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INVESTIGATIONS OF HYDRODYNAMIC PERMEABILITY CERAMIC MEMBRANES FOR MICROFILTRATION

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Abstract: This paper introduces the results of experimental investigations on the influence of operating parameters, such as feed flow rate, temperature, pressure difference in the microfiltration through the ceramic Kerasep membrane. The results confirmed earlier work on the same laboratory device for microfiltration, and they are the main condition for determination of kinetics juice clarification. Apart from investigations on the influence of operating parameters, the influence of membrane moisture on microfiltration was observed.

Key words: microfiltration, ceramic membranes, distilled water, permeate flux.

Introduction

Microfiltration (MF) has been extensively studied during the last 15 years, but MF is in use since 80's. Microfiltration is membrane separation process which makes possible macrocolutes in the range of 0.1 to 10 μm separated from the solvent and other smaller constituents with driving force in the range of 1 to 5 bar. The concept of membrane separation processes is in its essence very simple. Using appropriate driving force, from feed solution with semipermeable membrane all components which can not penetrate through the membrane have been separeted.

Solvent transport is executed through the membrane pores with hydraulic flow, where solvent molecules and suspended particles hold on membrane surface just like on a sieve, because membrane pores are too narrow and particles can't penetrate through the membrane.

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Compared to the conventional processes, microfiltration can bring the following benefits: separation can be executed without changing of temperature and pH of solution and without chemical additives, production costs and the problems of waste treatment are reduced, product quality is improved and labor costs are lower.

Microfiltration has wide application in different range of industries, such as biotechnology, pharmaceutical industry, dairy, food and beverage industry, chemical and petrochemical industry, microelectronics, metal finishing and power generation. Each industry has specific needs when it is necessary to use membranes for microfiltration. Microfiltration for food and beverage industry has applications in fruit juice clarification, recover of valuble products, filtration, concentrating of process streams.

Chemical structure of membranes does not have role in separation mechanism, so different types of membranes can be used, such as polymer membranes for microfiltration. Membranes for food and beverage industry needs have an alumina or zirconia coating, which is applied to the inside surface of a ceramic support. It is better to use ceramic membranes for microfiltration than polymer membranes. Even the capital cost is much higher than conventional polymeric membranes, in most cases a longer operational lifetime of ceramic membranes can be expected. These membranes can withstand high temperature, extreme acidity or alkalinity and high operating pressures, making them suitable for many applications where polymeric and other inorganic membranes can not be used.

In this work the effect of the operating conditions on the kinetics of microfiltration was investigated with ceramic Kerasep membrane. Ceramic membranes offer a perfect match for membrane installations due to their extremely high chemical and physical stability, outstanding separation characteristics, constant filtrate quality and long working life. The main requirements are process stability, high avalibility, low requirements for preliminary treatment and minimum need for support and maintenance.

Ceramic membranes are manufactured in different shapes (round, hexagonal) and with various channel diameters. Usually, ceramic membranes are constructed in multiple ceramic layers and formed into an asymetric, multi-channel element. Dependending of applications in food industry, ceramic membranes can be used as single-channel and multi-channel elements with channel diameters between 2 and 16 mm. The filter areas can range from 0.05 m^2 for test purposes up to 10 m^2 for a large-scale application.

Ceramic membranes are arranged in parallel in pressure housings to form modules. These pressure housings are produced from different types of stainless steel, coated steel or plastic, as required by the application. For applications in food industry, special casing designs are available which comply with strict

hygiene requirements. For microfiltration process tubular modules, flat membrane modules, spiral wound modules and hollow fiber modules can be used.

Permeate flux is a measure for rate of membrane separation processes. They are defined as permeate volume which has been collected in a time unit from m^2 of membrane surface. The permeate flux of pure water through the membrane can be written as:

$$J = \frac{Q_V}{A_m} = \frac{dV}{dt}\frac{1}{A_m} \tag{1.1.}$$

where Q_V (m^3/s) is volumetric rate of flow and A_m is the effective cross-sectional membrane area.

