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INORGANIC MEMBRANES IN FOOD PROCESSING

Micro- and ultrafiltration membrane processes are extremely useful in a food processing. Of numerous technological solutions of the micro- and ultrafiltration membranes, wide application has been found for inorganic membranes, especially those formed-in-place (FIP). The investigations undertaken in the field of protein separation on the microporous membrane with TiO₂ layer have allowed us to determine the conditions providing the lowest fouling index and the least irreversible fouling, while retaining BSA ionic strength solutions.

1. INTRODUCTION

Progress of civilisation, which since years has been causing problems with insufficiency of sources and energy, deficit of water, pollution of environment – paves the way for undertaking many efforts in order to develop the methods of processing raw materials into products (components) which are very easy to be used.

On the other hand, scientist's interests in a great deal are concentrated on the recovery of materials and media.

Production technology used in food processing can be a very good example of approaching this problem. Increasing demand for the processed food is conducive to the faster extension of studies related to improvement and development of new methods.

Such unique technological possibilities are offered by membrane processes.

Last years' achievements in this subject practically allow us to use them in all branches of industry where there is a need of separation, clarification, fractionation and concentration of both organic and inorganic matters.

The membrane technique was attractive to the food processing mainly owing to moderate operating temperatures, lack of phase transitions and low energy consump-

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tion. Membrane processes offer multiple porosity levels which could replace several traditional processes in a single operation.

Processes of the major importance among membrane technologies are the following: microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), dialysis (D), electrodialysis (ED), membrane distillation, facilitated transport and others. They differ in the sort of used membranes, the size of separated molecules, driving force and method of separation as well as the application. Some of them, for example: microfiltration, ultrafiltration, reverse osmosis, dialysis and electrodialysis, have widely been established since a long time. Application of such new processes as facilitated transport or membrane distillation is still under development [1].

In 1988, the annual sale of membranes and membrane modules for the food industry was estimated at the level of about 160 million US \$ or about 15% of the total annual sales, from which 75, 55, 45 and 15 million US \$ have fallen to MF, UF, RO and ED, respectively.

Most of the microfilters installed so far are run in the dead-end mode. The main applications are found in the beverage industry where microfiltration is used to achieve sterile filtration and clarification. The use of cross-flow microfiltration is increasing, leading to a better performance and a substantially longer membrane life. In this paper, only cross-flow applications will be discussed.

Dynamically formed "permanent" membranes that were designed by American Company Du Pont are very promising when their application in the food processing is taken into account. Such membranes have been tested by our research team for the last few years. Determination of the possibilities of separating the protein's solutions using such membranes is performed at present.

2. INORGANIC MEMBRANES

There are different methods for formation of the membranes; however, membranes can be divided into two main groups, i.e.: organic membranes and inorganic membranes. Inorganic membranes can be divided further into ceramic (mineral) ones and metallic ones.

Inorganic membranes consist of a porous support and one or more filtration layers. Because both the support and dispersed substances (in many cases) are of inorganic origin, those membranes are also called inorganic membranes. The porous supports of inorganic membranes are made out of powders which are sintered in order to obtain a unique structure, construction and rigidity. The filtration coating can be made out of the same material as the support or the other materials such as composites, for example.

Most of the industrial inorganic membranes are of tubular configuration. They mainly differ in pore diameter and thickness of support. Those membranes are asym-

metric, composed of thick, porous structure serving as a mechanical support for a thin filtration layer.

The construction of the membrane, the sintering process and the tubular configuration cause that those membranes have a very high resistance to organic and inorganic solvents, high pressure (10–30 bars) and high temperature (above 100 °C). The main disadvantages of inorganic membranes are: low packing density and relatively high cost of elementary surface production.

The first modules of inorganic membranes were put into operation in the processing industry at the end of 70's. They were made out of a porous carbon as a support and zirconium oxide (ZrO_2) as a filtration layer. A couple of years later a second membrane of this kind, alumina membrane, was reported [2]. Since then, there have been reports on various metallic membranes including stainless steel (SS), carbon-carbon and others. It should be noted that the idea of using a metallic membrane did not start with the carbon membranes. Other metallic materials such as Pt, Au, Ag were tested for the separation of gaseous streams, especially at the very high temperatures. Today, industrial installations are of three kinds, i.e., carbon with ZrO_2 , alumina-alumina and alumina with ZrO_2 .

2.1. TYPES OF INORGANIC MEMBRANES

2.1.1. CARBON- ZrO_2 - THE FIRST INORGANIC MEMBRANE

This membrane is the most versatile one. The filtering skin layer is made of ZrO_2 powder which forms a membrane of different pore sizes. The pores of these membranes have sizes typical of microfilter, 0.08–0.45 μm diameter, and usually the cut-off for UF ranges from 10,000 to 150,000 daltons (D). The membrane consists of a tube 1.2 m long, 6 mm inner diameter (ID) and 10 mm outer diameter (OD). Reported pure water flux (PWF) is 140–1,000 $dm^3/h \cdot m^2$ (4 bars at 25 °C). Maximum operating pressure is 10 bars and the membrane lifetime is 8,000–10,000 working hours. Cartridges of 1, 7, 37, 151 and 252 tubes are available.

