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The Influence of Electrochemical Properties of Membranes and Dispersions on Microfiltration

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1. Introduction

Membrane filtration processes are widely used in various water and wastewater treatment applications. Crossflow microfiltration is a pressure driven membrane process, which has been shown effective in a great number of processes, including the removal of colloidal inorganic and organic solids.

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. The steady value of permeate flux depends on various process variables such as cross-flow velocity, kind of membrane (pore size and chemical composition), the Reynolds number, shear stress and shear rate at the membrane surface in the membrane system and on physico-chemical particle-particle and particle-membrane interactions (Broussous et al., 2000; Huisman et al., 1999; Narong & James, 2006; Velikovská & Mikulášek, 2007). One way of characterizing these particle-particle and particle-membrane interactions is the knowledge of the ζ-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 ζ-potential gives the information of the stability of the system. Near the isoelectric point – IEP (the value of pH, where the charge and therefore ζ-potential of particles are equal to zero (Takagi & Nakagaki, 2001)) 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 (Baik & Seung, 2010; Gustafsson et al., 2000; Martín et al., 2003; Moritz et al., 2001; Mullet et al., 1997; Nazzal & Wiesner, 1994; Oo & Song, 2009).

Baik & Seung (2010) investigated surface charge properties of bentonite colloids to study their colloidal stability in a solution as a function of the pH and ionic strength. The results of ζ-potential measurements for the bentonite colloid showed that the bentonite colloids were stable at lower ionic strengths of 0.01 and 0.001M NaClO$_4$ but instable at a higher ionic strength of 0.1M NaClO$_4$ within the whole studied pH range.

Faibish et al. (1998) studied the effect of electrostatic double layer interaction on permeate flux decline and deposit cake formation in crossflow membrane filtration of colloidal

suspensions. They found that the rate of flux decline is strongly dependent on solution ionic strength and, to a much lesser degree, on solution pH (for the investigated pH range of 6.1-10.0). Variations in flux decline rate with solution ionic strength are especially significant as the particle size decreases. For given physical and chemical conditions, the cake layer porosity increased with decreasing particle size, while cake permeability decreased with decreasing particle size.

Franks (2002) investigated the influence of Li^+, Na^+, K^+ and Cs^+ on the surface properties of silica particles. Hofmeister series (Cs^+, K^+, Na^+, Li^+) order ions from the least hydrated ions to the most hydrated ions. He found that the adsorption sequence on the silica surface follows the Hofmeister series ($Cs^+>K^+>Na^+>Li^+$) with Cs^+ adsorbing in greater quantities than Li^+. The measurements of ζ-potential indicate that adding of these ions has influence on the magnitude of the ζ-potential. Obtained results show that Cs^+ produces lower magnitude than Li^+. The results also showed that there exists a shift in the IEP to higher pH values as the salt concentration is increased. This indicates that the alkali cations are adsorbing to the silica surface in quantities greater than required for charge neutralisation. The greatest shift in the IEP is found to follow the greatest shift to least IEP shift $Cs^+>K^+>Na^+>Li^+$.

TiO_2 belongs to the mineral oxide. It is well known that if the surface of a mineral oxide is exposed to water, it becomes hydrated. The presence of water causes forming of the hydroxide layer containing MOH groups on the particle surface (M stands for a cation such as Al^{3+}, Zr^{4+}, Si^{4+} or Ti^{4+}). These amphoteric MOH surface groups are capable to dissociate when the surface gets in contact with polar liquids. The dissociation of amphoteric surface groups strongly depends on the pH of the solution and causes positive or negative charge of the surface.

Many authors (Elzo et al., 1998; Greenwood & Kendall, 2000; Gustafsson et al., 2000; Kosmulski et al., 1999; Kosmulski, 2002) showed that the charge of surface of mineral oxides particles consists of two parts. One part is the particles charge due to the dissociation of the ionisable groups of particles, and the other part is the particles charge affected by the electrolytes in the bulk solution.

Elzo et al. (1998) studied the charge effects on inorganic membrane performance on a cross-flow microfiltration of silica particles. The microfiltration experiments showed that the permeate flux is affected significantly by the pH, the salt concentration and the salt valency. Steady-state flux was higher at high pH and low salt concentration. In contrast, the flux was lowered at high salinity, low pH and in the presence of a bivalent salt such as $CaCl_2$. The higher fluxes were obtained when particles were highly charged, i.e. when strong repulsive interactions between the particles occurred.

Greenwood & Kendall (2000) studied surface of alumina particles in the presence of KCl. They found that there exists a shift of the isoelectric point to higher values of pH when the concentration of KCl increases. This shift may be due to some adsorption of potassium ions at the alumina interface. Authors also found out that the ζ-potentials were smaller in magnitude in the suspensions where the salt was present. This is due to screening of the surface charge by the electrolyte. The same results were shown by Gustafson et al. (2000). They studied the influence of pH and NaCl on the ζ-potential of anatase dispersions and they also found that the isoelectric point is shifted to higher pH values with increasing salt concentrations. The results also showed that addition of electrolyte affects thickness of double layer and the magnitude of ζ-potential. The magnitude of ζ-potential will decrease with increasing concentration of added electrolyte.

Kosmulski (2002) studied the electrochemical properties of alumina in the presence of high concentration of certain 1-1 electrolytes. His results showed that the shift in the IEP induced by different salts comply with the following rules: Salts with large cations (Cs^+) have a rather insignificant and anion independent effect. Salts with small cations (Li^+, Na^+) have a significant and anion-dependent effect. Salts with small anions (Cl^-) have a rather insignificant and cation-dependent effect.

Nyström et al. (2001) investigated the influence of Na^+, Ca^{2+}, Ba^{2+} and La^{3+} on the ζ-potential of calcite dispersions. The obtained results showed that adding salt influences the electrostatic interactions between the particles and leads to a change in the shear-induced aggregation. For Na^+ a pure electrostatic screening was observed. The two divalent cations, Ca^{2+} and Ba^{2+}, showed a similar adsorption behavior. Up to a certain concentration they caused an increased ζ-potential, as a result of specific adsorption, after which it decreased. From the results it is obvious that the monovalent sodium shows the weakest and the trivalent lanthanum the strongest effect.