The following equation gives the ratio between permeate flux and permeability:

$$J = P\frac{\Delta\phi}{l} \tag{1.2.}$$

where $\Delta\Phi$ is driving force through the membrane and l (m) is membrane thickness.

The volumetric rate of flow, Q_V (m^3/s), for the permeation of pure water of viscosity, μ (Pa·s), through an isotropic membrane of thickness δ (m), pore diameter d_p (m), and tortuosity factor ξ under the applied pressure difference Δp (bar) is given by:

$$Q_v = vA_o = \frac{\Delta p\ d_p^{\,2} A_o}{32\mu\delta_m\xi} = JA_m = \frac{\Delta pA_m}{\mu R_m} \tag{1.3.}$$

where v is the average velocity of permeate through the pores, A_o is the mean cross-sectional area for flow, A_m is the effective cross-sectional membrane area, J is the permeate flux, R_m is the hydraulic membrane resistance.

Material and Methods

The experiments were performed on the laboratory device for microfiltration at the Faculty for Agriculture in Belgrade.

Laboratory device for microfiltration is designed to enable easy handling, process verification and changing of operating parameters (flow of distilled water through the module, pressure difference, temperature). The shematic view of the experimental device employed for the measurement of distilled water permeabilites of microfiltration membranes is shown in fig.1.

The distilled water (feed solution) was pumped from the reservoir to the module by a rotary pump and flow rate was monitored with a laboratory made rotameter. Temperature in the system was adjusted by passing water from a bypass line through the thermostat bath. Permeat was collected in a graduate cylinder placed on a Tehtnica model ET-111 digital balance. Overpressure in the system was adjusted by back-pressure regulator and measurement was done with a pressure gauge.

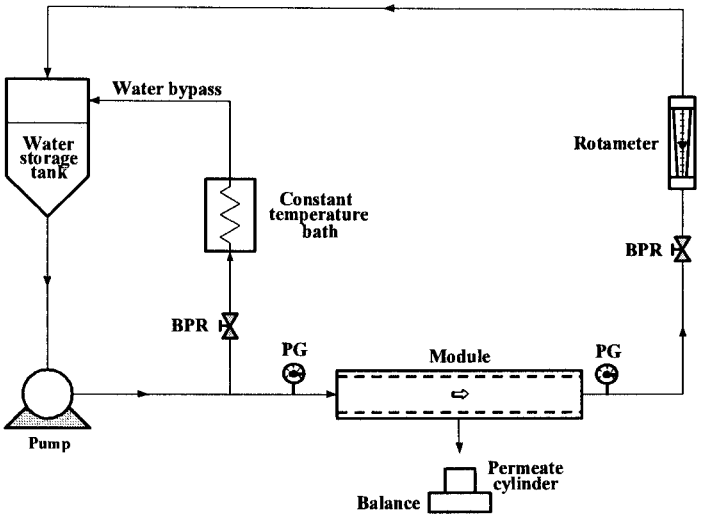

Fig. 1. - Scematic view of the experimental setup employed for the measurement of pure water permeabilities (PG-pressure gauge, BPR-back-pressure regulator)

The experiments were performed with inorganic ceramic Kerasep membrane with separation limit of 0.2 μm (Tech-Sep, Miribel, France). The effective length of this membrane is 270 cm, and it has 19 channels with 4 mm diameter. This membrane was installed inside a plastic module with a stopper tire. Characteristics of used membrane are given in table 1:

Tab. 1. Characteristics of used Kerasep membrane for microfiltration in the experiments

Selective layer	ceramic
Bearer	ceramic
Membrane type	tubular
Separation limit	0,2 μm
Permit pH	0 – 14
Max pressure	1.0 MPa
Internal diameter	0.004 m
Length	0.27 m
Effective area	0.0644 m^2
Number of channels	19
Max temperature	650°C

After we finished the process, Kerasep membrane was taken apart from the device and sank in hot NaOH solution. In this solution the membrane was left 12 hours. Before every new cycle of using, the membrane was sunk and washed with boiling distilled water and citric acid solution. The reason for washing the membrane with citric acid solution is to protect membrane character from acidity.