2.1.2. α -ALUMINA MEMBRANE

This membrane is made of an α - Al_2O_3 porous support. The membrane is of a multi-channel geometry with 19 tubes of 4 mm ID. The pressure drop of porous support is negligible. Another available geometry is a 6 mm ID multi-channel module for highly viscous fluids and a single tube of 7 or 15 mm ID for test purposes. The membrane is used as a microfilter with pore size of 0.2–5 μm when made only of α -alumina. The use of zirconia layer of the thickness of 50–100 nm with a very good corrosion resistance is also common. A filtration module can be constructed of several multi-channel blocks with varying from 0.01 to 3.8 m^2 membrane surface area. In addition to its high corrosion resistance, the alumina membrane as other inorganic

membranes is rigid and can withstand up to 40 bars. Some other constructions of such a kind of membrane were also reported. These were: a hollow-tube, spirally wound to form a self-supporting cylindrical unit of 100–200 fibres, 0.5–2 mm (ID) and a flat-sheet capillary pore structure, 45–60 μm thick.

2.1.3. CARBON-CARBON MEMBRANES

This is relatively new membrane with 6 mm inner diameter and 0.7 mm wall thickness. The filtering layer of the membrane is 0.1–1 μm and is claimed to be hydrophobic. It has high chemical resistance and is reported to operate up to 400 $^{\circ}\text{C}$. A module is composed of several 1.2 m long tubes. It was reported to operate as a microfilter with water flux of 455 $\text{dm}^3/\text{h}\cdot\text{m}^2\cdot\text{bar}$ [3].

2.1.4. STAINLESS STEEL MEMBRANES

The porous support is made of sintered SS welded tube. The IDs of the tubes are reported to be 1.56 mm and 3.12 mm, and the length of the tubes varies from 3.04 to 42.7 m. The zirconium oxide membrane was formed-in-place on the inner surface of the SS tubes.

In the first American and Japanese publications relating to this type of membranes, they were called, for the way of their formation, the dynamic membranes. These membranes are formed on the porous supports during the filtration of solutions containing an admixture of the dispersed material under the adequate conditions of the cross flow and pressure. The supports themselves have a nominal size of pores from 30 \AA to 50,000 \AA , but they do not have an ability to stop elements and ions of the dissolved substances of low molecular weight. However, because of the dispersed element sorption, which takes place on the support's surface turned towards the solution, a semi-permeable layer is formed. The formation of useful RO membranes by this procedure was first discovered by MARCINKOWSKI et al. [4]. Such membranes were originally called dynamic membranes because it was thought that a continuous feed of the membrane-forming substances was required. When it became clear that the membranes after their formation were really stable, they were described as "dynamically formed" membranes. However, the previous name was still used and after a couple of years the trade name of these membranes, formed-in-place or FIP membranes, was introduced. It practically stays so until now, at least in the USA.

Depending on the material used for dynamic layers and the nature of the porous support, one can obtain the dynamic membranes with different characteristics. There is a basic division of the dynamic membranes shown in table 1. The membranes were divided into three basic classes. The number, indicating the kind of membrane class from 1 to 3, was based on the prime geometrical dependences connected with a radius

of a particle of dissolved substance (the material of the dynamic layer) r_a and a radius of pore of the porous support r_0 .

Table 1

General division of the dynamic membranes

Type of the dynamic membranes	Relative pore size of support	Material of the dynamic layer	Support
Class 1	$r_0 < r_a$	polymers-forming gel and polyelectrolytes	ultrafiltration filter
Class 2	$r_0 \gg r_a$ $r_0 < r_a$	inorganic colloids	insoluble, selective, microporous supports
Class 3	$r_0 \approx r_a$	flexible polymers and polyelectrolytes	membranes with 0.05 mol/dm ³ NaCl, rejection of 5–50%

The deposition sequence can consist of several steps, depending on the type of membrane being prepared. The first step often consists in the deposition of one or more kinds of particles, normally inorganic. This is sometimes called precoating. At this point, a MF membrane (class 1) has been formed and it may be used as such. Inorganic gel or organic polymer layer may be applied to obtain an UF membrane. If the hydrous Zr (IV) oxide, for example, is used as the membrane-forming material, the resulting dynamic membrane will be in general UF dynamic membrane of class 2, in the USA the so-called ZOSS membrane. Reverse osmosis membranes, in the USA called ZOPA membranes that are dynamic membranes of class 3, one can obtain by sequential deposition of hydrous Zr (IV) oxide followed by poly/acrylic acid on suitable UF membrane as a substrate [5].

In comparison to polymeric membranes, that are widely used at the moment, dynamic membranes are considered much better and their advantages are as follows:

- high mechanical and chemical strength,
- a possibility of *in situ* membrane replacement,
- a very long life time of a supporting tube,
- a very high thermal stability,
- a high permeability reaching a value of hundreds of dm³ per m² of surface in an hour.

An additional essential virtue of the dynamic membranes is their simplicity in construction and structure of apparatus.

A crucial step in the development of this kind of membranes was a permanent membrane that was manufactured for the first time by Du Pont Company. It can be obtained by recirculation of a titanium dioxide solution through a stainless steel macroporous support. TiO₂ layer formed after being sintered makes up a new semi-permeable layer of a membrane.

At the moment this company performs wide research focused on formed-in-place (FIP) membranes with the ceramic and steel supports as well as with the organic and inorganic coatings of different configurations. Various materials used allow for construction of different kinds of membranes, i.e., MF, UF, NF and RO, that are foreseen to be tailored to a wide range of applications.

