EFFECT OF PHYSICOCHEMICAL CONDITIONS ON CROSSFLOW MICROFILTRATION OF MINERAL DISPERSIONS USING CERAMIC MEMBRANES

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This paper studies the influence of dispersion pH, ionic strength, and coagulant type on ceramic membrane microfiltration of TiO_2 dispersions. A series of crossflow microfiltration experiments were carried out at various pH values, ionic strengths and with various multivalent inorganic salts. The filtration behaviour was analyzed based on measurements of zeta potential of alumina membrane and TiO_2 particle and particle size distribution of the TiO_2 suspension. The results show that inorganic anions affect the microfiltration of TiO_2 dispersion by changing the surface properties of both the alumina membrane and TiO_2 particle. The solution environment affects the dispersion of TiO_2 particles and plays a major role in the filtration flux.

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Introduction

Crossflow microfiltration is a pressure driven membrane process for separating dispersed matters in the range of sizes from 0.05 to 10 μm from liquids. The principle of solid/liquid separation can be described as a pressing of pure liquid through the membrane pores and through the deposit of solid particles on the membrane wall. In the absence of membrane fouling, the increasing thickness of the deposit of particles (cake formation) causes the initial rapid decrease of flux, and limits the wider application of microfiltration. In spite of this, the separation process finds increasing use in water purification, wastewater treatment, brewing and biotechnology industries, amongst others.

The main factor limiting the application of crossflow microfiltration and other pressure-driven membrane processes is the flux decline due to membrane fouling and concentration polarization [1]. The steady state value of permeate flux depends besides hydrodynamic conditions (cross-flow velocity, the Reynolds number, shear stress and shear rate at the membrane surface) in the membrane system [2] on physico-chemical particle-particle and particle-membrane interactions [3]. One way of characterizing these particle-particle and particle-membrane interactions is the knowledge of the ξ-potential of both particle and membrane. This electrostatic characterization of membranes is a useful way to predict and interpret the performance of microfiltration process. The magnitude of the ξ-potential gives the information of the stability of the system. Near the isoelectric point – IEP (the value of pH, where the charge and therefore ξ-potential of particles are equal to zero) the system is unstable and the particles tend to flocculate. Therefore, the stability of the particles and the particle-membrane system could affect the separation process. Many studies showed that permeate flux, J, can be easily changed by pH, kind of added salt, and salt concentration of the microfiltration dispersion [4-7].

The feed pre-treatment prior to the application of crossflow microfiltration may be another option to increase the permeate flux, and coagulation can be one of the suitable pre-treatment methods. But the pre-treatment not only reduces the decline in permeate flux but also leads to superior removal of particulates [8].

Many authors [9-16] investigated the flocculation pre-treatment together with adsorption pre-treatment in wastewater reuse. The results of filtration experiments showed that the membrane fouling decreased and the membrane flux and permeate quality increased with flocculation as a pre-treatment.

The aim of present study is to show that pH, kind of salt and ionic strength significantly affect the electrochemical properties of dispersion and membrane and in this way influence the microfiltration process in general. Special attention was given to the ξ-potential measurements of the anatase dispersion in various solution environments. These measurements were combined with a series of crossflow microfiltration experiments at various pH values, salt concentrations and with

NaCl, Na_2SO_4 and Na_3PO_4 electrolytes. Moreover, in this study the influence of coagulation pre-treatment on crossflow microfiltration process of titanium dioxide dispersions was examined.

Experimental

Asymmetric tubular α-Al_2O_3 microfiltration membranes (TERRONIC, the Czech Republic) were used in the separation experiments. The characteristics of the membrane are: 0.25 m length, 6 mm inner diameter, 10 mm outer diameter. The nominal pore size of the membrane is 91 nm. A new membrane was used in each experiment, and before each run the pure water flux was measured with deionised water.

The microfiltration experiments were carried out with an aqueous dispersion of TiO_2 (anatase, PRECHEZA, the Czech Republic). The dispersions were prepared from powder and deionised water; the powder was dispersed in an ultrasonic bath. The concentration of dispersion was 5 wt %. The pH was adjusted to the target value by adding HCl. The microfiltration experiments were carried out without salt and in the presence of NaCl, Na_2SO_4 or Na_3PO_4 (the concentrations of the salts were 0.01 and 0.001 M).

