

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
7 (2001)

**THE INFLUENCE OF pH ON THE CROSS-FLOW
MICROFILTRATION OF DISPERSIONS
USING CERAMIC MEMBRANES**

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Received September 28, 2001

The influence of particle size and ζ -potential of particles and membrane surface with change of pH on permeate flux during the microfiltration of model dispersions on tubular ceramic membranes has been studied. The experiments include basic characteristics of alumina tubular membranes and model dispersions (aqueous titania dispersions). The description of the experimental system is also presented. The results of the experiments show that ζ -potential of membrane surface as well as of particles have impact on the permeate flux. This phenomenon is especially pronounced during the microfiltration of dispersion in isoelectric point, when permeate flux was nearly threefold in comparison with microfiltration of untreated dispersion.

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Introduction

The present cross-flow membrane processes for liquid feed streams are complicated by the phenomena of membrane fouling and of concentration polarisation in the liquid boundary layer adjacent to the membrane surface. Concentration polarisation and membrane fouling are major concerns in the successful use of a membrane-based separation operation, as their net effect is reduction of permeate flux, which results in loss of productivity. Therefore, it is important to reduce or control concentration polarisation and fouling in membrane processes and to enhance the permeate flux.

There are many intensification methods. One of them is based on influencing the electrochemical interaction between particles and between particles and membrane surface. This method plays an important role in microfiltration processes.

The pH value has significant influence on permeate flux, especially in the proximity of isoelectric point of some colloidal dispersions, which have tendency to instability and sedimentation. The effects of pH and salt concentration on microfiltration permeate flux have been reported by several authors.

Kwon *et al.* [1,2] were interested in the thickness of double diffuse layer and its influence on the microfiltration. They found that the thickness of diffuse layer is close-knit with ionic strength of solution.

Elzo and Huisman [3] were interested in filtration of the silica particles with the middle size of 0.5 μm . The inorganic membranes (middle size of pores 0.2 μm) used were made of $\alpha\text{-Al}_2\text{O}_3$. The authors studied the influence of some physical-chemical factors (e.g. pH, salt concentration and its valence) on the permeate flux. They found that permeate flux depends on surface charge of dispersed particles and on the surface charge of membrane surface. The conclusion of their research was expressed in the statement that the isoelectric point causes a decline of the permeate flux.

Huisman *et al.* [4] studied the influence of ζ -potential of three different ceramic membranes (Al_2O_3 , ZrO_2 , TiO_2) on the process of microfiltration of SiO_2 dispersion. The authors performed measurements for two values of pH, obtaining thus two ζ -potentials, one in acid area and the other in alkalic area. Inasmuch as, authors did not implicate in measurements the isoelectric point. They found that ζ -potential of dispersion and membrane surface has no influence on the process of microfiltration.

The aim of this study is to determine which operating parameters are involved in flux enhancement and to establish a link between electrochemical parameters and cake resistance.

Materials and Methods

Materials

Membranes

The membranes used in the filtration experiments were tubular asymmetric multi-layered membranes (Terronic, a.s., Czech Republic). They consist of a thin layer deposited on the internal surface of the alumina support. The characteristics of the membrane are: length, $L = 0.1$ m; internal diameter, $d_i = 6 \times 10^{-3}$ m; nominal pore size, $d_p = 0.91$ μm ; mean membrane resistance, $R_m = 1.17 \times 10^{12}$ m^{-1} (obtained from water flux measurements) and membrane surface area, $A_m = 18.86 \times 10^{-4}$ m^2 . A new membrane was used in each experiment, and before each run the pure water flux was measured with deionised water.

Dispersions

The microfiltration experiments were performed with an aqueous dispersion of titanium dioxide (Versanyl B-K7020) obtained from Ostacolor a.s., Pardubice, Czech Republic. The mean diameter of particles of pure dispersion (without acid or base) was 353 nm; however, the distribution of particles was very wide.

Filtration Unit

The microfiltration experimental apparatus used is shown schematically in Fig. 1. The circulating loop was constructed of stainless steel and contained ten litre feed suspension reservoir, pneumatic membrane pump (The Aro Corporation), damper (Almatec), for damping the beats of the pump, the membrane module and a flow control valve at the module outlet. The loop was also equipped with a temperature regulating system, and a pressure, temperature and flow monitoring system. The velocity and pressure in the retentate loop were varied independently by means of pump controller and a needle valve.

Methods

Particle Size and ζ -Potential Measurement

The experiments were carried out on the instrument Zeta PALS (fy. Brookhaven Instruments Corp., USA).