Zhao et al. (2005) studied the influence of pH and different concentrations of NaCl on microfiltration of TiO_2 suspensions. They found that the steady flux increased with increasing ionic strength and decreasing pH. This was mainly due to the influences of ionic strength and pH on the dispersity of the TiO_2 suspensions-that was confirmed by the results of particle size of dispersion TiO_2.

For the microfiltration of particulate dispersions, surface properties of both dispersions and membranes vary with the solution environments. Although considerable work on the effects of pH and ionic strength have been reported, contradicting results have been obtained due to the complicate interactions between related substances in such separation system. Moreover, the influence of multivalent salts on membrane performance has received little or no attention. In fact, different inorganic electrolytes are always encountered in the treatment of industrial dispersions by membrane technology (Mulder, 2000).

The aim of present study was to show that pH, kind of salt and ionic strength are very important parameters that significantly affect the particle size of the dispersion and electrochemical properties of dispersion and membrane and by this way influence the microfiltration process at all. Attention was given to the ζ-potential measurements of the membrane surface and anatase dispersion under different solution environments. These measurements were combined with a series of cross flow microfiltration experiments at various pH values, salt concentrations and with NaCl, $MgCl_2$, $AlCl_3$, Na_2SO_4 and Na_3PO_4 electrolytes. Due to measurements of the permeate flux and the ζ-potential of the system particle-particle the filtration behavior was analyzed.

2. Experimental

2.1 Materials

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, $L = 0.25$ m; internal diameter, $d_i = 6 \times 10^{-3}$ m; nominal pore size, $d_p = 0.091$ μm; mean membrane resistance, $R_m = 1.17 \times 10^{12}$ m^{-1} (obtained from water flux measurements) and membrane surface area, $A_m = 43.35 \times 10^{-4}$ m^2. A new membrane was used in each experiment, and before the run the pure water flux was measured with deionised water.

The microfiltration experiments were performed with an aqueous dispersion of anatase obtained from Precheza a.s., Přerov, Czech Republic. The mean diameter of particles of pure dispersion (without acid or electrolyte) was 310 nm; however, the distribution of particles was very wide.

Selection of electrolytes used in this study was application-oriented. All chemical used were analytical grade and the solutions were prepared with ultra-pure water of conductivity less than 1 μScm^{-1}.

For investigating the effect of ionic strength on the performance of the ceramic membrane, NaCl solutions at different ionic strengths of 0.001 and 0.01M were prepared, respectively. To investigate the influences of different valent cations, NaCl, $MgCl_2$ and $AlCl_3$ solutions were used at an ionic strength of 0.001 and 0.01M. Na_2SO_4 and Na_3PO_4 solutions at an ionic strength of 0.001 and 0.01M were prepared for investigating the influence of different valent anions on the performances of the ceramic membrane. The pH of the solution was adjusted with NaOH and HCl solutions.

2.2 Experimental methods
2.2.1 Separation experiments
The microfiltration experimental apparatus used is shown schematically in Figure 1.
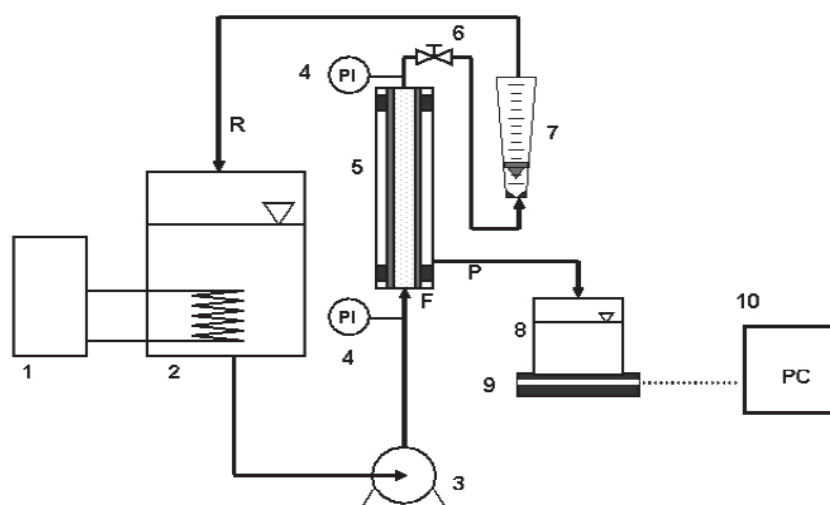

Fig. 1. Schematic diagram of crossflow microfiltration system
1 - tempering system with thermostat, 2 - stock tank, 3 – pump, 4 - sensor of pressure,
5 - membrane module, 6 - needle valve, 7 – rotameter, 8 – beaker for permeate,
9 – scale, 10 - output on PC. F – feed, P – permeate, R – retentate.

The circulating loop was constructed of stainless steel and contained a three litre feed suspension reservoir, pump and the membrane module. This loop was also equipped with a pressure and flow monitoring system. The crossflow velocity was controlled using the speed of the pump and the operating pressure (and hence transmembrane pressure) in the loop was controlled by a needle valve at the module outlet; both parameters were varied independently. The loop was also equipped with a temperature regulating system.

In the experiments anatase suspensions were used with a concentration of 5% by weight at various pH and with or without electrolyte NaCl. During all the tests, the filtration was run at a constant crossflow velocity of 1 m s^{-1} and a constant pressure of either 100 or 200 kPa.

Before each filtration experiment the resistance of membrane was measured. The membrane was placed into the membrane module, and deionised water was circulated in the test loop at a pressure 100 kPa and a velocity of 1 m s^{-1} for about 30 minutes. During this time a stable value of the permeability of the membrane to water was observed. From the measured permeate flow rate, the membrane resistance R_m was calculated from:

$$R_m = \frac{\Delta P}{\mu_p J_w} \tag{1}$$

where μ_p is dynamic viscosity of the permeate, J_w is the permeate flux for deionised water and ΔP is the transmembrane pressure.

After this measurement, the dispersion was placed into the reservoir and the filtration was started, the operating pressure as well as feed velocity was adjusted by the regulation system. The stock dispersion was kept at a constant temperature of 25°C. 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.