The experiments confirmed earlier work on the same laboratory device for microfiltration. Investigations were carried out on the influence of operating parameters (flow of distilled water through the module, pressure gradient and temperature gradient) on microfiltration of distilled water through the Kerasep membrane.

Results and Discussion

The results of the experiments show the condition for defining kinetics of juice clarification. It is important to determine membrane resistance (R_m) with distilled water and then we can determine polarization resistance (R_P) and total resistance (R) with juice. In other words, we can determine influence of concentration polarization. That is why the experiments were made, depending of pump capacity, under different operating conditions:

Flow of distilled water through the module, Q_V (l/min): 0.5 to 3,
pressure gradient, Δp (bar): 0.5, 1 and 1.5,
temperature, t (°C): 22, 35, 45, 55.

First of all, it is necessary to make the device „operating diagrams" and membrane operating characteristic. Operating diagrams can be made with distilled water. Determine operating diagrams to establish operating interval for making investigations. After making of operating diagrams, we performed measurements of distilled water permeabilites. The mass of collected permeate was measured with an accuracy of ± 0.1 g every minute for periods of 80 min.

Max overpressure of pump for Kerasep membrane is 1.5 bar because mass permeate flow (Q_m) is very high, which results from lower membrane resistance.

Influence of membrane moisture on kinetics of microfiltration distilled water through the Kerasep membrane

Besides the experiments carried out to investigate the influence of operating parameters (flow of distilled water through the module, pressure difference and temperature) on kinetics of microfiltration distilled water through the Kerasep membrane, the effect of membrane moisture was investigated too. The experiments were performed under the same conditions (flow of distilled water through the module, pressure difference and temperature) on two ceramic membranes with identical characteristics. One of them was always sunk in distilled water, while the other one was kept dry.

In fig.2. it is shown the cumulative permeate mass of distilled water as a function of time for Kerasep membranes at different pressures, where dry and moisture membranes were used for the experiments. It was quite expected and confirmed that permeate flux measurement with dry membrane was higher than permeate flux measurement with moisture membrane. If we use dry membrane, than fluid must flow through the membrane for a definite period of time. In that way, all membrane pores will wet and permeate flow will be constant. Stationary conditions are established after 40 min. After more than 80 min permeate flux measurement with dry membrane can be equalized with permeate flux measurement with moisture membrane. That time is about 120 min.

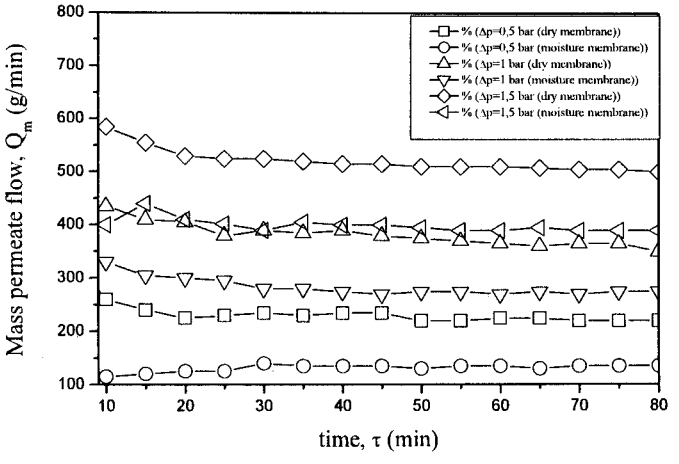

Fig. 2. - The mass permeate flow of distilled water, Q_m (g/min) for Kerasep membrane, where one of two mwmbranes was sunk and other one was kept dry, at different pressure, flow of distilled water through the module, Q_V=1 l/min and temperature t=22°C

With increase of pressure difference, permeate flux increases too. If the pressure difference is high (1 and 1.5 bar), then permeate flux will be higher because membrane pores are not wet. This phenomenon is more expressive in the experiments with dry membrane.