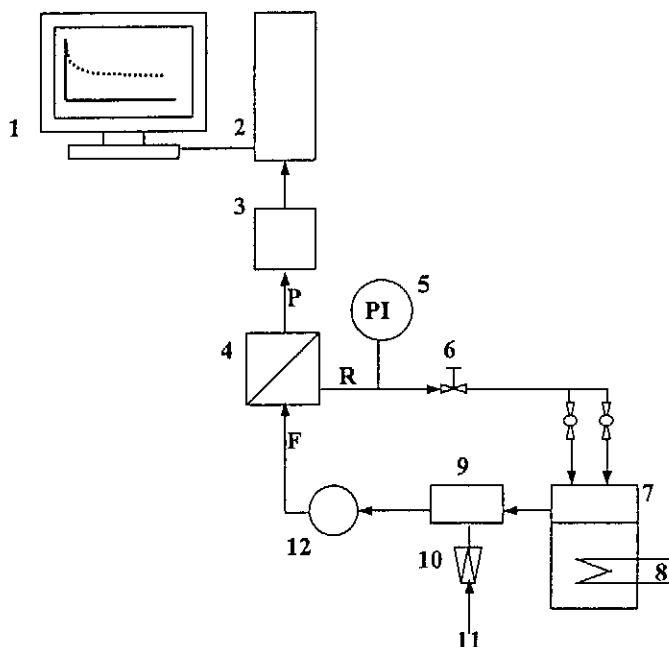


Fig. 1 Scheme of experiments: 1 – monitor; 2 – output on PC; 3 – scale; 4 – membrane module; 5 – sensor of pressure; 6 – needle valve; 7 – stack with dispersion; 8 – temperature system with thermostat; 9 – pneumatic membrane pump; 10 – reducing valve of the pump; 11 – entrance of air from compressor; 12 – damper; F – feed; P – permeate; R – retentate

Before performing the microfiltration experiments, one membrane was ground in the oscillatory mill. This powder was dispersed in water by ultrasound at pH value ranging from 2.5 to 11.5, and ζ -potential of the dispersion was measured.

A dispersion of titanium dioxide was scaled in the same range of pH values like a membrane surface. The original dispersion was diluted to the concentration of 1 kg m^{-3} , and then the particle size and ζ -potential were measured.

Microfiltration Measurements

The experiments concerned the cross-flow microfiltration of the titanium dioxide particles with concentrations 5 and 10% wt at various pH values. During all the tests, the filtration was run at a constant cross-flow velocity of 1 or 2 m s^{-1} and constant transmembrane pressures of 100 or 200 kPa.

After the membrane was placed in the membrane module, deionised water

was circulated in the test loop at moderate operating pressure for about 1 hour. During this time a stabilisation of the membrane was observed giving relatively stable water permeability. A concentrate of feed substance was then introduced to the unit, preheated to the desired temperature (25 °C), and the operating pressure as well as retentate velocity were adjusted by the regulation system.

The flux through membrane was measured by weighing permeate and timing the collection period (by use of a balance interfaced with a computer). Both the retentate and permeate were recirculated back into the reservoir. Therefore, the concentration in the recirculation loop remained virtually constant. After each set of experiments the circuit and membrane were rinsed with water and the pure water flux was measured again under the conditions of initial tests until the steady state was attained. The differences in the steady state pure water flux were taken as a measure of the fouling tendency of the membrane.

Results and Discussion

ζ-Potential and Particle Size

The results obtained are plotted as the ζ -potential of the titania particles or membrane material vs. the range of pH values.

From Figs 2 and 3 we observed that the particle size and ζ -potential of dispersion and ζ -potential of membrane material are strongly dependent on the pH value of the solution in which they are immersed.

Figure 2 shows the ζ -potential and the particle size of the titanium dioxide

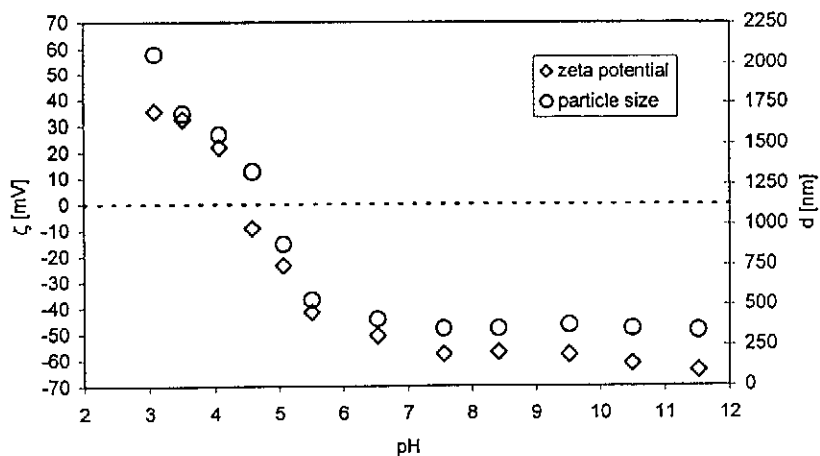


Fig. 2 Influence of pH value on particle size and ζ -potential of aqueous dispersion