3. MICRO- AND ULTRAFILTRATION PROCESSES

These processes are extremely useful in the case of biological substances that are sensitive to temperature.

Microfiltration process is used for separation of micro- and macromolecules of 0.5–50 μm sizes.

The microporous membranes with the pore radius ranging from 0.05 to 10 μm are used as the separating barriers. A driving force of the microfiltration process is the difference of hydrostatic pressure in the range of 0.01–0.1 MPa. In this case, a mass distribution occurs according to a sieve mechanism.

Typical transmembrane flows obtained in MF are in the range from $1.39 \cdot 10^{-4}$ to $55.56 \cdot 10^{-4} \text{ m}^3/\text{s}$.

UF membranes are applied to separation, fractionation as well as concentration of solutions containing micro- and macromolecules with diameters of 1–50 nm. The continuous process of the substance separation is driven by transmembrane pressure and there is no change of phase or interfacial mass transfer. The ultrafiltration is used for separation of the particles of a dissolved substance with a relatively large molecular weight, i.e., proteins, resins of natural polymers and other complex organic compounds or colloidal substances such as: alumina, cytochromes, minerals, microorganisms, from their solutions, most often water solutions. The mentioned substances generate rather low osmotic pressure in water solutions so there is only a need for operation at hydrostatic pressure in the range of 0.05–0.5 MPa.

The asymmetric membranes are used in industrial UF. They consist of highly consolidated, but very thin skins (0.1–5 μm) supported by relatively thick (2–10 mm) porous support. These membranes demonstrate a very high hydraulic permeability combined with a good ability to reject some of the dissolved substances. They withstand high pressures and are resistant to liquids with a high friction coefficient. They do not clog and do not contaminate the substances being filtered. They are also distinguished by high pH and temperature resistance and they show much higher permeate rate than the symmetric structures with a comparable thickness.

Ultrafiltration often presents some unique separation properties. This occurs when ultrafiltration serves for fractionation. In other applications, ultrafiltration is an alter-

native to conventional separation processes. When used for concentration, ultrafiltration sometimes competes with evaporation.

4. INORGANIC MEMBRANE'S APPLICATION IN THE FOOD PROCESSING

A list of various applications of membrane technologies in food processing is presented below. Some of these as well as some additional potential applications are presented more widely in the next part of this chapter [6], [7].

Dairy industry

RO processes: concentration of milk and whey, demineralisation of whey.

ED processes: demineralisation of whey.

UF processes: protein standardisation, cheese production, whey protein concentrate production.

MF processes: bacteria removal, defatting of whey.

Other animal protein processing

RO processes: concentration of hen's egg-white.

UF processes: concentration of blood serum proteins, concentration of gelatin, concentration of whole egg.

MF processes: prefiltration of gelatin.

Fruit juice industry

RO processes: concentration of fruit juice (apple, orange, tomato, etc.).

UF and MF processes: clarification of fruit juice (apple, orange, grape, pear, pineapple, cranberry), concentration of pectin (UF).

Wine and beer

RO processes: concentration of grape must, stabilisation of tartrates, concentration of wine, reduction of alcohol content in beer.

UF processes: protein stabilisation and colour reduction in wine.

MF processes: "cold" pasteurisation of beer, "rest" beer recovery, clarification of wine.

Sugar industry

RO processes: concentration of thin juice.

UF processes: purification of raw juice.

Inorganic membranes have been in use in the dairy industry since the early 1980s, initially for the concentration of whey proteins (1980) and for protein standardisation of milk for automated cheese-making (1981). In recent years, their application has emerged as microfilters for whey and milk and as ultrafilters for highly viscous fluids such as milk at high volume concentration factor (VCF).

It is well known that the largest membrane area in the food industry is installed in the dairy industry. It has been estimated that about 150,000 m² were installed by the end of 1988 for the ultrafiltration of milk and whey, the annual growth being about 30%. About 65% of the membrane area installed in the dairy industry is used for the treatment of whey and about 35% for milk.

Ultrafiltration of milk is carried out, for example, in the manufacture of yoghurt, pre-concentration at farms. One of the more common uses of milk concentration by UF is milk standardisation for continuous mechanised cheesemaking.

In traditional cheesemaking, coagulation occurs after the addition of starter culture and rennet to the cheese milk. The whey proteins are lost in the whey which is drained off from the curd. By concentrating the milk proteins, using ultrafiltration before cheesemaking, this loss can be prevented or reduced as the whey proteins are included in the final product, giving a considerably increased yield.

It should be noted that membrane concentrated precheese having a protein content of 21% or higher could only be obtained using inorganic membranes.

Intensive work has been and is being done on ultrafiltration for the manufacture of fresh, soft, semihard and hard cheeses, e.g., Quarg, Feta cheese, Mozzarella, Blue cheese and Cheddar cheese.