Influence of pressure difference on kinetics of microfiltration distilled water through the Kerasep membrane

In fig.3. and fig.4. it is shown the cummulative mass permeate flow of distilled water as a function of time, and in fig.5. the mass of permeate as a function of time for Kerasep membranes at different driving forces, Δp (bar), flow of distilled water through the module, Q_V=1 l/min and at the temperatures 22°C, 35°C, 45°C and 55°C. In all series collected permeate mass of distilled water

decreased in time until stationary conditions were established. Decrease of permeate flux and mass permeate flow is at the beginning very high and all the time of the microfiltration process they both decreased. As the process passes, decrease of permeate flux and mass permeate flow is very small and those are considered to be stationary conditions. In this case stationary conditions begin after 80 min.

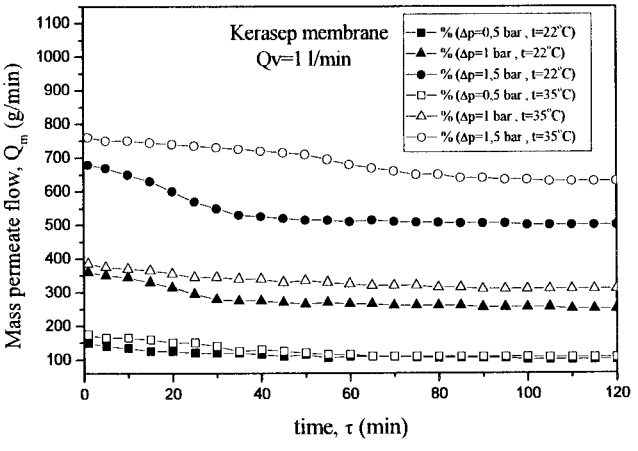

Fig. 3. - Influence of pressure difference,Δp (bar) on the mass permeate flow, Q_m (g/min) of distilled water as function of time for Kerasep membrane
(flow of distilled water through the module, Q_V=1 l/min and temperature t=22°C and t=35°C)

Initial values of permeate flow will be higher if microfiltration is performed at high temperature. Permeate flow increases linearly in the function of driving force (pressure difference). The mass of permeate collected after a definite period of time increases with the pressure difference, but if pressure difference is constant, in time the mass of permeate will linearly increase. This means that the mass permeate flow of distilled water is constant. It is quite expected because the feed water does not contain suspended solids that would lead to a reduction in mass permeate flow.

In fig.3. and fig.4. certain decrease of mass permeate flow of distilled water is noticeable between 40 and 80 min. The reason for deacrease of mass permeate flow is that the experiments are performed with dry membrane and disstiled water must flow through the membrane for a definite period of time, because of wetting of membrane pores. Ceramic membranes used in these experiments were used for earlier experiments on the same device with juice. They were not idealy clean even though they were washed with various chemicals. After two days, when membranes were sunk in distilled water, mucous layer on the membrane surface was noticed, and the reason was probably the presence of some microorganisms.

Stationary flux and stationary mass permeate flow are independent of increase of driving force (Δp). Under stationary conditions, after 80 min, all series showed the same results. Then it is not an important value of driving force.

Collected mass of permeate is the highest at the pressure difference of Δp=1.5 bar and that applies to mass permeate flow.