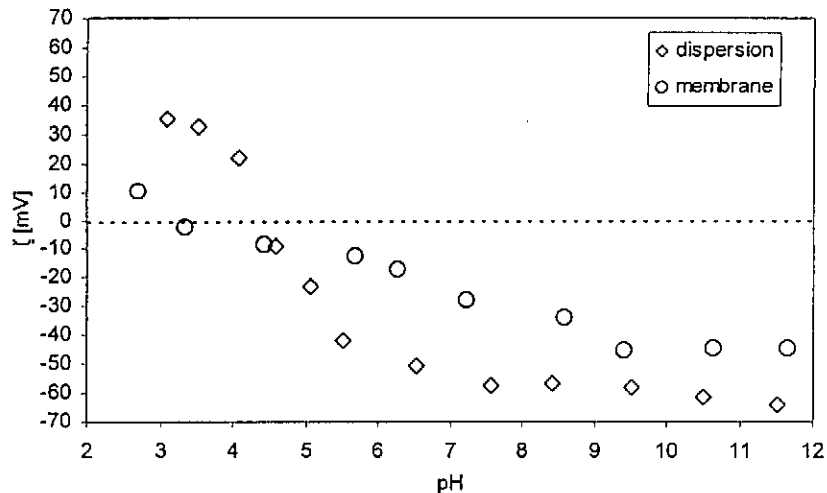


Fig. 3 Influence of pH value on ζ -potential of the dispersion (TiO_2) and the membrane (Al_2O_3)

particles. The particle size is nearly constant in the base area, 300 nm. The ζ -potential is invariable too, of about -50 mV. With decreasing of pH value the particle size increases up to a value of 1800 nm. The isoelectric point, i.e. the pH at which the ζ -potential is zero, of dispersion was at about pH 4.5.

The variation of ζ -potential with the pH of dispersion is shown in Fig. 3. The isoelectric point of the α -alumina particles (membrane) was obtained to be about pH 3.2. For higher values of pH, the ζ -potential is negative.

Filtration Experiments

Effects of pH on Permeate Flux

Figure 4 shows results from the cross-flow microfiltration experiments performed at various pH values. The transmembrane pressure, 100 kPa and 200 kPa, and the velocity of feed, 1 m s^{-1} and 2 m s^{-1} , were constant.

The steady permeate flux is nearly constant in the alkalic area. Decreasing pH of the dispersion (acid area) resulted in a higher steady permeate flux and a shorter period to attain the equilibrium state. At pH 4.5 the steady permeate flux reached the maximum value. Below this pH value the steady permeate flux declined. At pH value of about 3.5 the steady permeate flux reached a local minimum. In the most acid area the steady permeate flux increased. Similar experiments were carried out with the same TMPs and velocities for higher concentration, 10% wt. The results are presented in Fig. 5. The general tendencies observed before were confirmed.

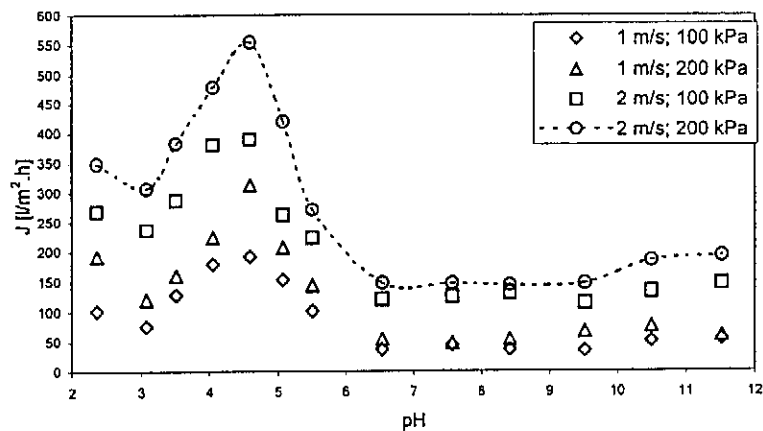


Fig. 4 Influence of pH value on steady state permeate flux (5% wt dispersion)