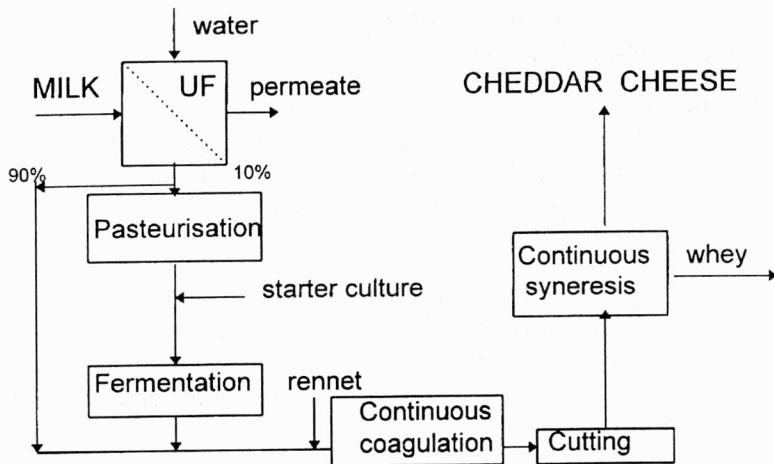


Fig. 1. Flow scheme for the Cheddar cheese production

So far, the use of ultrafiltration for the production of semihard and hard cheeses is very limited. Cheddar cheese is, however, being successfully made commercially from UF retentates by a process developed in Australia. In this process, there is a certain whey drainage, which is not the case when fresh and soft cheeses are produced. A flow scheme for the Cheddar cheese process is shown in figure 1.

Ultra- and microfiltration modules equipped with dynamic membranes are produced by French Company TECH-SEP. They are world-wide applied in the dairy industry. TECH-SEP has approximately 15% of the total world-wide membrane surface area in operation and 1/4 of this area exists as the inorganic membranes. Some typical applications of these membranes in dairy industry are as follows: milk concentration for liquid pre-cheese, coagulated milk concentration for fresh cheese and milk protein standardisation.

Installation for UF concentration of milk using CARBOSEP modules is presented in figure 2. Two UF modules were the main elements of this installation. Housing of each module was manufactured with a stainless steel tube of 0.174 m diameter. Carbon tubes of 6 mm diameters providing the total area of 3.4 m² were used as the membranes. The modules can work in the wide range of operational parameters:

temperature: up to 350 °C,

pressure: 0.4–0.8 MPa,

pH: 0–14.

High volume concentration coefficient (6-fold) and velocity in the range $81 \cdot 10^{-6}$ – $104 \cdot 10^{-6}$ m³/m² · s were obtained for full fat milk as well as skim milk.

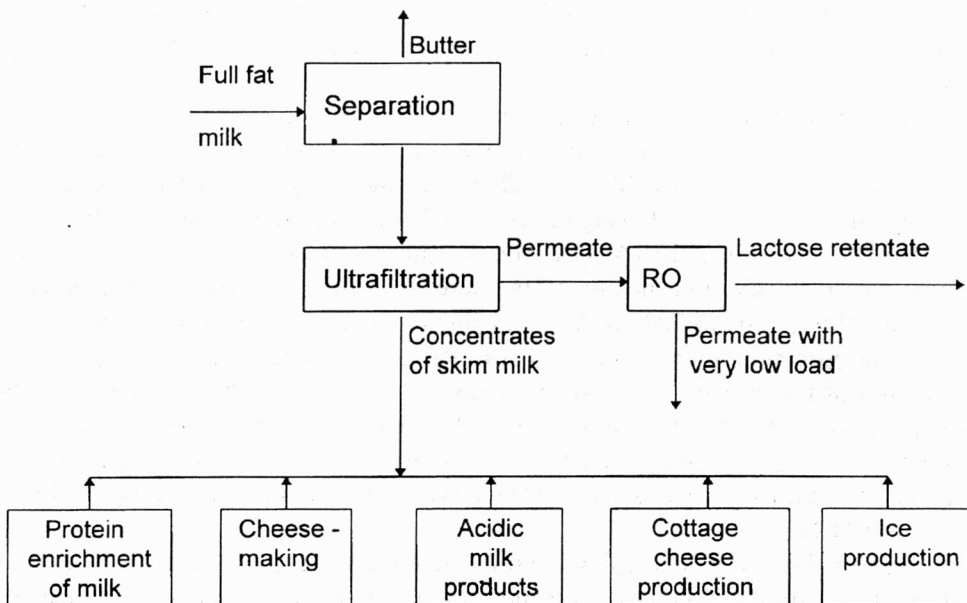


Fig. 2. Scheme for clean processing of milk when RO and UF are applied

CARBOSEP modules are also used for protein recovery from the whey [8], [9]. Whey contains about 0.7% of proteins, 5% of lactose, some salts and about 93% of water. The whey proteins, having excellent functional properties, can be recovered and concentrated by ultrafiltration. Lactose and salts can be removed simultaneously. Depending on the degree of volume concentration, whey protein concentrates (WPC) with different protein contents can be obtained; the most common types contain 35%, 60% and 80% of protein per gram of total solids (TS). In order to obtain a high protein content in the retentate, the retentate is diluted with additional water in the last ultrafiltration stage and then further ultrafiltered in order to obtain a selective removal of lactose and salts.

Flux rates are affected by pre-treatment, volume reduction factor, pH, etc. Typically, flux rates ranging from 25 to 50 dm³/m²·h are obtained with sweet whey. Permeation rates for acid whey are lower than for sweet whey, and the UF flux for hydrochloric acid whey at pH 4.1–4.4 is reported to be about 60% of the flux for Cheddar cheese whey in the pH range of 5.7–6.4.