The experiment was stopped after obtaining a constant permeate flux. The adjustment of pH value was performed 18 hours before the filtration experiments, to allow stable equilibration conditions to be reached in the dispersion (that is, an equilibrium state of particle-particle interactions). After each set of experiments the unit and the membranes were rinsed with deionised water and the pure water flux was measured again under condition of initial test until the steady state was attained. From this value was the membrane resistance was calculated again. The fouling tendency of the membrane can be calculated from the difference between the two resistances (that is the "before" and "after" filtration resistances). The total filtration resistance R_t was calculated from:

$$R_t = \frac{\Delta P}{\mu_p J_\infty} \tag{2}$$

where J_∞ is the steady state permeate flux. The difference between the total filtration resistance and the membrane resistance is filter cake resistance R_c.

2.2.2 Particle size and ζ–potential measurements

The particle size and ζ-potential measurements were carried out on the instrument Zeta PALS (Brookhaven Instruments Corp., USA).

The stock dispersion was diluted to the concentration of 1 kg m^{-3} using permeate, in order to retain the same solution conditions (pH, salt concentration) that existed during filtration. The ζ- potential of the particles was calculated from a measurement of the electrophoretic mobility using:

$$\zeta = \frac{\mu \upsilon}{\varepsilon_o \varepsilon_r} \tag{3}$$

where υ is the mobility of the particles, μ is the dynamic viscosity and ε_o and ε_r are permittivity of vacuum and relative permittivity of the liquid.

One membrane was ground in the oscillatory mill. This powder was dispersed in permeate by the help of ultrasonic bath and than the ζ-potential of this sample was measured. The sample concentration was 1 kg m^{-3}, too.

3. Results and discussion

3.1 The pH dependence of the ζ–potential of TiO$_2$ particles in the presence of various electrolytes

The Fig. 2 shows the pH dependence of the ζ-potential of TiO$_2$ particles in the presence of NaCl, MgCl$_2$, AlCl$_3$, Na$_2$SO$_4$ and Na$_3$PO$_4$ (at two ionic strengths of 0.001 and 0.01M), and without any salt. Fig. 3 shows the same pH dependence of the ζ-potential of TiO$_2$ in the presence of the rest of studied electrolytes - Na$_2$SO$_4$ and Na$_3$PO$_4$ (at two ionic strengths of 0.001 and 0.01M).

As shown in the Fig. 2 and Fig. 3, the surface charge of the particles is strongly dependent on the pH, kind of salt and ionic strength of the electrolyte solution. With the increase of the pH from 2 to 8, the ζ-potential of the TiO$_2$ particles decreased and became negative at the isoelectric point (IEP); exception is AlCl$_3$ for which there is no IEP and the ζ-potential is always positive.
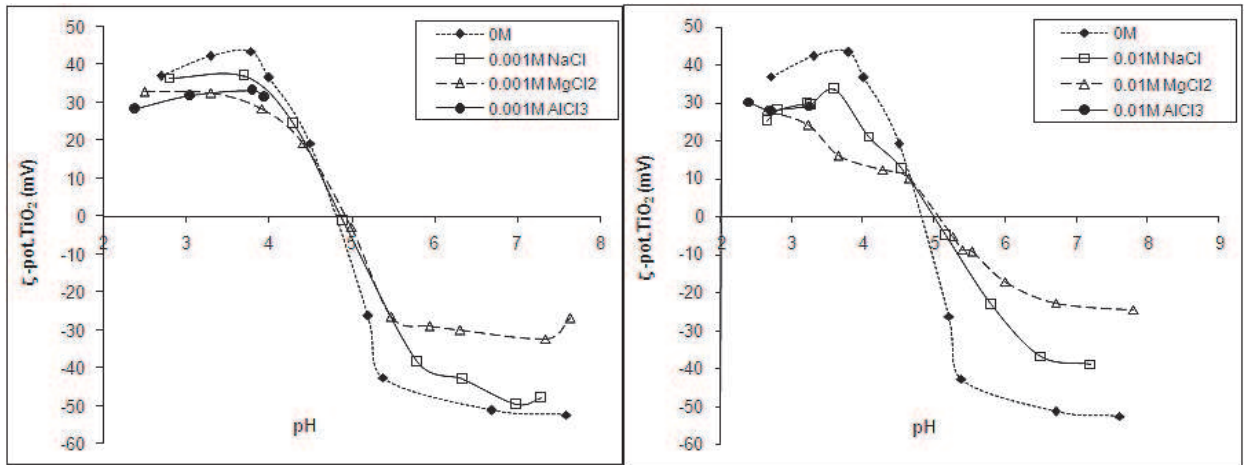

Fig. 2. The pH dependence of the ζ-potential of TiO$_2$ particles in the NaCl, MgCl$_2$ and AlCl$_3$ solution under different ionic strengths
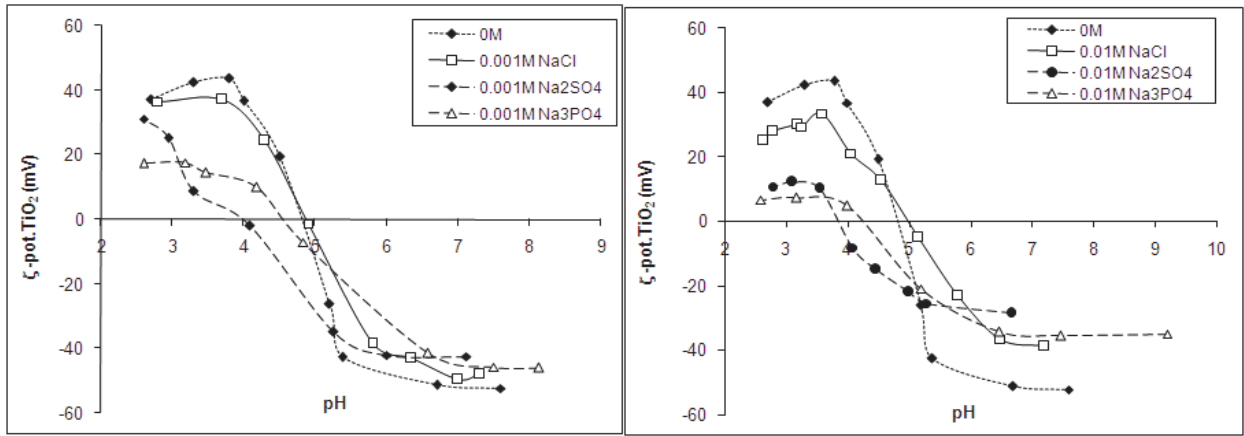