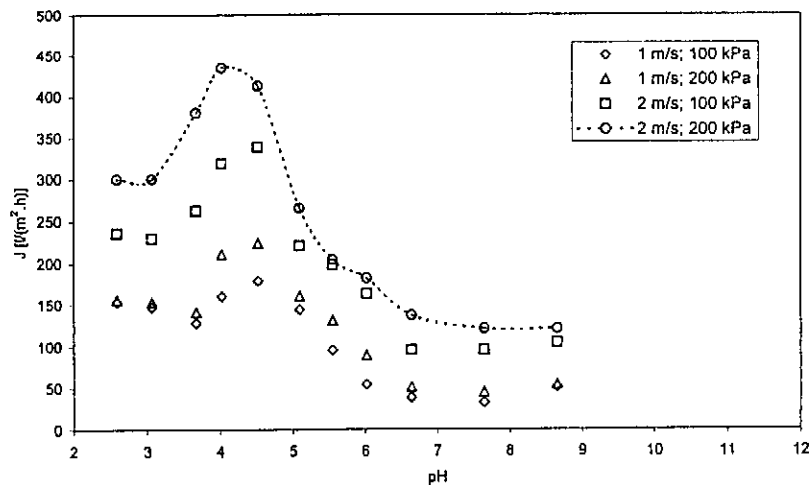


Fig. 5 Influence of pH value on steady state permeate flux (10% wt dispersion)

The highest permeate flux was obtained at the isoelectric point of dispersion.

Because the steady permeate flux was nearly constant in alkalic area for 5% wt dispersion, we did not measure this area with the 10% wt dispersion.

As it can be seen in Figs 4 and 5 all the dependencies embody similar trend in the whole range of pH values. The maximum of stable value of permeate flux occurs near pH 4.5. Particles of dispersion occur in isoelectric point at this value

of pH. Neither the value of ζ -potential (-55 mV) nor particle size (300 nm) changes in pH interval from 6.5 to 11.5 . Therefore, permeate flux remains nearly constant. Below values of pH 6.5 the particle size as well as ζ -potential begin to increase. Thereupon the permeate flux is increasing too, until the isoelectric point. In pH interval from 4.5 to 3.0 the particle size is increasing and ζ -potential of particles reaches positive values. But the ζ -potential of membrane surface has isoelectric point at pH value 3.2 . On that account, the particles are attracted to the membrane surface. Thereupon the thickness of filter cake increases; therefore the resistance of filter cake increases, too. As a result, the stable value of permeate flux decreases. The ζ -potential of membrane surface reaches positive values for $\text{pH} < 3.0$. Therefore, the stable value of permeate flux is increasing in consequence of repulsion of particles and membrane surface.

Influence of pH on Filter Cake Resistance

Figures 6 and 7 show the influence of pH value on resistance of filter cake. We can see all the dependencies embody similar trend in the whole range of pH values. The minimum of resistance value of filter cake occurs in the proximity of pH 4.5 .

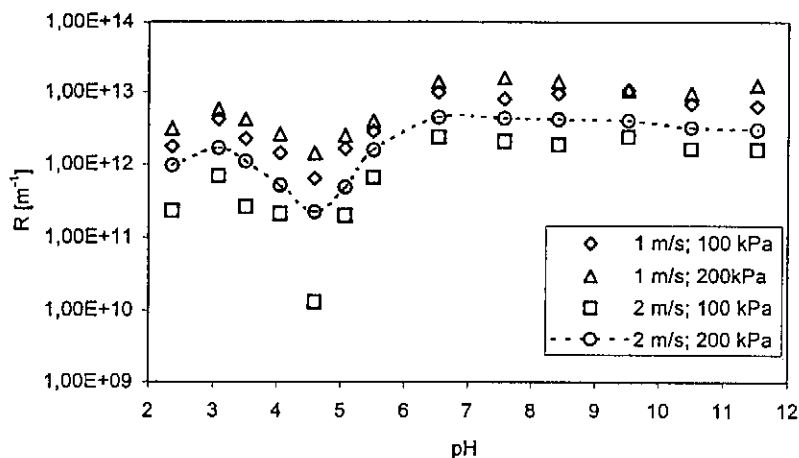


Fig. 6 Influence of pH value on filter cake resistance (5% wt dispersion)

Because the particle size is about one order greater in the most acid area of pH, the stable value of permeate flux is higher in this area. The bigger particle sizes cause higher porosity and lower value of resistance of filter cake.