Ultrafiltration recovery of whey protein using dynamic membranes is a typical example of a cleaner technology. After leaving a module, the permeate is directed to thermal concentrator where the protein concentration of 0.3·10⁻³ kg/m³ is achieved. Finally, the concentrated protein is sold away as swine fodder. Retentate, in the form of separated proteins, is dried for quality improvement using small, flat-bottomed columns.

Since their first introduction to the market in 1984, the MEMBRALOX ceramic membranes have been used in dairy for both ultrafiltration and microfiltration [10]. Cross-flow microfiltration (CF-MF) of milk to prolong its shelf life through reducing its bacterial content is performed using the BACTOCATCH process developed by ALFA-LAVAL with special MEMBRALOX modules. In this process, which involves a very accurate control of the transmembrane pressure difference, skimmed milk is microfiltered with a flux of 500 to 700 dm³/h·m² maintained over a period of 6 to 7 hours. This results in the reduction by more than 99.6% of the number of bacteria in the milk.

The aim of this process is to prepare consumer milk which has a shelf life, when refrigerated, of 16 to 21 days instead of 6 to 8 days for pasteurised milk and this without heating the milk substantially, thus avoiding the typical "boiled" taste of UHT products. A number of industrial systems are now operating in Europe with the BACTOCATCH processes.

It is reported that due to keeping the transmembrane pressure at a constant and low level, microfiltration can continue for more than 6 hours at a constant, high capacity with a bacteria (total count) retention of > 99%.

Most of the milk components pass through the membrane, while most of the micro-organisms are retained in the retentate. A correctly chosen membrane allows us to retain more than 99.6% of the bacteria. The retentate is sterilised, mixed with the low-bacteria skim milk permeate, and then the mixture is pasteurised.

By maintaining a constant transmembrane pressure, the pressure difference between retentate and the permeate as well as capacities of 400–600 dm³/h·m² can be obtained.

Similarly, whey can be microfiltered with a constant transmembrane pressure. Micro-organisms and part of the fat are retained. Such a plant is in operation in Sweden. Using a suitable type of pre-treatment to avoid calcium phosphate precipitation, the fluxes of 1,250–1,500 dm³/h·m² have been obtained at 50 °C for up to 16 hours. Ceramic membranes are used in these applications.

In table 2, there are presented the applications of CF-MF on an industrial scale. It can be concluded that only a few applications are now established (mainly wine and vinegar).

Table 2

Industrial applications of CF-MF in the food industry (1988)

Food industry feed	Installed membrane area (m ²)	Separation of	Aim
Beverage	wine	colloids/bacteria	clarification
	vinegar	colloids/bacteria	clarification
	beer	microorganisms/colloids yeast/bacteria	clarification "rest" beer recovery
Dairy	gelatin		
	milk	bacteria	cold pasteurisation
	whey	proteins/fat bacteria	high-quality protein recovery cold pasteurisation

As an example, MEMBRALOX membranes are used to further recovery of beer from a tank bottom sediments or centrifuge concentrates of wine.

MEMBRALOX as well as CARBOSEP membranes are also used for "rest" beer recovery and clarification of beer.

Removal of bacteria by cross-flow microfiltration is an interesting alternative to heat treatment. The thermal load is avoided, and the beer clarification is also improved since particles passing through the traditional filter can be removed by microfiltration. The only disadvantage of microfiltration is the risk of losing colour, bitter flavour components and foam stabilising proteins.

Fruit juices are concentrated in order to prolong their shelf lives and to minimise the costs of distribution and storage. Before retailing the concentrated juice is diluted, pasteurised and packaged. Concentration normally takes place by means of vacuum evaporation in one or more stages. During this operation many of the volatile aroma compounds of the juice are lost in the vapour, resulting in reduced product quality. To maintain a high quality, aroma compounds must be recovered and

added to the juice concentrate. For juices from such fruits as apples, pears and some berries, the vapour from the first of the evaporation stages is often taken to a distillation column where it is concentrated and cooled to a low temperature. The aroma concentrate is stored separately and then added to the diluted juice concentrate before pasteurisation. On the industrial scale such a distillation technique results in a very low yield. Besides, the aroma compounds are treated at a relatively high temperature for quite a long time which has a negative effect on the quality of the final product.

Separa Systems, a joint venture of the FMC Corporation and Du Pont Company, have developed a "Freshnote" system with which juice can be concentrated to about 55° Brix. After clarification the juice is processed in a series of hollow fine fiber reverse osmosis permeators at pressures between 10 and 14 MPa. The retentate is then recombined with the stream of pasteurised bottom solids.

Industrial systems with MEMBRALOX membranes for juice clarification are located in Germany, Eastern Europe and the USA.

Today many other established membrane manufactures supply the commercial CF-MF systems. Commercially available CF-MF inorganic membranes are the membranes with the trade names: ANAPORE, MPG, UCARSEP and CERAFLO.

The installed membrane surface for CF-MF in food processing in 1988 is estimated at about 9,000 m². Although the capacity installed in CF-MF is still very small as compared to RO and UF it can be considered as a coming technique. However, it is to be expected that the capacity of membranes installed in CF-MF systems never reaches the level of RO or UF because: 1) the total potential feedstream for CF-MF in the food industry is probably less than that for RO and UF and 2) CF-MF is only economic when flux performance is better than using ultrafiltration, hence the membrane surface required for the processing of a given feedstream will be less.

At the present stage of the membrane technique development it seems that the inorganic membranes are one of the best solutions to be used in food processing.

