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ULTRAFILTRATION OF CHEESE WHEY USING ENZYME MEMBRANE

The experimental results on the improvement of cheese whey ultrafiltration process pretreatment by enzymatic prevention of a tubular membrane flux decrease resulting from concentration polarization phenomenon have been presented in the paper. Mathematical model of the membrane flux decrease with the process duration time was also discussed and experimentally verified. Better results have been achieved when applying addition of enzyme to the bulk solution of the wastewater over the precedent immobilization of the enzyme on tubular membrane.

1. INTRODUCTION

Cheese whey is a by-product in milk processing to cheese, cottage cheese, and casein. Cheese whey can be acidic or rennet depending on the coagulant used. Cheese whey is a water solution of proteins, lactose, lactic acid, and mineral salts. As a result of high contents of water its nutritive value is often underestimated. On the other hand, when it is not utilized in the proper way, it becomes very harmful waste which causes pH decrease, considerable oxygen shortage, and pollution of sewage and water. One of the main processes leading to cheese whey utilization is its concentration by water removal. Ultrafiltration process in concentrating cheese whey is used recently on an industrial scale. During ultrafiltration a great part of lactic acid and mineral salts are removed which allows to obtain cheese whey concentration of high practical values. The main impediment to cheese whey ultrafiltration lies in the serious fouling of the membrane which decreases the permeate flux within a short period of operation. Fouling of membranes has been identified as a result of the gelling of macromolecular or colloidal solutes on the membrane surface when the solutes are being accumulated by the concentration polarization phenomenon. One of the methods proposed to remove the gel layer is immobilization of enzymes to hydrolyze gel layer, thereby reducing the overall membrane resistance and causing increase in permeate flux. Such experiments with immobilization of trypsin and papain

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in a cellulosic membrane were carried out by DEJMEK and HALLSTRÖM [2] for cheese whey ultrafiltration, but the results were not encouraging. On the other hand, VELINCANGIL and HOWELL [5] obtained a 20% improvement of flux using the papain membrane. Increase in membrane flux was also observed by DRIOLI et al. [3] in ultrafiltration of oil emulsion using microorganisms which can decompose hydrocarbons and oil derivatives. Enzyme membranes were used for sewage ultrafiltration by JENQ et al. [4] with a good effect.

The purpose of the authors' investigation is to estimate the possibility of application of industrial grade protease Klox c5 to counteract increase of membrane resistance as a result of the concentration polarization. Klox c5 is used either in solution of cheese whey in recirculating system as a free enzyme or it is immobilized by physical sorption on membrane surface.

2. EXPERIMENTAL

The experiments were carried out in an ultrafiltration device with or without recirculation. Polyacrilonitrile tubular membranes were used with the fibers of 0.73 to 0.81 mm in diameter and the length of 75 to 88 cm. These fibers possess sharp cut off characteristic; they completely reject substances of molecular weight above 1000 and pass solutes of molecular weight below 300. The experiments were carried out at a temperature of 293 ± 1 K and at transmembrane pressure difference of 0.1 MPa. Two flow intensities of bulk solution were used, i.e. 0.16 cm^3/min and 2.35 cm^3/min which correspond to axial flow velocity of 0.85 m/min and 14.0 m/min, respectively. Before experiments the pure water permeation rate was determined for each membrane. The UF process was performed using acidic and rennet cheese wheys. Cheese wheys were initially pasteurized at a temperature of 348 K for 15—18 s. Next, both kinds of cheese wheys were adjusted to pH 7.4 with 0.1 N NaOH and then centrifuged to collect the supernatant.

Three kinds of experiments were performed, the first one when a cheese whey was used as a bulk solution, the second one in which cheese whey with enzyme was used, and third one in which the enzyme was immobilized on the UF membrane. The enzyme Klox c5, product of Sembodja Chemicals, Amsterdam, Holland, was applied in the experiments and used as the additive of detergents. In the second set of experiments the enzyme was added to cheese whey to reach its concentration in a bulk solution of cheese whey within 20 mg/dm^3. In the third set of experiments water solution of enzyme at a concentration of 20 mg/dm^3 was ultrafiltrated for 1 hour in UF recirculating system to form the enzyme layer on the pressurized membrane surface by physical sorption. The permeate samples of fixed volume were collected and time was measured in every case.

