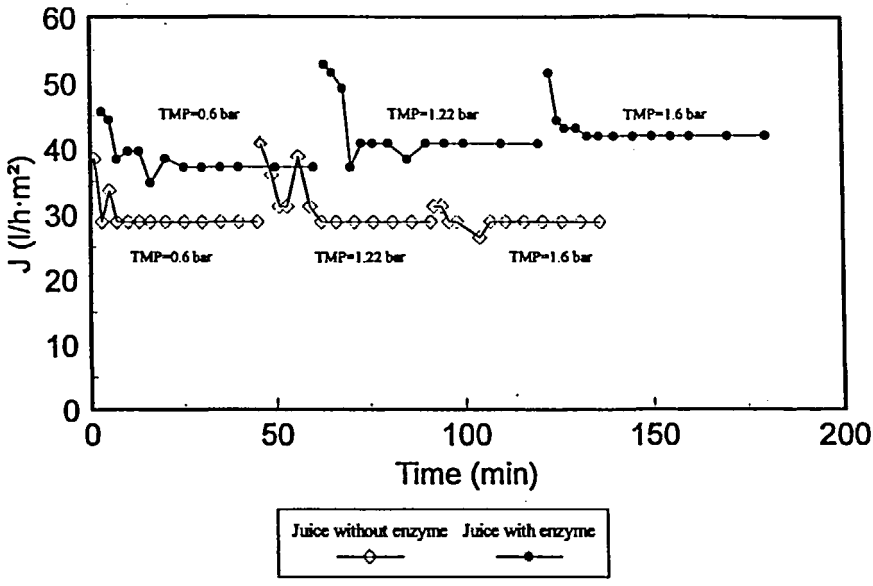

FIG. 7 Ultrafiltration of treated and untreated juice through 18 kDA membrane at an axial flow rate of 1000 L/h and different TMPs.

(20) as described in detail in previous work (21). For each set of J–t experimental data, a series of four optimization runs was performed sequentially by assigning n (n = 0, 1, 1.5, 2) and the corresponding steady-state value J_{lim} which had already been observed experimentally. The procedure for the estimation of parameter k consisted essentially of an iterative process of numerical solution of Eq. (1) by adaptive-step-size Runge–Kutta algorithms. The process was repeated until the minimum for the sum of squares deviation (SSD) between numerical predictions and experimental data was found. The minimum value of SSD was the criterion used to single out the optimum value of n and establish the fouling mechanism.

In Fig. 8 a comparison between numerical predictions and the experimental data is shown for a given feed flow rate and TMP values for refined raw juice with and without enzyme treatment. As reported in the figure, from the estimated value of n it can be seen that when no enzyme is added to the juice, the ultrafiltration process is governed by a "cake filtration" fouling mechanism. This means that the convective flux, which moves from the bulk solution toward the membrane, prevails on the rate of shear-induced backdiffusion of the rejected material, thus leading to the formation of a cake on the membrane surface.