Fig. 3. The pH dependence of the ζ-potential of TiO2 particles in the NaCl, Na2SO4 and Na3PO4 solution under different ionic strengths

From the curves shown in Fig. 2 and Fig. 3 it is obvious that the ζ-potential decreased with increasing ionic strength. These results may be explained by a decrease in the effective

thickness of the diffuse layer as the ionic strength increases. From the results it can be also found that IEP of TiO_2 dispersion without any salt and with addition of NaCl is nearly the same for both the concentrations 0.001 and 0.01M. This fact indicated that there is absence of a specific adsorption of Cl^- and Na^+ ions on the particle surface.

From the curves shown in Fig. 2 and Fig. 3 it is apparent, that in comparison with the results obtained for TiO_2 dispersion without any salt the adding of NaCl and $MgCl_2$ induces the shift of IEP to higher values of pH, while the adding of Na_2SO_4 and Na_3PO_4 causes the shift to lower pH values. The results indicate the specific adsorption of cations in the case of NaCl and $MgCl_2$, respectively the specific adsorption of anions in the case of Na_2SO_4 and Na_3PO_4.

For electrolytes NaCl and $MgCl_2$ and both of the studied concentrations of added electrolyte the magnitude of ζ-potential of TiO_2 was found in the order $MgCl_2$< NaCl. The difference in the magnitude of ζ-potential is in the area pH>pH(IEP) caused by the adsorption of cations. The diameter of these cations as different, and therefore exists the difference in hydration of these cations. The bigger and therefore poorly hydrated ion (Mg^{2+}) adsorbs in greater quantity to the TiO_2 surface than the smaller and well-hydrated ion (Na^+) and by this way Mg^{2+} causes bigger compression of the diffuse layer than Na^+ and produces lower magnitude of ζ-potential of TiO_2 particles. At the same time the valence of Mg^{2+} is two time bigger than in the case of Na^+. From this is obvious, that the same amount of Mg^{2+} cation affects the magnitude of ζ-potential more than Na^+ cation.

In the area where is the pH<pH(IEP), the difference in the magnitude of ζ-potential is caused by the anions. The concentration of Cl^- anions is in the case of $MgCl_2$ two times higher than in the case of NaCl. The adding of $AlCl_3$ has the same effect as the addition of $MgCl_2$.

In the area of pH where is the pH<pH(IEP), the magnitude of ζ-potential of TiO_2 particles is influenced by adsorption of the anions. The bigger and poorly hydrated anion PO_4^{3-} adsorbs in greater quantity to the surface of TiO_2 than small and well-hydrated anion Cl^- and produces lower magnitude positive ζ-potential. This result was found for both studied concentrations of the electrolytes (see Fig. 3).

In the area where the pH>pH(IEP), the magnitude of ζ-potential is affected by adsorption of cations. For 0.001M concentration of added electrolyte (see Fig. 3) the magnitude of ζ-potential was nearly the same for all kind of electrolytes. For 0.01M concentration of NaCl, Na_2SO_4 and Na_3PO_4 was found that in comparison with the results obtained for TiO_2 dispersion without any salt the adding of NaCl, Na_2SO_4 and Na_3PO_4 produces lower magnitude of ζ-potential of TiO_2 particles.

3.2 The pH dependence of the particle size of TiO_2 particles in the presence of various electrolytes

The dependences of diameter of TiO_2 particles on the value of pH are shown in Fig. 4 and Fig. 5.

From the curves shown in Fig. 4 and Fig. 5 it is obvious that the diameter of TiO_2 particles increased with decreasing value of pH. By the comparison of results obtained for 0.001M and 0.01M concentration of electrolytes and was found that increasing ionic strength of the added electrolyte causes increase in the particle diameter.

For all studied systems there was found a step change in the particle size. In all cases these step change of particle size happened near the value of pH corresponding to the IEP.

The size of the particles tend to increase in the order NaCl < $AlCl_3$ < <$MgCl_2$ < Na_2SO_4 < Na_3PO_4. These results may be explained by adsorption of the counter ions into the Stern layer of the TiO_2 particle.
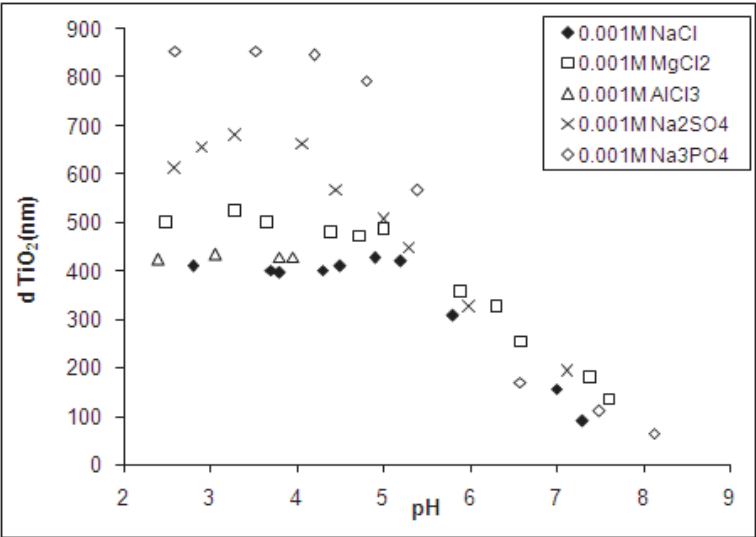
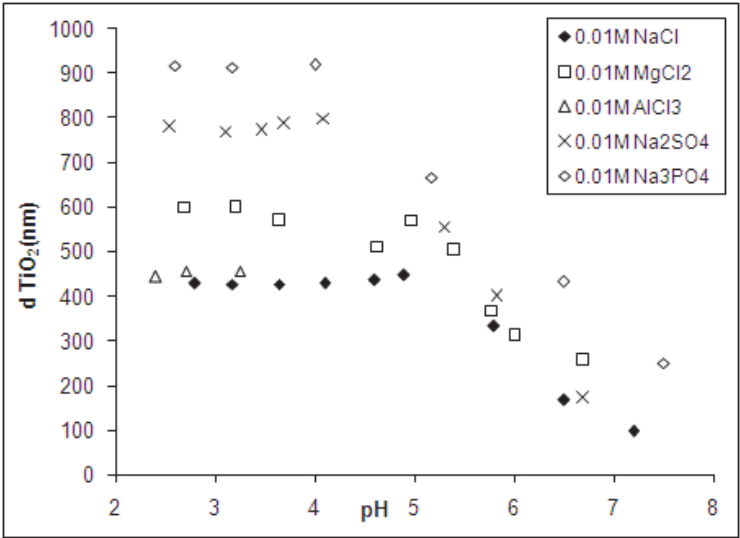Fig. 4. Particle diameter of TiO_2 as a function of pH and kind of electrolyte; electrolyte concentration 0.001M