At the beginning of investigation membranes were tested at various transmembrane pressure differences ranging from 0.05 MPa to 0.11 MPa for both water and cheese whey (fig. 1). The decrease of membrane flux is caused by gel layer formation when cheese whey is used as a feed solution. Figure 1 shows that the flux appears to be approaching

a pressure-independent value at a pressure of about 0.09 MPa. It indicates that above this pressure macrosolutes concentration at the membrane surface reaches a limiting value of a gel concentration. The flux observed during ultrafiltration operation taking place in this "gel polarized" region is far lower than that expected to occur through the membrane alone. For example at the pressure of 0.1 MPa the reduced solvent flux is about 40% lower than that of pure water.

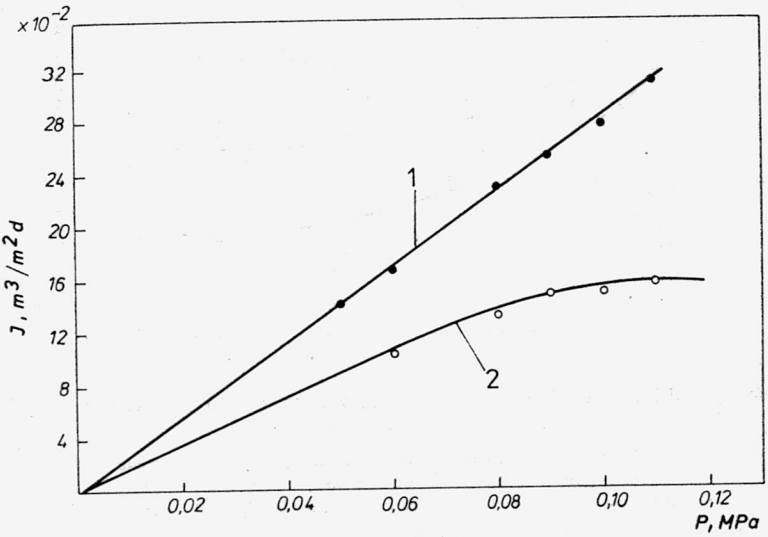

Fig. 1. Dependence of membrane flux on pressure
1 — pure water, *2* — cheese whey

Rys. 1. Zależność strumienia membranowego od ciśnienia
1 — czysta woda, *2* — serwatka

3. MATHEMATICAL MODELLING

The back-diffusion-controlled concentration polarization model for macrosolute ultrafiltration predicts a very rapid drop in UF flux occurring in a time period not longer than a few seconds as the gel layer is built up. As it is indicated in figs. 2—5 a gradual decay in flux is observed during a long-term operation. A probable cause of this effect is an irreversible consolidation of the solute gel with time which reduces the hydraulic permeability of the gel continuously with time. The consolidation of particles in the gel layer is a relatively slow process. We can measure only one value — the membrane flux. From the practical point of view the most interesting information is its magnitude and its decline with time.

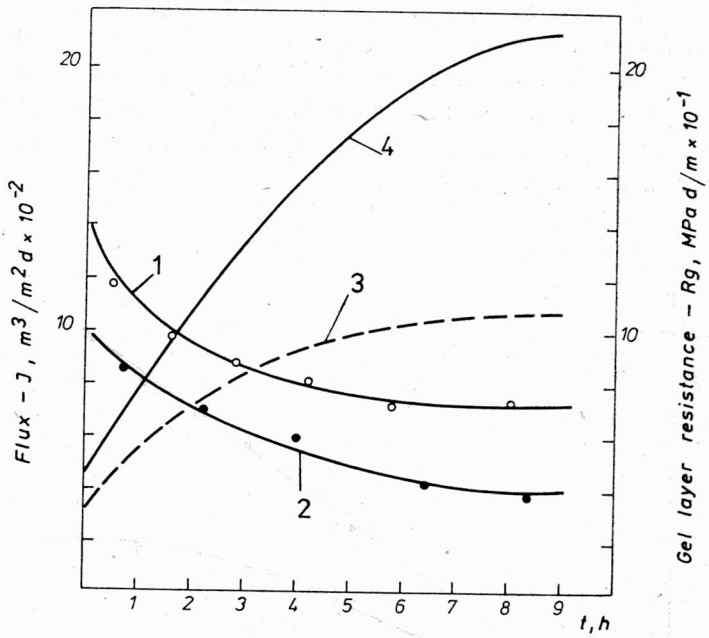

Fig. 2. Flux decay and increase of gel layer resistance with time for rennet cheese whey in recirculating system