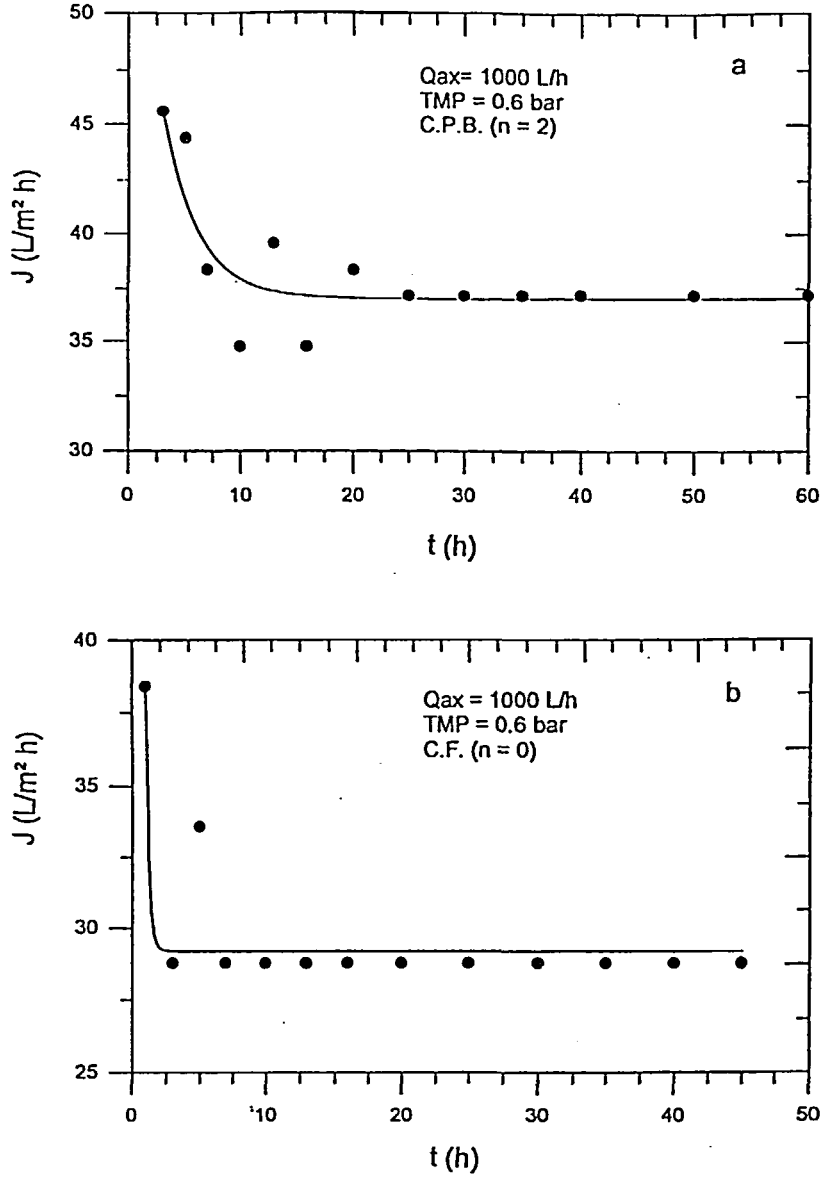

FIG. 8 Flux decay during UF of juice treated with enzyme (a) and untreated juice (b). Comparison between experimental data (solid circles) and theoretical predictions (lines).

On the other hand, in the presence of the enzyme the prevailing fouling mechanism is "complete pore blocking." In other words, as a consequence of the hydrolytic action of the enzyme, caking on the membrane does not take place and additional transport resistance is reduced.

CONCLUSIONS

A study on the treatment of apple juice in enzyme membrane reactors has been carried out in the present work. Membranes with different nominal molecular weight cut-off, (NMWCO) were used. Our membrane reactors combined a stirred tank reactors (enzyme-free) and an ultrafiltration process or immobilized the enzyme on the membrane surface.

We observed that the most suitable membrane in terms of flux, enzyme retention, and pectin fractions recovered were membranes with an NMWCO of 10 kDa.

The use of pectolytic enzymes improves the permeate flux. In particular, when treating the refined juice with 0.5% of free enzyme at an applied pressure, a permeate flux of about 15 $L/m^2 \cdot h \cdot bar$ was obtained; when using refined raw juice treated with an immobilized enzyme (30 mg in 34×10^{-4} m^2), the resulting permeate flux was about 20 $L/m^2 \cdot h \cdot bar$.

Experiments carried out on a semipilot scale (PVDF tubular membrane, 18 kDa, 5×10^{-2} m^2 membrane area) confirmed that the permeate of refined juice is higher when it is treated with enzyme; the flux increases with increasing axial flow rate but it does not increase for increasing TMP.

The experimental results confirm the possibility of controlling the fouling mechanism in apple juice treatment by an enzyme membrane reactor. In general, the ultrafiltration process is governed by a cake filtration fouling mechanism when an enzyme is present, while the prevailing fouling mechanism is complete pore blocking when these enzymes are added. An accurate analysis of flux decay with time for extrapolation of asymptotic values is also necessary.

The fluxes observed in the fluid dynamics conditions explored appear of potential interest for industrial development of the process.

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