Fig. 5. Particle diameter of TiO_2 as a function of pH and kind of electrolyte; electrolyte concentration 0.01M

3.3 Steady value of the permeate flux as a function of pH, kind of electrolyte and ionic strength

To investigate the influences of pH, kind of electrolyte and its concentration a set of microfiltration experiments was carried out. All experiments were performed at the same conditions. The cross-flow velocity was $1 m.s^{-1}$, the temperature was set to 25°C. The transmembrane pressure was 100 or 200kPa. Fig. 6 shows the results from the cross-flow microfiltration experiments as a function of pH for 0.001M concentration of electrolytes NaCl, $MgCl_2$ and $AlCl_3$. The studied transmembrane pressure was 100 and 200kPa. Fig. 7 shows the same dependencies this time for the 0.01M concentration of mentioned electrolytes.

As can be seen from Fig. 6 and Fig. 7, all the dependencies had a similar trend. The values of steady permeate flux decreased as the pH value increased in a pH range of 2 to 8. All

dependencies have maximum permeate flux near the isoelectric point of dispersion. From Fig. 6 and Fig. 7 it is obvious, that the steady flux increased with increasing ionic strength of NaCl, MgCl$_2$. Exception is AlCl$_3$; increasing concentration of AlCl$_3$ caused decrease in the steady of permeate flux.

From the curves shown in Fig. 6 and also from Fig. 7 it is apparent, that increase in the value of transmembrane pressure causes growth of the steady value of permeate flux.
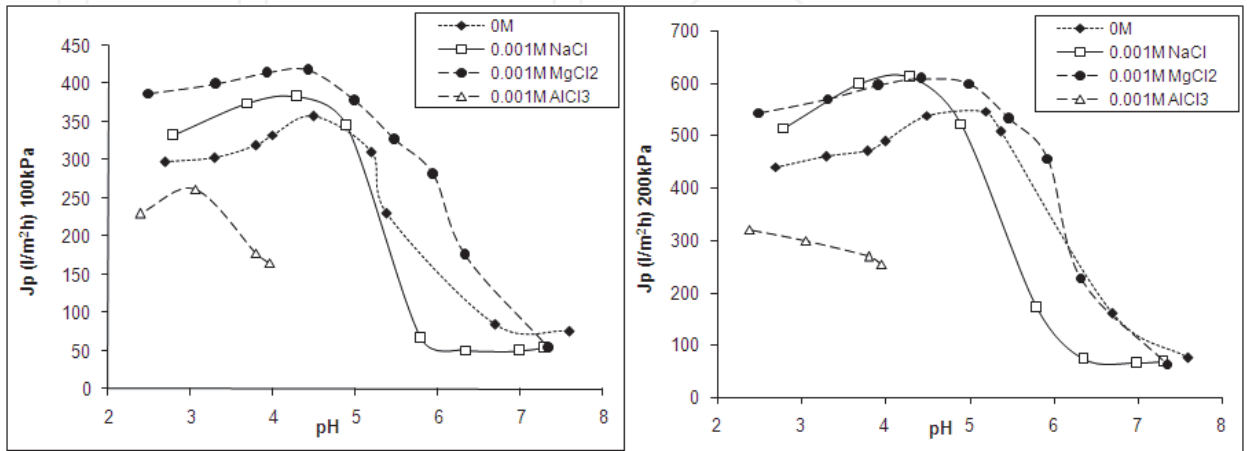

Fig. 6. Effect of pH, transmembrane pressure and 0.001M concentration of NaCl, MgCl$_2$ and AlCl$_3$ on steady permeate flux
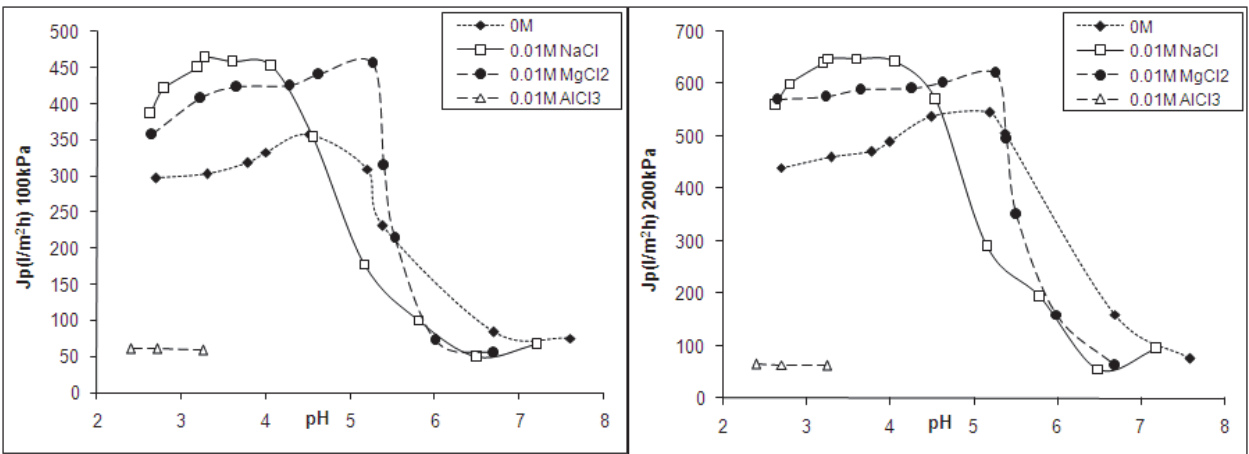