Flux: *1* — with enzyme in bulk solution, *2* — without enzyme
Gel layer resistance: *3* — with enzyme, *4* — without enzyme
Points indicate experimental data, curves are calculated for $Q = 0.16$ cm³/min

Rys. 2. Spadek strumienia i wzrost oporności warstwy żelowej w zależności od czasu dla serwatki chymozynowej w układzie recyrkulacyjnym

Strumień: *1* — z enzymem w całym roztworze, *2* — bez enzymu
Oporność warstwy żelowej: *3* — z enzymem, *4* — bez enzymu
Punkty wskazują dane eksperymentalne, krzywe są obliczone dla $Q = 0{,}16$ cm³/min

The first order equation is proposed to describe the rate of ultrafiltrate flux reduction:

$$-\frac{dJ}{dt} = k(J - J_\infty), \tag{1}$$

where:

J_∞ is the ultimate flux of the membrane when $t = \infty$,
k is a first order rate constant.
Equation (1) can be integrated to give:

$$\int_{J_0}^{J} \frac{dJ}{J - J_\infty} = \int_{0}^{t} -k\,dt, \tag{2}$$

where J_0 is the initial membrane flux just after the gel layer is built up at $t = 0$.

The resulting expression for the membrane flux as a function of time is given by equation (3):

$$\frac{J-J_\infty}{J_0-J_\infty} = \exp -kt. \tag{3}$$

Dependence of flux on time was calculated according to equation (3). Curves which were obtained by digital simulation as well as points showing experimental data are presented in figs. 2—5. These plots show strong correlation with the results of experiments.

According to BLATT [1] the solvent transport across a membrane can be expressed by equation:

$$J = \frac{\Delta P}{R_m + R_g}, \tag{4}$$

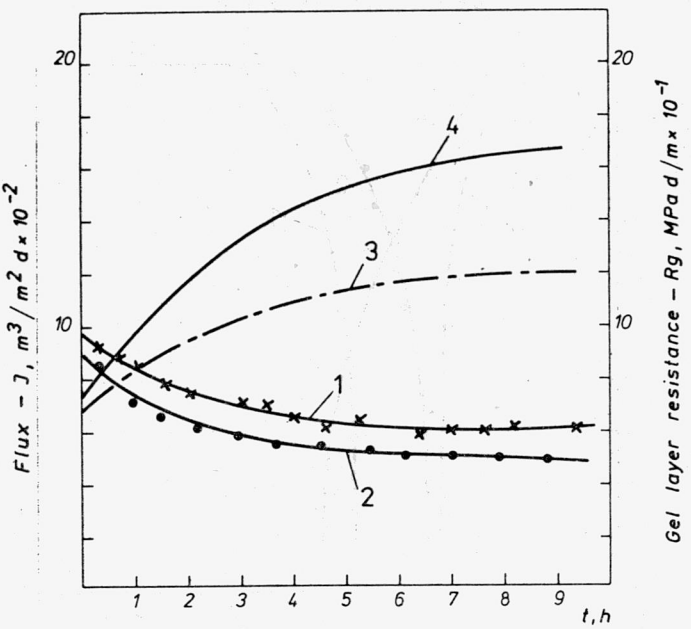

Fig. 3. Flux decay and increase of gel layer resistance with time for acid cheese whey in system without recirculation

Flux: *1* — with immobilized enzyme, *2* — without enzyme
Gel layer resistance: *3* — with enzyme, *4* — without enzyme
Points indicate experimental data, curves are calculated for $Q = 0.16$ cm³/min

Rys. 3. Spadek strumienia i wzrost oporności warstwy żelowej w zależności od czasu dla kwaśnej serwatki w układzie bez recyrkulacji

Strumień: *1* — z unieruchomionym enzymem, *2* — bez enzymu
Oporność warstwy żelowej: *3* — z enzymem, *4* — bez enzymu
Punkty wskazują dane eksperymentalne, krzywe są obliczone dla $Q = 0{,}16$ cm³/min

where:

ΔP is the total pressure drop,

R_m is hydraulic resistance of membrane,

R_g is hydraulic resistance of gel layer.

