Effect of physicochemical conditions on crossflow microfiltration of mineral dispersions using ceramic membranes

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Effect of physicochemical conditions on crossflow microfiltration of mineral dispersions using ceramic membranes

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Abstract

In this paper the influence of dispersion pH, ionic strength, and coagulant type on ceramic membrane microfiltration of TiO₂ dispersions were studied. A series of crossflow microfiltration experiments was carried out at various pH values, ionic strengths and with various multivalent inorganic salts. Filtration behaviours were analyzed based on measurements of zeta potential of alumina membrane and TiO₂ particle and particle size distribution of the TiO₂ suspension. Results showed that inorganic anions affect the microfiltration of TiO₂ dispersion by changing the surface properties of both the alumina membrane and TiO₂ particle. The solution environment affects the dispersion of TiO₂ particles and plays a major role in the filtration flux.

Keywords: microfiltration, pH, ionic strength, coagulation, membrane fouling

1. Introduction

Crossflow microfiltration is a pressure driven membrane process for separating dispersed matters in 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.

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The main factor limiting the application of crossflow microfiltration and other pressure-driven membrane processes is flux decline due to membrane fouling and concentration polarization (Schafer et al., 2000). 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 (Broussous et al., 2000) on physico-chemical particle-particle and particle-membrane interactions (Huisman et al., 1999). One way of characterizing these particle-particle and particle-membrane interactions is the knowledge of the \( \xi \)-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 \( \xi \)-potential gives the information of the stability of the system. Near the isoelectric point – IEP (the value of pH, where the charge and therefore \( \xi \)-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 (Nazzal et al., 1994; Mullet et al., 1997; Moritz et al., 2001; Martín et al., 2003).

The feed pre-treatment prior to the application of crossflow microfiltration may be another option to increase the filtration flux and coagulation can be one of the suitable pre-treatment methods. But the pre-treatment not only reduces the decline in filtration flux but also leads to superior removal of particulates (Kwon et al., 1997).

Many authors (Abdessemed et al., 2000, 2002; Chapman et al., 2002; Zhong et al., 2003; Guo et al., 2004, 2005; Shon et al., 2004, 2005) 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 was to show that pH, kind of salt and ionic strength are very important parameters that significantly affect the electrochemical properties of dispersion and membrane and by this way influence the microfiltration process at all. Special attention was given to the \( \zeta \)-potential measurements of the anatase dispersion under different solution environments. These measurements were combined with a series of crossflow microfiltration experiments at various pH values, salt concentrations and with NaCl, \( \text{Na}_2\text{SO}_4 \) and \( \text{Na}_3\text{PO}_4 \) electrolytes. Moreover, in this study the influence of coagulation pre-treatment on crossflow microfiltration process of titanium dioxide dispersions was examined.

2. Experimental

Asymmetric tubular \( \alpha\text{-Al}_2\text{O}_3 \) microfiltration membranes (TERRONIC, Czech Republic) were used in the separation experiments. The characteristics of the membrane are: 0.25m length, 6mm inner diameter, 10mm outer diameter. The nominal pore size of the membrane is 91nm. A new membrane was used in each experiment, and before each run the pure water flux was measured with deionised water.
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The microfiltration experiments have been carried out with an aqueous dispersion TiO$_2$ (anatase, PRECHEZA, Czech Republic). Dispersions were prepared from powder and deionised water; the powder was dispersed in an ultrasonic bath. The concentration of dispersion was 5wt%. The pH was adjusted to the target value by adding HCl. The microfiltration experiments have been carried out without salt and in the presence of NaCl, Na$_2$SO$_4$ or Na$_3$PO$_4$ (the concentrations of the salts were 0.01 and 0.001M).