Fig. 7. Effect of pH, transmembrane pressure and 0.01M concentration of NaCl, MgCl$_2$ and AlCl$_3$ on steady permeate flux

The last phenomenon resulted from Fig. 6 and Fig. 7 is the effect of kind of the electrolyte on the steady value of permeate flux. Adding of the NaCl and MgCl$_2$ in comparison with the results obtained for TiO$_2$ dispersion without any salt produces higher values of steady permeate flux. For the 0.001M concentration and 100kPa transmembrane pressure value the maximum of steady value of permeate flux observed with the MgCl$_2$ is higher than that observed with NaCl electrolyte. In all other cases (0.001M NaCl and MgCl$_2$ 200kPa; 0.01M NaCl and MgCl$_2$ 100 and 200kPa) the maximum steady value of permeate flux was higher in the presence of NaCl.

The growth of the steady permeate flux in the presence of electrolyte is caused by the specific adsorption of counter ions on the particle surface what results in less repulsive

forces between the particles and in increasing size of the particles. Both of these factors improve the conditions for effective microfiltration.

The Fig. 8 shows the results from the cross-flow microfiltration experiments as a function of pH for 0.001M concentration of electrolytes NaCl, Na_2SO_4 and Na_3PO_4. The studied transmembrane pressure values were 100 and 200kPa. The Fig. 9 shows the effect of pH and transmembrane pressure for 0.01M concentration of electrolytes NaCl, Na_2SO_4 and Na_3PO_4.

The same way as the curves shown in Fig. 6 and Fig. 7, all the dependencies from Fig. 8 and Fig. 9 had a similar trend. The values of steady permeate flux decreased as the pH value increased in a pH range of 2 to 8. All dependencies have maximum permeate flux near the isoelectric point of dispersion.
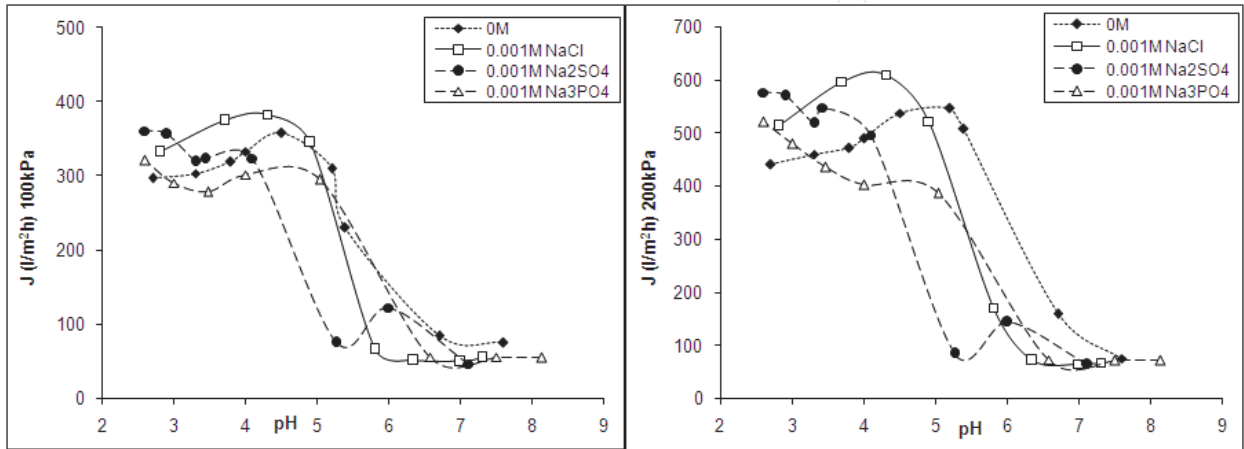

Fig. 8. Effect of pH, transmembrane pressure and 0.001M concentration of NaCl, Na_2SO_4 and Na_3PO_4 on steady permeate flux
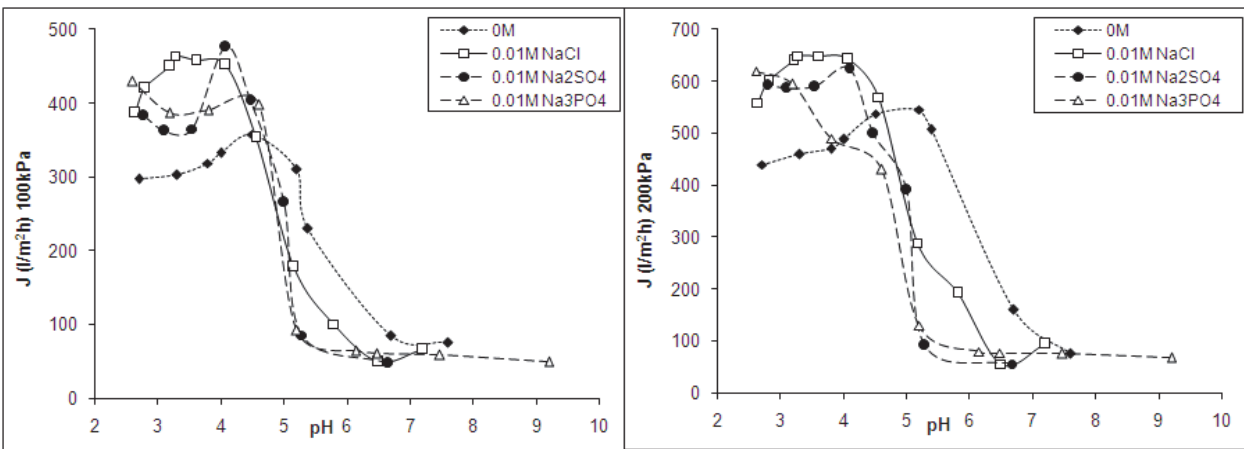