Membrane resistance R_m was determined for each membrane from pure water flux measurements J_w:

$$R_m = \frac{\Delta P}{J_w}. \tag{5}$$

Then, the gel layer resistance R_g was calculated according the following equation:

$$R_g = \frac{\Delta P}{J} - R_m, \tag{6}$$

where values of J obtained from equation (3) were introduced. $R_g = f(t)$ relationship is presented in figs. 2—5.

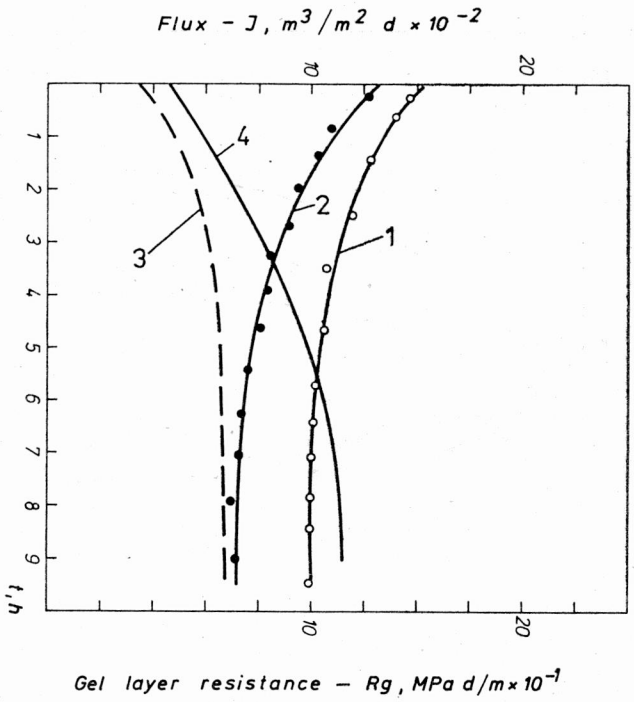

Fig. 4. Flux decay and increase of gel layer resistance with time for acid cheese whey in recirculating system

Flux: *1* — with enzyme in bulk solution, *2* — without enzyme
Gel layer resistance: *3* — with enzyme, *4* — without enzyme
Points indicate experimental data, curves are calculated for $Q = 2.35$ cm³/min

Rys. 4. Spadek strumienia i wzrost odporności warstwy żelowej w zależności od czasu dla kwaśnej serwatki w układzie recyrkulacyjnym

Strumień: *1* — z enzymem w całym roztworze, *2* — bez enzymu
Odporność warstwy żelowej: *3* — z enzymem, *4* — bez enzymu
Punkty wskazują dane eksperymentalne, krzywe są obliczone dla $Q = 2{,}35$ cm³/min.

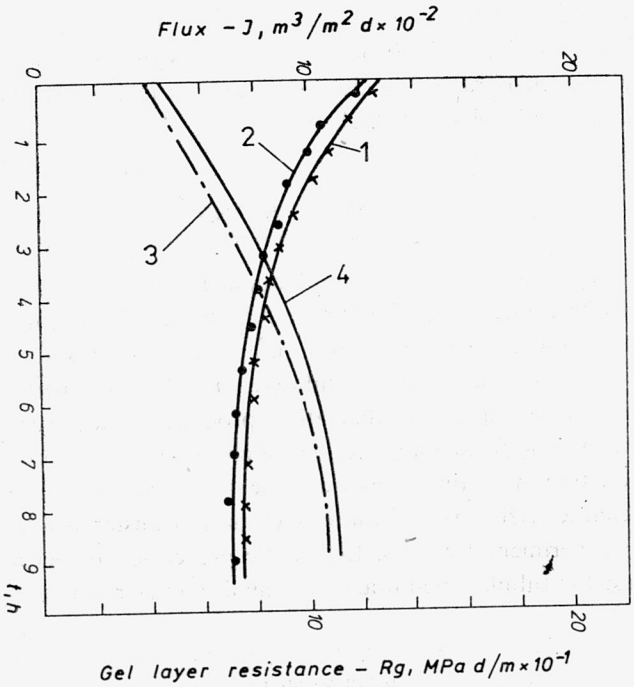

Fig. 5. Flux decay and increase of gel layer resistance with time for acid cheese whey in recirculating system

Flux: *1* — with immobilized enzyme, *2* — without enzyme
Gel layer resistance: *3* — with enzyme, *4* — without enzyme
Points indicate experimental data, curves are calculated for $Q = 2.35$ cm³/min