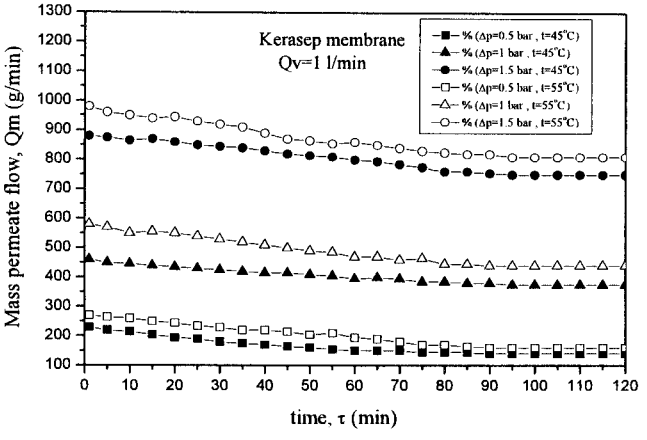

Fig. 4. - Influence of pressure difference, Δp(bar) on the mass permeate flow, Q_m (g/min) of distilled water as function of time for Kerasep membrane
(flow of distilled water through the module, Q_V=1 l/min and temperature t=45°C and t=55°C)

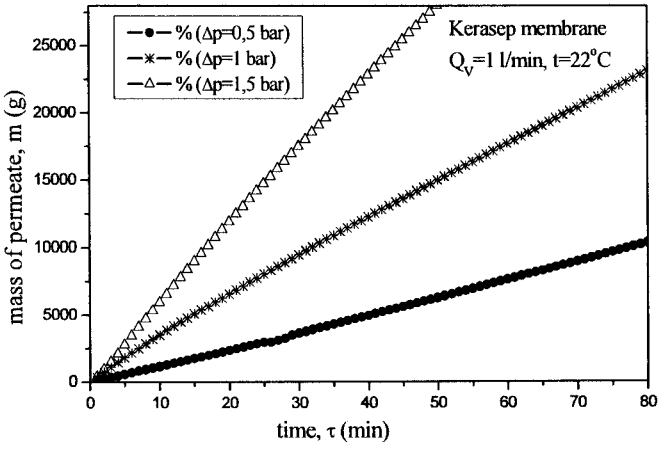

Fig. 5.- Influence of pressure difference, Δp (bar),on the mass of permeate distilled water, m (g), as function of time for Kerasep membrane
(flow of distilled water through the module, Qv = 1 l/min and temperature t = 22°C)

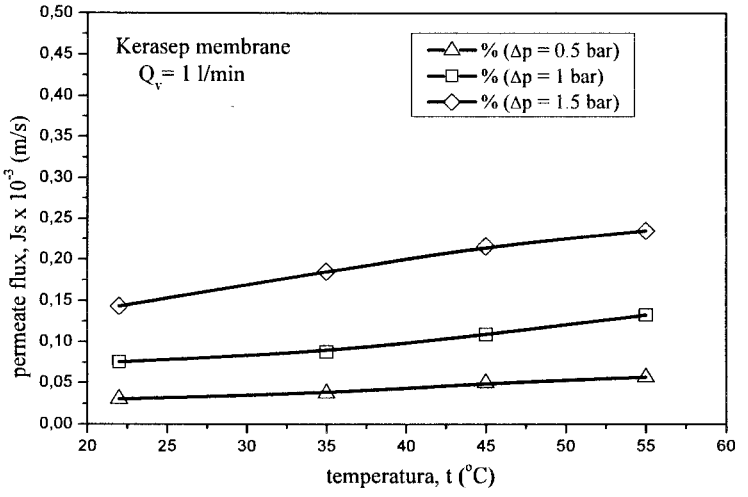

Fig. 6. - Influence of pressure difference, Δp (bar) and temperature, t (°C), on the permeate flux, J_S (m/s), for Kerasep membrane (flow of distilled water through the module, Q_V=1 l/min)

Influence of flow distilled water through the module on kinetics of microfiltration distilled water through the Kerasep membrane

The performed experiments show that flow of distilled water, Q_V in module does not have influence on the velocity of permeate separating and permeate flux. That is shown in fig.7.