The experiments concerned the cross-flow microfiltration of the TiO_2 particles with a particle concentration of 5 wt % at various pH values, salt concentrations and salt type. During all tests, the microfiltration process was run at a constant cross-flow velocity of 1 m s^{-1} and constant transmembrane pressure of 100 kPa. The temperature of the dispersion was 25 °C. The volume of dispersion was 2.5 l. The permeate flux was measured by the electronic balance and the permeated volume was recirculated to the feed tank to keep a constant feed concentration. The experiment was stopped after obtaining constant permeate flux. The adjustment of pH value was performed 18 h before the filtration experiments to reach the stable conditions of interactions between particles. After each set of experiments the unit and the membranes were rinsed with deionised water. The tests were performed in duplicate and showed a high reproducibility.

The ξ-potential of titania particles was determined using Zeta PALS (Brookhaven Instruments Corp., USA). The principle of measurement consists in the migration of charged particles under the influence of an electric field. The ξ-potential can be derived from the electrophoretic mobility

$$\xi = \frac{\mu_M \eta}{\varepsilon_0 \varepsilon_r} \tag{1}$$

where ξ is the zeta potential, μ_M is the electrophoretic mobility, η is the dynamic viscosity of liquid, ε_0 is the permittivity of vacuum and ε_r is the relative permittivity of the liquid. All the experiments were carried out at 25 °C.

For some series of cross-flow microfiltration experiments two types of coagulant (inorganic and organic) were used. Aluminium sulphate was used as an inorganic coagulant and PRAESTOL 511K (polyacrylamide) was used as an organic coagulant. Preliminary tests were performed before crossflow microfiltration experiments, and three different doses of these coagulants were chosen on the basis of the results of these preliminary tests. The influence of different doses and coagulant type on crossflow microfiltration process was examined. The concentrations of 30, 40 and 50 mg l^{-1} of aluminium sulphate and the concentrations of 30, 50 and 70 mg l^{-1} of PRAESTOL 511K were tested.

The experiments were carried out on laboratory-scale, and the experimental apparatus is shown in Fig. 1. The feed dispersion was pumped from a feed tank to the membrane module by a screw pump and the retentate was returned to the feed tank. The permeate flux was measured by an electronic balance and the permeated volume was recirculated to the feed tank to keep a constant feed concentration. The pressure was adjusted to the target value by a regulating valve, and the transmembrane pressures were measured by manometers.
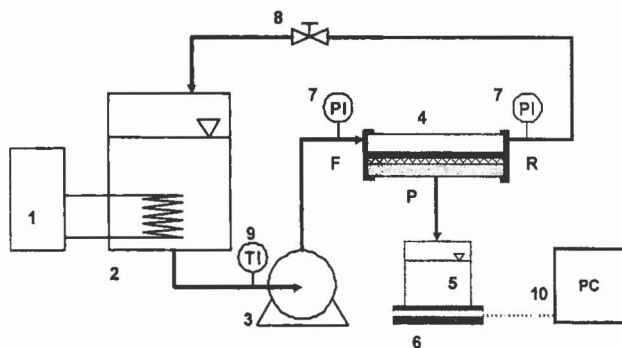

Fig. 1 Schematic diagram of the experimental apparatus: 1 – thermoregulator; 2 – feed tank; 3 – screw pump; 4 – membrane module; 5 – permeate tank; 6 – electronic balance; 7 – manometers; 8 – regulating valve; 9 – temperature sensor; 10 – PC; F – feed; P – permeate; R – retentate

Results and Discussion

Table I represents the values of IEP of TiO_2 dispersions for the different ionic strengths of NaCl, Na_2SO_4 and Na_3PO_4. According to the results, the IEP in the presence of Na_2SO_4 and Na_3PO_4 shifts to lower values of pH as the concentration increases. The results indicate that the specific adsorption may occur with the