Rys. 5. Spadek strumienia i wzrost oporności warstwy żelowej w zależności od czasu dla kwaśnej serwatki w układzie recyrkulacyjnym

Strumień: *1* — z unieruchomionym enzymem, *2* — bez enzymu
Oporność warstwy żelowej: *3* — z enzymem, *4* — bez enzymu
Punkty wskazują dane eksperymentalne, krzywe są obliczone dla $Q = 2{,}35$ cm³/min

4. DISCUSSION

In all cases curves $J = f(t)$ tend asymptotically to ultimate values J_∞ which are higher for experiments with enzyme. These higher values of J_∞ result from lower concentration of the gel layer due to hydrolytic activity of the enzyme. It is well illustrated by figs. 4 and 5, where the influence of the enzyme on the ultimate membrane flux was higher when the enzyme was added to the bulk solution than for experiments with enzyme immobilized on the membrane surface. The immobilized enzyme is located on the membrane surface only and its activity is limited to that region. The free enzyme is transported like other macrosolutes and that is why it is uniformly distributed with in the whole gel layer. A diminishing effect of the enzyme on membrane resistance is connected with the rate

of mass transport in close surroundings of the enzyme. This effect can be intensified by increasing axial flow (figs. 2 and 4). From experiments with cheese whey without enzyme it can be seen that the membrane flux increases with the increasing axial flow due to results from the decrease of gel layer thickness.

5. CONCLUSIONS

It appears that depending upon the method applied, the enzyme used, Klox c5, caused up to 25% or up to 75% increase of membrane flux during ultrafiltration of cheese whey. The results obtained indicate that the addition of enzyme to a bulk solution is more effective than previous immobilization on membrane. The former method is simpler and aalows to omit time consuming immobilization process, it, however, cannot be useful in every case having in mind further applications of concentrate. The proposed equation (3), modelling flux reduction with time, gives a close approximation to experimental data. Rate constant k characterizing the conditions of mass transfer inside the gel layer can be estimated from experimental results. Enzymatic prevention of gel layer consolidation is of special interest for tubular membranes of small diameter where it is difficult to use other methods.

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ULTRAFILTRACJA SERWATKI PRZY UŻYCIU MEMBRAN ENZYMATYCZNYCH

Przedstawiono dane doświadczalne z badań nad próbą usprawnienia procesu ultrafiltracji serwatki przez zastosowanie enzymów, które zapobiegają spadkowi przepustowości membrany. Spadek ten jest wywołany przez polaryzację stężeniową. Poddano weryfikacji i dyskusji matematyczny model opisujący spadek przepustowości membrany jako funkcji czasu trwania procesu ultrafiltracji. Lepsze wyniki od tych, które zapewnia membrana z immobilizowanymi enzymami, uzyskano w przypadku dodawania enzymu do obrabianej serwatki.

ULTRAFILTRATION VON MOLKE DURCH ENZYMATISCHE MEMBRANEN

Im Bericht werden Versuche dargestellt, die zu einer Rationalisierung der Ultrafiltration von Molke durch Anwendung von Enzymen führen. Sie sollten vor allem einem Abfall der Leistungsfähigkeit der Membrane entgegenwirken. Diese Leistungsabnahme wird durch die Konzentrationspolarisation verur-

sacht. Bewahrheitet und diskutiert wird ein mathematisches Modell, das die Abnahme der Leistungsfähigkeit als Funktion der Zeit darstellt. Bessere Resultate als die, die eine Membrane mit immobilisierten Enzymen lieferte, wurden in solchen Fällen erhalten, wenn Enzyme der Molke direkt zugegeben wurden.

УЛЬТРАФИЛЬТРАЦИЯ СЫВОРОТКИ ПРИ ИСПОЛЬЗОВАНИИ ЭНЗИМАТИЧЕСКИХ МЕМБРАН

В работе представлены опытне данные об исследованиях по попытке усовершенствования процесса ультрафильтрации сыворотки путём применения энзимов, которые предотвращают снижению пропускной способности мембраны. Это снижение вызвано концентрационной поляризацией. Подвергнута верификации и обсуждению математическая модель, описывающая снижение пропускной способности мембраны как функции продолжительности процесса ультрафильтрации. Лучшие результаты, чем те, которые обеспечивает мембрана с иммобилизированными энзимами, были получены при добавлении энзима к обрабатываемой сыворотке.