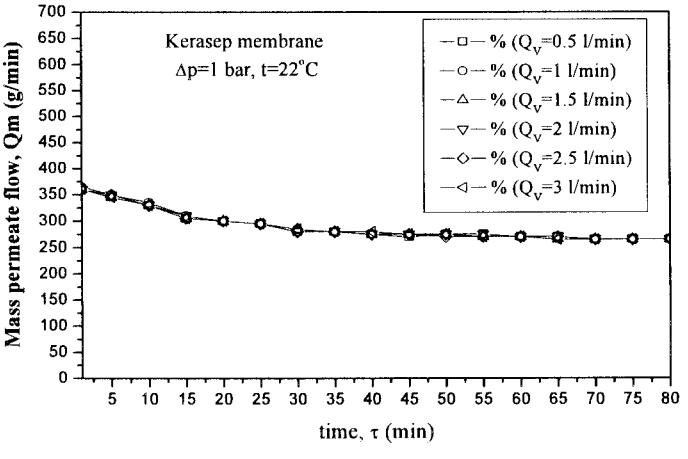

Fig. 7. - Influence of the mass flow of distilled water through the module on the mass permeate flow of distilled water as function of time for Kerasep membrane (pressure difference of Δp=1 bar and temperature t=22°C)

Because of the absence of concentration polarization, the hydraulic resistances are notified inside the membrane. These hydraulic resistances depend on the membrane structure (pore diameter, thickness of selective and bearer layer, etc.).

The mass permeate flow of distilled water is independent as a function of time, and it is higher than the mass permeate flow of juice, although driving force is low (Δp=0.5 bar). The cause is the absence of concentration polarization and the absence of appearing of second dynamic layer on the membrane surface.

Hydraulic resistance (R_m) of inorganic Kerasep membrane for microfiltration is $0.1454 \cdot 10^{13}$ 1/m. Hydraulic membrane resistance is independent of pressure difference, retentate flow and temperature.

Influence of temperature on kinetics of microfiltration distilled water through the Kerasep membrane

In fig.8. and fig.9. are shown the mass permeate flows, Q_m as a function of time, and in fig.10. the mass of permeate distilled water m as a function of time, at different temperatures: 22°C, 35°C, 45°C, 55°C and driving force Δp: 0.5, 1, 1.5 bar for Kerasep membrane where flow of distilled water through the module is Q_V=1 l/min. It is observed that with increase of temperature increase of the permeate mass becomes evident. With increase of temperature, liquid viscosity is reduced and this is reason for this occurence. If pressure difference (Δp) and temperature increase, then permeate flux will increase too, fig.11. It is obvious that increase of permeate with temperature is proportional with reducing of water viscosity. Hydrulic resistance is independent if changing of temperature and pressure difference is constant.

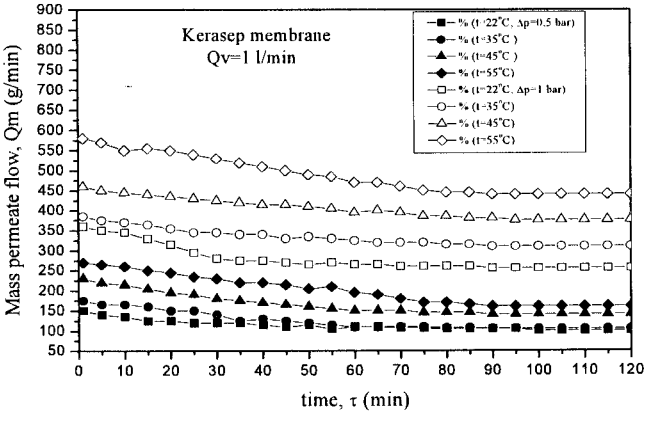

Fig. 8. - Changing of the mass permeate flow of distilled water, Q_m (g/min), on different temperature for Kerasep membrane
(flow of distilled water through the module, Q_V=1 l/min and pressure difference, Δp=0.5 bar and Δp=1 bar)