The experiments concerned the cross-flow microfiltration of the TiO$_2$ particles with a particle concentration of 5wt% at various pH values, salt concentrations and salt type. During all tests, the microfiltration process was run at a constant cross-flow velocity of 1m.s$^{-1}$ and constant transmembrane pressure of 100kPa. The temperature of the dispersion was 25°C. The volume of dispersion was 2.5L. 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 18h before the filtration experiments, by virtue of 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 $\zeta$-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 $\zeta$-potential can be derived from the electrophoretic mobility:

$$\zeta = \frac{\mu_M \cdot \eta}{\varepsilon_0 \cdot \varepsilon_r}$$

where $\zeta$ is the zeta potential, $\mu_M$ is the electrophoretic mobility, $\eta$ is the dynamic viscosity of liquid, $\varepsilon_0$ is the permittivity of vacuum and $\varepsilon_r$ is the relative permittivity of the liquid. All 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, respectively. Preliminary tests were performed before crossflow microfiltration experiments and from results of these tests were chosen three different doses of these coagulants. The influence of a different doses and coagulant type on crossflow microfiltration process was examined. Concentrations of 30, 40 and 50 mg/l of aluminium sulphate and concentrations of 30, 50 and 70 mg/l of PRAESTOL 511K were tested.

Experiments were carried out at 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 retentate was returned to the feed tank. 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. Pressure was
adjusted to the target value by a regulating valve and transmembrane pressures were measured by manometers.

![Figure 1: Schematic diagram of the experimental apparatus](image)

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.


3. Results and discussion

Table 1 represents the values of IEP of TiO$_2$ dispersions for the different ionic strengths of NaCl, Na$_2$SO$_4$ and Na$_3$PO$_4$. According to the results, the IEP in the presence of Na$_2$SO$_4$ and Na$_3$PO$_4$ shifts to lower values of pH as the concentration increases. The results indicate that the specific adsorption may occur with the SO$_4^{2-}$ and PO$_4^{3-}$ ions on the membrane surface. In addition, the shift of IEP increases with increasing salt concentrations.

<table>
<thead>
<tr>
<th>Kind of salt</th>
<th>Ionic strength</th>
<th>Value of the IEP (TiO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no salt</td>
<td>-</td>
<td>4.8</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.001M</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>0.01M</td>
<td>5.0</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.001M</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>0.01M</td>
<td>3.9</td>
</tr>
<tr>
<td>Na$_3$PO$_4$</td>
<td>0.001M</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>0.01M</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Table 1: The isoelectric point of TiO$_2$ dispersions
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Figure 2: Steady state value of the permeate flux as a function of pH and different ionic strengths of NaCl, Na$_2$SO$_4$ and Na$_3$PO$_4$

To investigate the influences of pH and ionic strength a set of microfiltration experiments was carried out. All experiments were performed at the same conditions. The transmembrane pressure was 100 kPa and the cross-flow velocity 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 range of 2 to 8, and all curves have maximum permeate flux near the isoelectric point of dispersion. The steady state flux increased with increasing ionic strength of NaCl, Na$_2$SO$_4$ and Na$_3$PO$_4$.

The influence of the optimal dose of coagulant has been carried out in another set of microfiltration experiments. The results of the experiments show that the coagulation could decrease the membrane fouling and increase the filtration 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 influence of PRAESTOL 511K. We can also see from Fig. 3A that optimal dose is 40mg/l. However, the results with higher dose (50mg/l) are very similar to results with this dose mainly for the lower pressures (50 – 150 kPa). The optimal dose of another coagulant (see Fig. 3B) is 50mg/l in spite of the fact, that the better results were achieved with concentration of 70mg/l. 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 better coagulant for titanium dioxide dispersion. The results of the experiments show that the pre-treatment of the feed by 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 by the PRAESTOL 511K.
Figure 3: Steady state value of the permeate flux as a function of pressure difference, type and dose of coagulant

Figure 4: The comparison of the effects of optimal dose of coagulants on permeate flux
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4. Conclusions

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 strengths) and by the presence of coagulant. The steady-state flux increased with increasing ionic strength in the presence of electrolytes, NaCl, Na$_2$SO$_4$ and Na$_3$PO$_4$, and 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. More suitable coagulant for flux enhancement during TiO$_2$ microfiltration is aluminium sulphate with the optimal dosage of 40mg/l. The results also show that the value of steady state permeate flux significantly increase with pressure difference and the limit pressure difference was not be achieved.

Acknowledgements

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References