Table I   Isoelectric point of TiO$_2$ dispersions

Kind of salt	Ionic strength	Value of IEP (TiO$_2$)
No salt	-	4.8
NaCl	0.001 M	4.9
	0.01 M	5.0
Na$_2$SO$_4$	0.001 M	4.0
	0.01 M	3.9
Na$_3$PO$_4$	0.001 M	4.5
	0.01 M	4.2
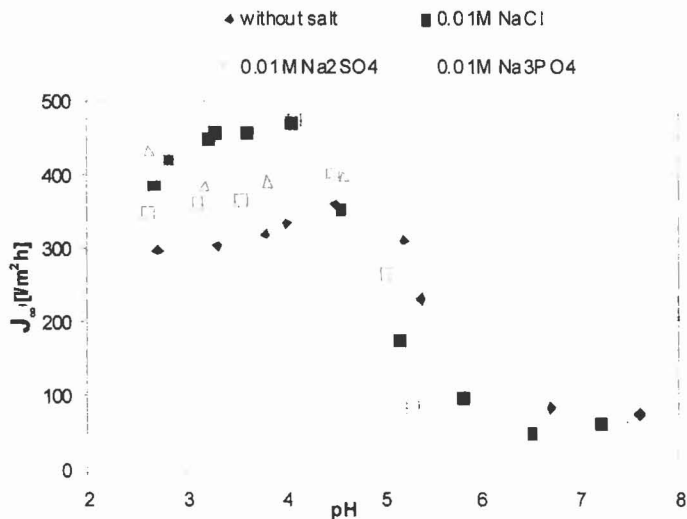
Fig. 2   Steady state value of the permeate flux as a function of pH at the same ionic strengths of NaCl, Na$_2$SO$_4$ and Na$_3$PO$_4$

SO_4^{2-} and PO_4^{3-} ions on the membrane surface. In addition, the shift of IEP increases with increasing salt concentrations.

A set of microfiltration experiments were carried out to investigate the influences of pH and ionic strength. All the experiments were performed at the same conditions. The transmembrane pressure was 100 kPa and the cross-flow velocity was 1 m s^{-1}. Figure 2 shows the results from the cross-flow microfiltration experiments as a function of pH at the same ionic strengths of NaCl, Na$_2$SO$_4$ and Na$_3$PO$_4$.

As can be seen from Fig. 2, all the dependencies had a similar trend. The value of steady state permeate flux decreased as the pH value increased in a pH
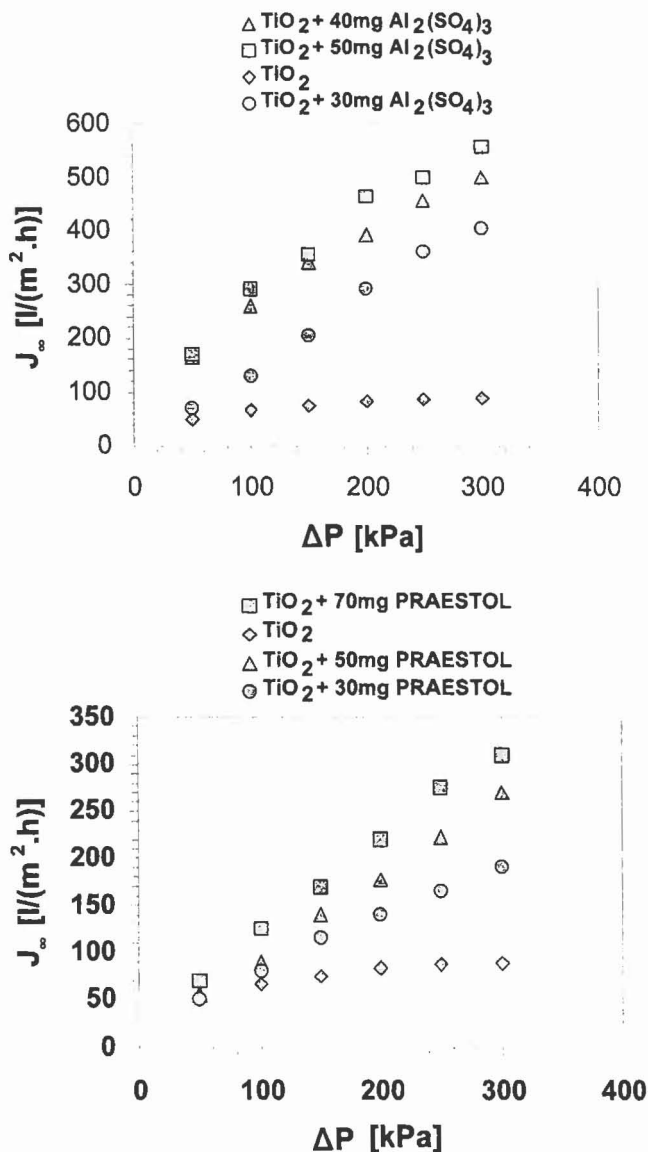
Fig. 3   Steady state value of the permeate flux as a function of pressure difference, type and dose of coagulant