Although they have a great deal of the disadvantages, especially the costs of producing an elementary surface and unsatisfactory packing density (except "permanent" membranes), in general they are promising. High mechanical and biological resistance, wide range of the pore sizes and also solutions, which allows us to use liquids of high viscosity, place them high among techniques which can be used in processing. The future of the inorganic membranes looks very promising. The production of ready-to-cook food is expanding strongly, therefore search for new, safe methods to reach the goal must fulfil the expected requirements.

The development of membrane techniques should proceed to evolve the modern high-selective membranes with the sharp cut-off which will be able to separate particles with a close molecular weight at high streams.

In the future, new techniques of manufacturing the membranes, setting new materials, introducing new hydraulic solutions and constantly expanding connected engineering sciences should be developed.

Cross-flow microfiltration offers significant potential if fouling problems can be reduced. Much more research is needed to obtain a better understanding of the phenomena involved. The hydrodynamics and the start-up procedure are also of great importance.

5. EXPERIMENTAL

The high-molecular animal and plant proteins are present in the form of the so-called quaternary structure (digomer, protomer) creating a spherical form of a diversified size. Not all the proteins can therefore pass during the filtration of solutions through the membranes.

Changing the structure of proteins from the globular to the linear form as the result of performance of physicochemical series can lead to their effective separation on the membranes. The change of the protein structure can be obtained through treating them by the denaturing agents, e.g., a variable pH, the salts of heavy metals or a temperature.

Problems connected to the basic mechanisms of this type of separation with the use of inorganic membranes are not well recognised in comparison to other scientific problems. Therefore there exists a wide spectrum of studies and applications of novel methods which can be performed.

The investigations undertaken in the field of protein separation are an integral part of the research program which is carried out by our Sanitary Research Group and focused on membrane methods.

The following investigations were performed so far:

1. Tests of the structure of TiO₂ layer under scanning electron microscope (SEM). The water permeability of this membrane was also tested and as a result of both mentioned tests the structural parameters (porosity, pore density and its average diameter as well as thickness of the TiO₂ layer) were calculated [11].

2. Tests with a model substance (Dextran 70, Dextran 200, Dextran 500) in order to determine the optimal parameters of the membrane process.

3. Tests on single protein solution with high ionic strength performed in order to investigate UF characteristic of protein (BSA). These tests are reported in this paper.

The "permanent" titanium dioxide membrane with the average pore size of ~32 nm is used. The membrane was supplied by Du Pont Separation Systems Co. and was a titania microfiltration membrane permanently affixed to the inside surface of a porous sintered stainless steel.

The protein (BSA-albumin fraction V) was obtained from Sigma Chemical Co. All other compounds were reagent grade and the water was deionized with a mixed bed, MB-8, Amberlite ion exchange.

The ultrafiltration experiments were run for 180 min at 27 °C with 1.0 g/dm³ BSA solutions buffered at pH = 3.8, pH = 4.8, and pH = 6.8, the cross-flow velocity of 2.0 m/s and at the pressures of 0.20 and 0.70 MPa. The flux and concentrations of BSA in the permeate and retentate were determined at intervals during the course of the experiment. Such process parameters have been recognised as optimal on the basis of the tests performed with model substance (Dextran).

The protein concentration was determined by means of the spectrophotometric method [12].

Hydraulic tests were carried out before and after each of the tests of the process of protein separation. The hydraulic tests were done in order to define irreversible fouling.

After each experimental cycle, i.e. 1) hydraulic test, 2) test with separation, 3) hydraulic test, the chemical cleaning of the installation took place and it was done according to the CIP (Clean-In-Place) procedure which is widely used, usually in food industry in the USA.

6. RESULTS AND DISCUSSION

A series of experiments with BSA solutions using a titanium dioxide "permanent" FIP module produced the results presented in figures 3–6.

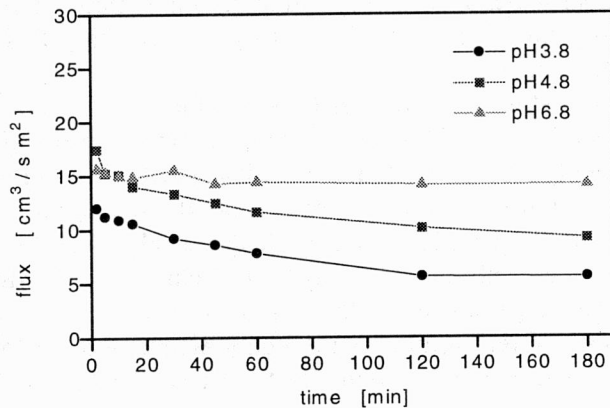


Fig. 3. Flux decline versus time for various pH values at $P = 0.20$ MPa

According to the analysis of the results shown in these figures, the fundamental principle of membrane processes was confirmed, i.e., together with the increase of

a working pressure on the high pressure side, the flux increases, hence the rejection of the dissolved solution also increases (a concentration of the protein in permeate decreases). Generally, the above statement is confirmed through all comparisons of the flux and the concentration decrease of albumins in permeate, which is shown in the presented figures.