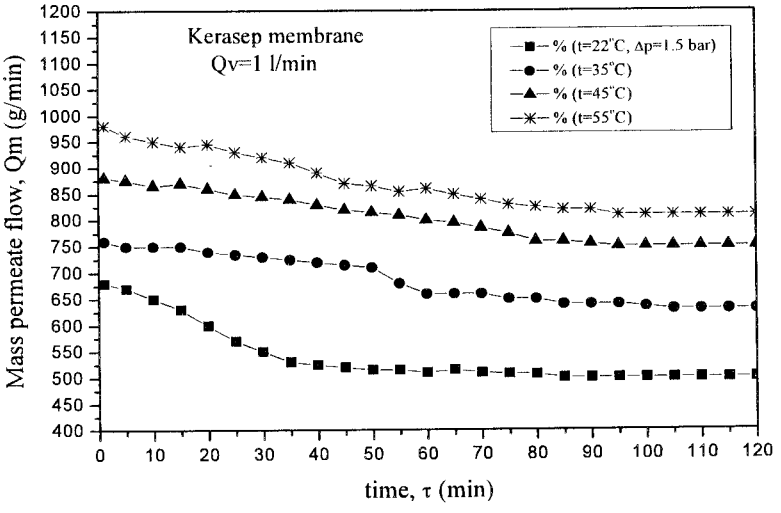

Fig. 9. - Changing of the mass permeate flow of distilled water, Q_m (g/min), on different temperature for Kerasep membrane
(flow of distilled water through the module, Q_V=1 l/min and pressure different, Δp=1.5 bar)

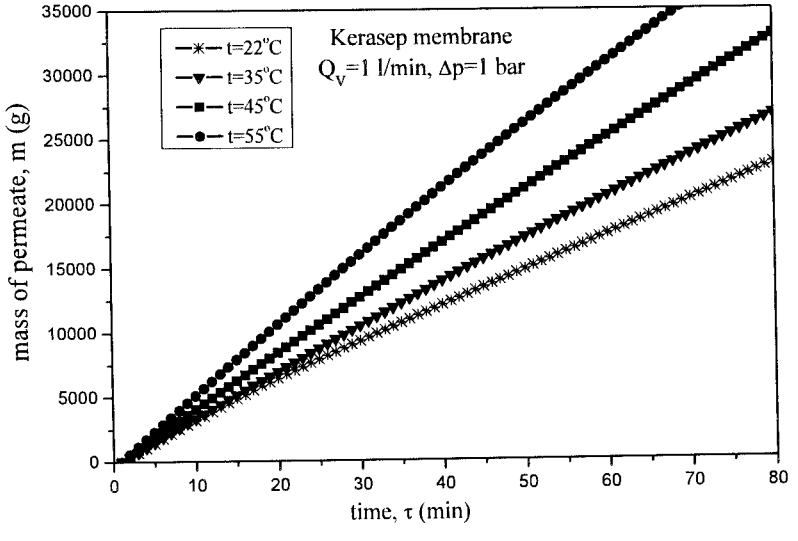

Fig. 10. - Collected mass permeate of distilled water, m (g), as function of time for Kerasep membrane on different temperatures (flow of distilled water through the module, Q_V=1 l/min and pressure difference Δp=1 bar)