range of isoelectric point to 8, and all the curves have the maximum permeate flux near the isoelectric point of dispersion. The steady state flux increased with increasing ionic strength of NaCl, Na_2SO_4 and Na_3PO_4.

The influence of the optimum dose of coagulant was investigated in another set of microfiltration experiments. The results of the experiments show that the coagulation could decrease the membrane fouling and increase the permeate flux.

The dependence of the steady state permeate flux on pressure difference is shown in Fig. 3. From Fig. 3 is evident that the influence of aluminium sulphate is greater than that of PRAESTOL 511K. We can also see from Fig. 3A that the optimum dose is 40 mg l^{-1}. However, the results with higher dose (50 mg l^{-1}) are very similar to those with this dose mainly for the lower pressures (50-150 kPa). The optimum dose of other coagulant (see Fig. 3B) is 50 mg l^{-1} in spite of the fact, that the better results were achieved with concentration of 70 mg l^{-1}. But the influence of this coagulant is significant for the higher pressures (higher than 100 kPa).

The comparison of these two types of coagulant is shown in Fig. 4. From Fig. 4 is evident that aluminium sulphate is a better coagulant for titanium dioxide dispersion. The results of the experiments show that the pre-treatment of the feed with aluminium sulphate led to four or five times higher permeate flux than that without any pre-treatment, and more than two times higher permeate flux than with pre-treatment with the PRAESTOL 511K.
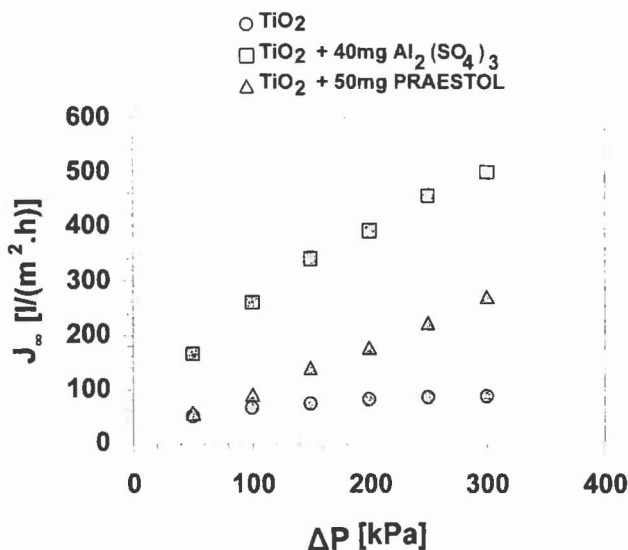

Fig. 4 The comparison of the effects of the optimum dose of coagulants on permeate flux

Conclusion

The permeate flux of the ceramic membrane in the microfiltration of TiO_2 suspension was affected significantly by the solution environment (including pH and ionic strength) and by the presence of coagulant. The steady-state flux increased with increasing ionic strength in the presence of electrolytes, NaCl, Na_2SO_4 and Na_3PO_4, and with decreasing pH. This was mainly due to the influences of ionic strength and pH on the dispersity of TiO_2 suspensions. The

results showed that the influences of inorganic salts on the microfiltration of TiO_2 dispersion were related to changes in the surface properties of both the ceramic membrane and TiO_2 particles. A more suitable coagulant for flux enhancement during TiO_2 microfiltration is aluminium sulphate with the optimum dosage of 40 mg l^{-1}. The results also show that the value of steady state permeate flux significantly increases with the pressure difference and the limit pressure difference was not be achieved.

Acknowledgements

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