Fig. 9. Effect of pH, transmembrane pressure and 0.01M concentration of NaCl, Na_2SO_4 and Na_3PO_4 on steady permeate flux

From Fig. 8 and Fig. 9 it is obvious, that in comparison with the results obtained for TiO_2 dispersion without any salt addition of NaCl produces higher values of steady permeate flux no matter what the concentration of NaCl or the value of the transmembrane pressure is. Addition of electrolyte Na_2SO_4 and Na_3PO_4 caused the growth of permeate flux only in narrow range of pH values. This range of pH values for 0.001M electrolytes Na_2SO_4 and Na_3PO_4 is from pH 2 to pH 3 and for 0.01M concentration of Na_2SO_4 and Na_3PO_4 from pH 2

to pH 5. From this result it is obvious that the 0.01M concentration of electrolyte affected the microfiltration process much more than the concentration of 0.001M.

This result is in contrast to that observed with microfiltration of silica particles (Elzo et al., 1998). The authors found that high permeate fluxes were obtained at low salt concentrations and they attributed this event to the strong repulsion between the silica particles at low salt concentrations. Such a contradiction may be attributed to the different nature of the particles. There was no flocculation of silica particles in their work. However, TiO_2 particles flocculated easily as the solution environment changed in our study.

As mentioned before the growth of the steady permeate flux in the presence of electrolyte is caused by the specific adsorption of counter ions on the particle surface what results in less repulsive forces between the particles and in increasing size of the particles.

3.4 Modeling of the value of permeate flux as a function of ζ–potential of TiO_2 particles

The dependence of the values of permeate flux as a function of ζ-potential of TiO_2 particles was modeled by the following equation reported in the literature (Doran, 1995):

$$y = y_0 + y_\infty \cdot e^{a \cdot e^{b(x-x_o)}} \qquad (4)$$

Which was because of the modeling of the values of permeate flux as a function of ζ-potential of TiO_2 particles arranged into the following form:

$$J = J_D + J_H \cdot e^{a \cdot e^{b(\zeta - zeta_o)}} \qquad (5)$$

where | J | is | steady value of permeate flux [l m²h⁻¹],
| J_D | - | parameter [l m²h⁻¹],
| J_H | - | parameter [l m²h⁻¹],
| a | - | parameter [-],
| b | - | parameter [mV⁻¹],
| ζ | - | ζ-potential of TiO_2 particles [mV],
| $zeta_o$ | - | parameter [mV⁻¹].

For single electrolyte and its concentrations, by the transmembrane pressure difference value of 100 and 200kPa, were by the minimizing the function $((J_{exp.} - J_{cal.})/J_{exp.})^2$ observed values of the parameters J_D, J_H, a, and b ($J_{exp.}$ are the experimental values of steady permeate flux, $J_{cal.}$ are values of permeate flux calculated by model described by Eq. (2)).

The resulting values of the parameters J_D, a, b, and J_H are presented in Table 1.

	100 kPa	200 kPa
J_D[lm⁻²h⁻¹]	55.10	55.10
a [-]	-10.55	-10.55
b [mV⁻¹]	-0.41	-0.41
J_H[lm⁻²h⁻¹]	340.1	507.9

Table 1. The resulting values of parameters J_D, a, b a J_H (Eq. (5)) as a function of transmembrane pressure

While the parameters J_D, a, b and J_H are independent of the kind of electrolyte and its concentration and theirs values changed only with the change of the value of transmembrane pressure, the parameter $zeta_o$ is very dependent on the kind and

concentration of the electrolyte. The kind and the concentration of the electrolyte can be express by the ionic strength.

The values of parameter $zeta_o$ as a function if ionic strength of dispersions are presented in Table 2. The parameter $zeta_o$ is independent on the value of transmembrane pressure and therefore for the transmembrane pressure value of 100 and 200kPa are the values of parameter $zeta_o$ the same.

The dependence of the value of parameter $zeta_o$ on the ionic strength of TiO$_2$ dispersion is possible to describe by following Eq. (6):

$$zeta_o = - 8496\ I^2 + 850.8\ I - 43.24 \tag{6}$$

where $zeta_o$ is parameter [mV^{-1}],

I - ionic strength of dispersion of TiO$_2$ [mol/l].

	c [mol/l]	I [mol/l]	zeta$_0$ [mV]
without electrolyte	0	0	-47.36
NaCl	0.001	0.001	-41.18
MgCl$_2$	0.001	0.003	-39.95
Na$_2$SO$_4$	0.001	0.003	-39.95
Na$_3$PO$_4$	0.001	0.006	-36.24
NaCl	0.01	0.01	-35,64
MgCl$_2$	0.01	0.03	-25.94
Na$_2$SO$_4$	0.01	0.03	-25.94
Na$_3$PO$_4$	0.01	0.06	-22.52

Table 2. Values of the parameter $zeta_o$ for different ionic strength

The deviations between the experimental results and values of steady permeate flux calculated by using Eq. (5) (for the values of the parameters presented in Tables 1 and 2) for chosen electrolyte and its concentration are presented in Tables 3 and 4.

	100 kPa		200 kPa	
ζ(TiO$_2$)	$J_{exp.}$ [lm^{-2}h^{-1}]	$J_{cal.}$ [lm^{-2}h^{-1}]	$J_{exp.}$ [lm^{-2}h^{-1}]	$J_{cal.}$ [lm^{-2}h^{-1}]
25.20	386.3	395.2	559.4	562.9
28.00	420.6	395.2	600.5	562.9
29.90	450.0	395.2	640.3	562.9
29.40	464.4	395.2	649.0	562.9
33.56	458.3	395.2	649.0	562.9
21.18	452.0	395.2	643.0	562.9
12.70	353.8	395.2	569.8	562.9
-4.90	178.2	395.2	288.9	562.9
-23.14	100.6	374.9	192.6	532.7
-36.60	49.7	55.1	55.3	55.1
-38.70	66.3	55.1	94.0	55.1

Table 3. Comparison of experimental and calculated values of steady permeate flux as a function of ζ-potential of TiO$_2$ dispersion in the presence of 0.01M NaCl

The deviations between the experimental results and values of the steady permeate flux calculated by using Eq. (5) (for the values of the parameters presented in Tables 1 and 2) are caused by the fact, that the model reflects parameters as the ζ-potential of dispersion, kind and concentration of electrolyte (by using the ionic strength). The model does not reflect the parameters like the particle size of the dispersion, ζ-potential of the membrane or physicochemical particle-particle and particle-membrane interactions.