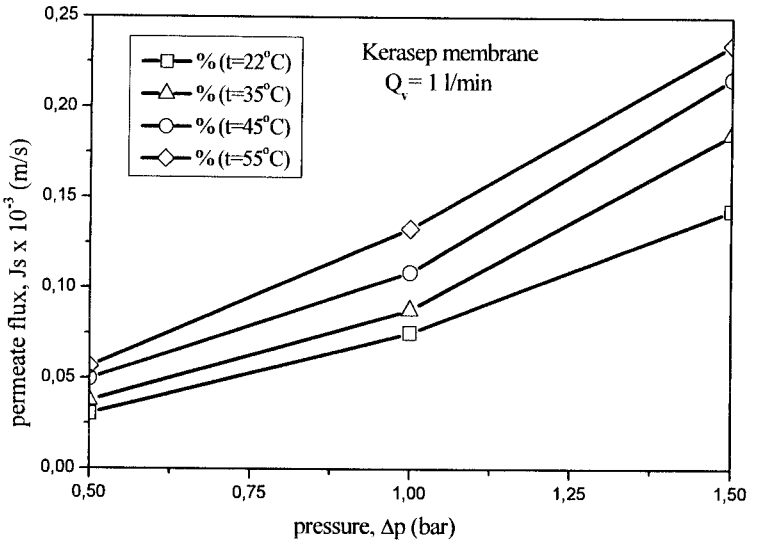

Fig. 11. - Effect of temperature, t (°C) and pressure difference, Δp (bar) on permeate flux, J_S (m/s), for Kerasep membrane with flow of distilled water through the module, Q_V=1 l/min

In all figures, it can be seen that the mass permeate flow slowly decreases as a function of time. This happens because resistances of membrane pores are very small. These resistances are caused by dry membrane pores or by membrane pores where there are air bubbles. So, to eliminate these resistances it is important that distilled water flows through membrane 40 min. After this time, permeate flow becomes stable and this means that all membrane pores are wet and air bubbles are lost.

Conclusion

The results of the performed experiments, where investigation was carried out on the influence of operating conditions (pressure difference, temperature, flow of distilled water through the module) on microfiltration of distilled water through the Kerasep membrane show that permeate flow linearly increases with increase of driving force (pressure difference). The mass of permeate collected after a definite period of time increases with increase of pressure difference. Also, if pressure difference is constant, then the mass of permeate will linearly increase with the time. This means that mass permeate flow of distilled water is constant.

Water flow in membrane flow does not have influence on permeate flux. Because of the absense of concentration polarization, hydraulic resistance will exist only inside the membrane. These resistances depend only of membrane structure.

If temperature increases, then the mass of permeate will increase too. The reason for this is the reduction of liquid viscosity at high temperature.

The experiments carried out to investigate the influence of membrane moisture show that membrane which was kept dry gave higher permeate flux than membrane sunk in distilled water. If membrane is sunk in distilled water, then all membrane pores will become wet and permeate flow will become stable earlier. If membrane was kept dry, then feed solution must flow for a definite period of time, because of wetting of membrane pores. When all membrane pores become wet, permeate flow will be stable.

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ISPITIVANJE HIDRODINAMIČKE PROPUSTLJIVOSTI KERAMIČKIH MIKROFILTRACIONIH MEMBRANA

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R e z i m e

U ovom radu su prikazani rezultati eksperimentalnog ispitivanja uticaja radnih parametara (protok destilovane vode kroz modul, temperatura, razlika pritisaka) na kinetiku mikrofiltracije kroz keramičku Kerasep membranu. Dobijeni rezultati su potvrdili ranija ispitivanja koja su obavljena na istoj aparaturi i predstavljaju uslov za određivanje kinetike bistrenja soka. Pored ispitivanja uticaja radnih parametara ispitan je i uticaj vlažnosti membrane na kinetiku mikrofiltracije.

Na osnovu izvršenih eksperimenata uticaja radnih parametara na mikrofiltracju destilovane vode kroz Kerasep keramičku membranu, može se zaključiti da se protok linearno povećava sa povećanjem pogonske sile tj. razlike pritisaka.

Protok vode u modulu nema nikakvog uticaja na brzinu izdvajanja permeata, tj. fluks permeata. Zbog odsustva koncentracione polarizacije hidraulički otpori se javljaju samo unutar membrane.

Uočeno je da povišenjem temperature dolazi do povećanja mase permeata. Razlog je u smanjenju viskoziteta tečnosti na povišenoj temperaturi.

Vlažnost membrane odražava se tako da suva membrana daje veći fluks permeata od potopljene membrane. To je posledica zapušenosti pora membrane u slučaju kada je ona potopljena. Kod suve membrane neophodno je da fluid struji neko vreme kako bi se sve pore u membrani nakvasile, nakon čega će se protok permeata ustaliti.

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