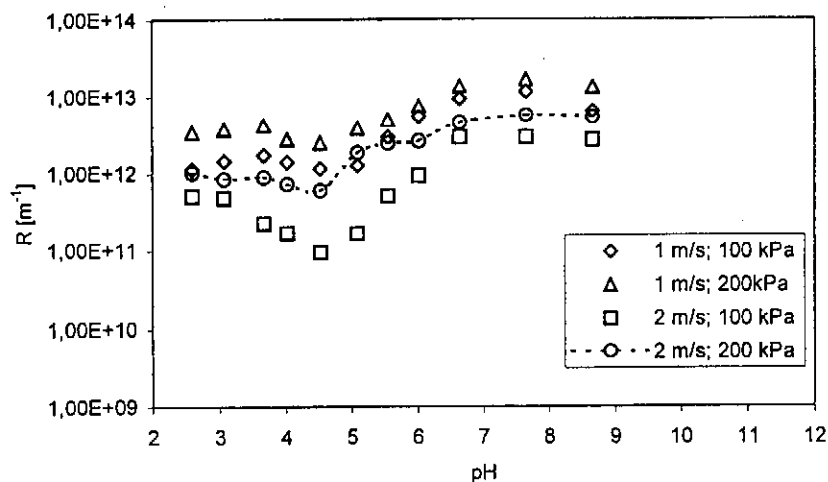


Fig. 7 Influence of pH value on filter cake resistance (10% wt dispersion)

Description of the Microfiltration Process

The development of permeate flux in time may be divided into three periods (see Fig. 8). At the beginning of the process, during the first period, a rapid decrease of the permeate flux is observed. The permeate flux is dependent on physicochemical parameters already during the first period. This can be explained by assuming that the flux during this period is so high and that all particles that get near the membrane surface are pressed onto the membrane. Characteristics thereby rising filter cake are dependent upon electrokinetic forces between the arriving particles and the membrane or between the arriving particles and those already deposited. The membrane characteristics have great influence on permeate flux during this first period too, e.g. permeability and transmembrane pressure. The build-up of filter cake decreases the permeate flux.

When the second period starts, the interactions particle — particle and particle — membrane surface have the most important effect in the build-up of the filter cake. The particle size and ζ -potential of particles and membrane surface affect the porosity of the growing filter cake. With lower porosity of filter cake the permeate flux is declining.

The third period begins when the steady-state flux regime is reached. The permeate flux is independent on the filtration time. A dynamic equilibrium between the convected particles and the removed particles is reached.

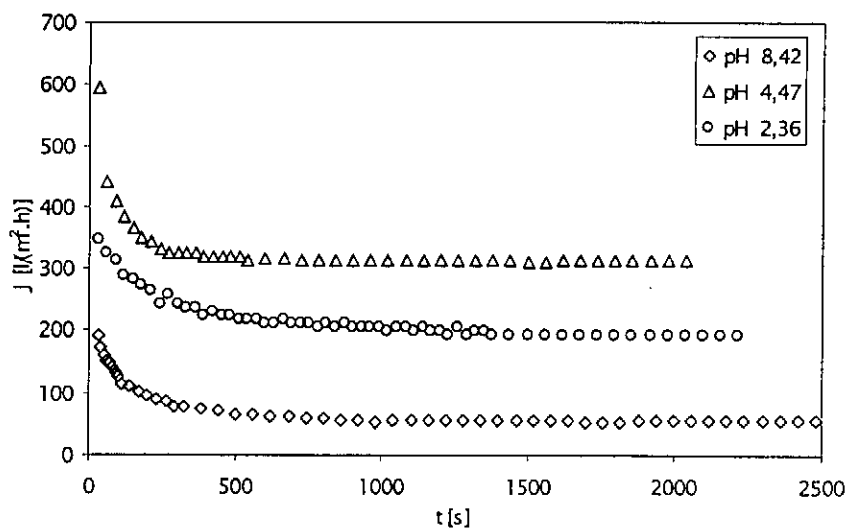


Fig. 8 Influence of pH value on permeate flux ($u_F = 1 \text{ m s}^{-1}$, $\Delta P = 200 \text{ kPa}$, concentration 5% wt)

Conclusion

The results of the experiments show that ζ -potential of membrane surface as well as that of particles have impact on the permeate flux. This phenomenon is especially pronounced during the microfiltration of dispersion at isoelectric point, when permeate flux was nearly threefold in comparison with microfiltration of untreated dispersion.

This process seems to be very promising, so further research and development on other dispersion systems (inorganic or organic) are under-way to optimise the process and to promote a better understanding of the underlying mechanisms.

Acknowledgements

The Ministry of Education, Youth and Sports of the Czech Republic, Project CI MIS 253100001, financially supported this work.

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