Based on the results presented in Tables 3 and 4 (and the others comparison of experimental and calculated values of steady permeate flux, which are not presented in this work) is possible to say that the model represented by Eq. (5) presents good correlation between experimental and prediction values of steady permeate flux.

	100 kPa		200 kPa	
$\zeta(TiO_2)$	$J_{exp.}$ [$lm^{-2}h^{-1}$]	$J_{cal.}$ [$lm^{-2}h^{-1}$]	$J_{exp.}$ [$lm^{-2}h^{-1}$]	$J_{cal.}$ [$lm^{-2}h^{-1}$]
31.16	360.8	395.2	576.0	562.9
25.34	356.1	395.2	570.2	562.9
8.64	319.3	395.2	517.8	562.9
-1.87	323.8	395.2	496.5	562.9
-34.91	74.6	145.3	83.5	189.7
-41.99	121.8	55.1	144.5	55.1
-42.42	45.7	55.1	63.7	55.1

Table 4. Comparison of experimental and calculated values of steady permeate flux as a function of ζ-potential of TiO_2 in the presence of 0.001M Na_2SO_4

4. Conclusion

The present study is focused on the study of the influence of electrochemical properties of dispersions and membranes on the microfiltration of model dispersion of TiO_2 on asymmetric tubular α-Al_2O_3 microfiltration membranes.

The permeate flux of the ceramic membrane in the microfiltration of TiO_2 suspension was affected significantly by the particles environment including pH and ionic strengths. The steady-state flux increased with increasing ionic strength in the presence of electrolytes, NaCl, Na_2SO_4 and Na_3PO_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.

The results of the experiments show that the ζ-potential of particles as well of membrane surface have important effects on the permeate flux. This is especially pronounced during microfiltration of the dispersion when it is close to its isoelectric point, when the value of permeate flux increased to about fivefold the value of non-treated dispersion. This is due to the particle interactions; close to the isoelectric point the dispersion had a tendency towards instability, the particle aggregation was evident. It resulted in either deposition of a lower thickness of cake or of one with a higher porosity, thereby leading to higher values of permeate fluxes and lower filter cake resistances.

From the presented results the following general conclusions may be drawn:

- ζ-potential of the TiO_2 particles and also ζ-potential of membrane surface decreased with increasing ionic strength;
- Addition of electrolytes caused the shift of the value of the IEP (to lower pH values in case of Na_2SO_4 and Na_3PO_4 and to higher values of pH in the case of NaCl and $MgCl_2$; addition of $AlCl_3$ did not cause any shift, because there is no IEP and the value of ζ-potential of membrane and particles is always);
- The shift of IEP to lower pH values indicate the specific adsorption of anions, while the shift of IEP to higher values of pH indicate specific adsorption of cations;
- The diameter of TiO_2 particles increased with decreasing value of pH;
- Increasing ionic strength of the added electrolyte caused increase in particle diameter (because of the adsorption of counter ions on the particle surface);
- For all studied systems the steady permeate flux decreased as the pH value increased and the maximum permeate flux was near the isoelectric point of dispersion;
- The addition of electrolytes NaCl and $MgCl_2$ in concentration of 0,001 and 0,01M produces higher values of steady permeate flux in comparison with the results obtained for TiO_2 dispersion without any salt;
- Addition of electrolytes Na_2SO_4 and Na_3PO_4 in the concentration of 0.001M caused the growth of permeate flux only in narrow range of pH values (pH 2 - 3);
- Addition of electrolytes Na_2SO_4 and Na_3PO_4 in concentration of 0.01M caused the growth of steady values of permeate flux in the range of pH 2 - 5.

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 particle. The influence of solution environment on the dispersity of the TiO_2 dispersion played a major role in the permeate flux. When the particles were well dispersed, changes in the surface charge of the membrane would be important in determining membrane performance. Electroviscous effects are more complicated both on membrane and cake layer. Further investigations are deserved.
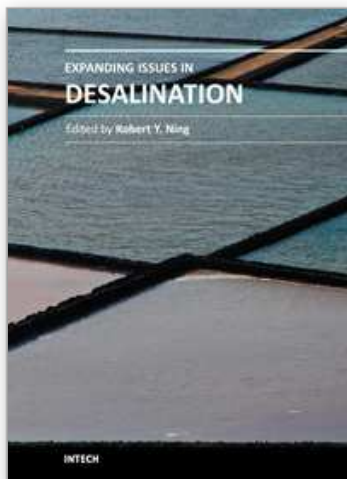
5. Acknowledgement

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Expanding Issues in Desalination

Edited by Prof. Robert Y. Ning

For this book, the term â€œdesalinationâ€ is used in the broadest sense of the removal of dissolved, suspended, visible and invisible impurities in seawater, brackish water and wastewater, to make them drinkable, or pure enough for industrial applications like in the processes for the production of steam, power, pharmaceuticals and microelectronics, or simply for discharge back into the environment. This book is a companion volume to â€œDesalination, Trends and Technologiesâ€, INTECH, 2011, expanding on the extension of seawater desalination to brackish and wastewater desalination applications, and associated technical issues. For students and workers in the field of desalination, this book provides a summary of key concepts and keywords with which detailed information may be gathered through internet search engines. Papers and reviews collected in this volume covers the spectrum of topics on the desalination of water, too broad to delve into in depth. The literature citations in these papers serve to fill in gaps in the coverage of this book. Contributions to the knowledge-base of desalination is expected to continue to grow exponentially in the coming years.

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