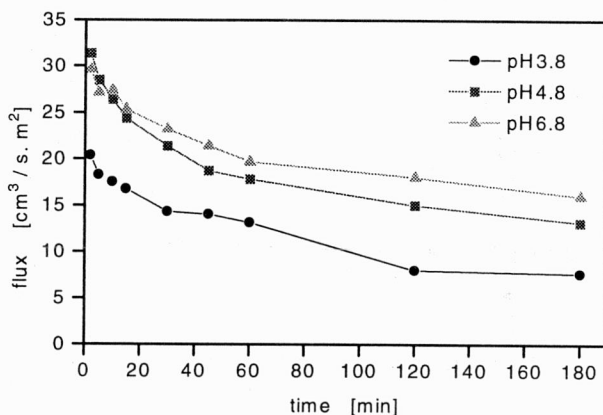


Fig. 4. Flux decline versus time for various pH values at $P = 0.70$ MPa

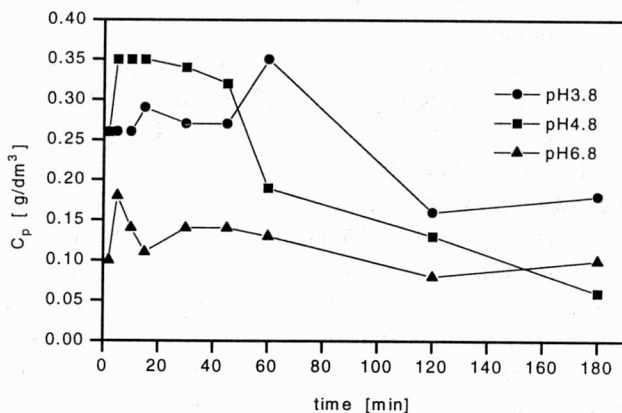


Fig. 5. Protein concentration in permeate versus time for various pH values at $P = 0.20$ MPa

The higher flux at the working pressure of 0.70 MPa was obtained and the protein separation was higher than at 0.20 MPa pressure at the same pH values.

Special attention should be paid to the typical flux decline, especially at 0.70 MPa pressure, during the first minutes of the process. The distinct flux decline is noticed, it can be a result of formation of an extra filtration layer built up by absorption of the high molecular proteins on the membrane. Figures 5 and 6 show the changes of protein concentration in the permeate that have a positive effect on separation results.

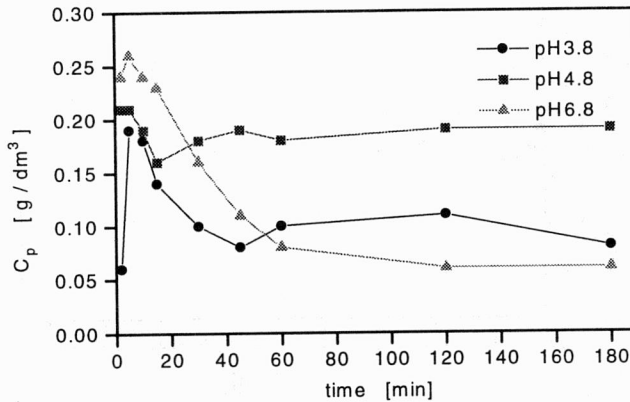


Fig. 6. Protein concentration in permeate versus time for various pH values at $P = 0.70$ Mpa

The significant differences were obtained for the solutions at various pH values which were subjected to an examination at the same pressures (0.20 MPa and 0.70 MPa).

As it is shown in figures 3 and 4, while conducting the process at the pressures of 0.20 MPa and 0.70 MPa, the highest flux was obtained at pH = 6.8, and the lowest one at the pH = 3.8. The curve for the flux at pH = 4.8 lays in both cases between curves for the fluxes at pH = 3.8 and 6.8. This pattern of flux curves shows quite clear the electrostatic interaction between protein and membrane; pH = 4.8 is the isoelectric point of BSA. At this value of pH, BSA is dissolved at the lowest rate and is considered as electrically neutral. So the protein remains as the typical macromolecular compound whose filtration is not disturbed by anything. Both cases, pH = 3.8 as well as pH = 6.8, however, refer to the situation of the same charges of the BSA and the membrane, i.e., positive charge at pH = 3.8 and negative charge at pH = 6.8, and the obtained values of the fluxes are different. The hypothesis about increase of the flux in the case of the same charge of both protein and membrane, as a consequence of the mutual repulsion, was fully confirmed in the research at the pH = 6.8. The extreme curve position for flux at pH = 3.8 most likely results from much higher fouling which occurs at this value.

Those curves, as it was mentioned, follow a pattern similar to that of two pressure values applied. The flux increase, however, is higher at the pressure of 0.70 MPa and it is an obvious consequence of higher fluxes at higher pressures.

The curves representing the concentration change for albumin have the similar character at the same pressure values and various pH of solutions (figures 5 and 6). For the pressure of 0.20 MPa and steady state process conditions, the lowest concentration of proteins in permeate was obtained for solutions at pH = 6.8, and the highest one for solutions at pH = 3.8. The protein concentration changes at 0.70 MPa were slightly different. In principle, the lower protein concentrations in a permeate were measured at pH = 6.8 and 3.8, and the lowest concentration level was obtained, similarly as at the pressure of 0.20 MPa, for solutions at pH = 6.8. The results obtained for the pressure of 0.70 MPa are comparable with those obtained for the separation of BSA in solutions with low ionic strength and performed for the similar membranes [13]. In this case, the solutions at pH = 4.8 show the lowest ability of the protein to separate. The smaller increase in the rejection at the higher pressure at the isoelectric point (pI) of albumin is the opposite of the greater increase at the higher pressure observed at lower pH. This fact suggested that at the pI the protein was immobilised in the membrane pores at the lower pressure but remained mobile at the higher pressure in the associated higher convective flow rate.

The volume flux (J) decreased with time during the BSA ultrafiltration experiments as shown in figures 3 and 4. The equations :

$$J = J_c - b \ln t \quad \text{and} \quad J/J_c = 1 - B \ln t$$

were used to describe the dependence of J on t where J_c is a characteristic flux obtained by extrapolating J/J_c versus $\ln t$ to $\ln t = 0$, or $t = 1$ (min). The coefficient B , i.e., the negative of the slopes of the plots of J/J_c versus $\ln t$, represents a fouling index where $B = 0$ means no decrease in flux with time, and an increase in B indicates

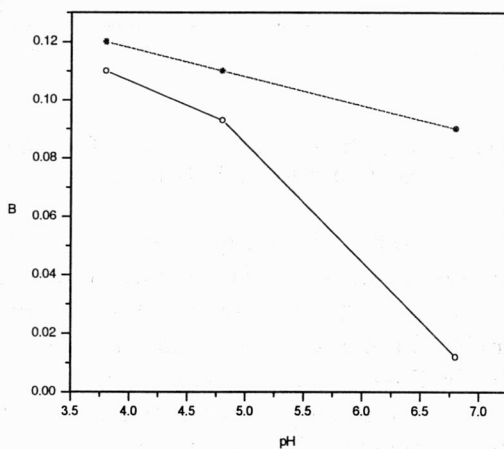


Fig. 7. Fouling index (B) versus pH for $P = 0.20$ MPa (open circles) and $P = 0.70$ MPa (filled circles)

an increase in the rate of the flux decline. The values of B obtained from the slopes are shown in figure 7. In general, the fouling index was much higher for experiments at $P = 0.70$ MPa than for those at $P = 0.20$ MPa and decreased with increasing pH for both pressures. Its value ranges from 0.09 to 0.12 for all experiments except those at $P = 0.20$ MPa and $\text{pH} = 6.8$, where it much smaller (0.021).

The ultrafiltration experiments at $P = 0.70$ MPa and 180 min duration produced larger total volumes of the permeate than those at $P = 0.20$ MPa at the same pH even when the fouling indexes were higher.

Additional and very firm confirmation of the effect of pH values on the separation of albumins were the water tests in which the membrane permeabilities measured before and after each of the separation tests were taken into account.

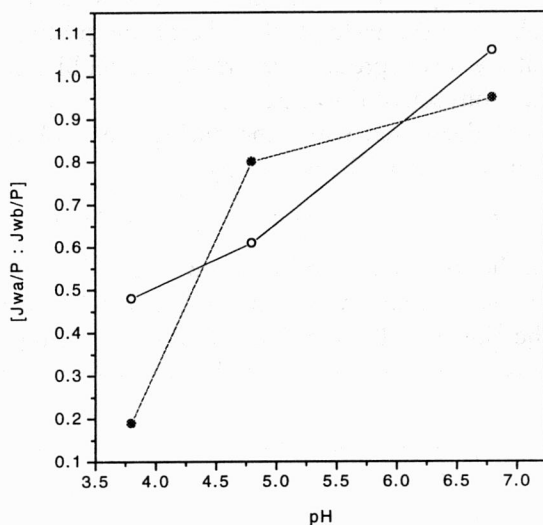


Fig. 8. Ratio $[J_{wa}/P]/[J_{wb}/P]$ versus pH for $P = 0.20$ MPa (open circles) and $P = 0.70$ MPa (filled circles)

A ratio of the water flux after the BSA experiment (J_{wa}) to the water flux before the BSA experiment (J_{wb}) as a measure of the fouling that could not be removed by the treatment or cross-flow of water (whatever was used) after the ultrafiltration experiment, i.e., irreversible fouling, was estimated. The results obtained due to this estimation are presented in figure 8. They differ from the fouling indexes which included all types of fouling and not just the part that is not removed by water cross-flow wash or other treatment. The irreversible fouling is less for both pressures at $\text{pH} = 6.8$.

7. CONCLUSIONS

BSA rejections in the 0.92–0.94 range can be obtained on the macroporous titania membrane at ionic strength greater than 0.05 mol/dm^3 and under controlled conditions of pH and pressure. High rejection accompanied by the smallest flux decline observed and irreversible fouling were obtained at the highest pH = 6.8 and the lower pressure $P = 0.20 \text{ MPa}$. Such results allow us to recommend those conditions for concentrating BSA by means of macroporous titania membrane.

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MEMBRANY NIEORGANICZNE W PRZETWÓRSTWIE SPOŻYWCZYM

Procesy membranowe z wykorzystaniem membran mikro- i ultrafiltracyjnych znalazły szerokie zastosowanie w przetwórstwie spożywczym. Spośród wielu rozwiązań technologicznych szczególnie przydatne okazały się nieorganiczne membrany dynamiczne. Przeprowadzono badania dotyczące separacji białek z wykorzystaniem mikroporowatej membrany pokrytej warstwą tlenku tytanu. Doświadczenia pozwoliły określić warunki procesu separacji roztworu BSA o określonej sile jonowej, dla których indeks foulingu jest najmniejszy.

