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Microfiltration of Concentrated Suspensions of a Microparticulate Ion-Exchanger Through a Ceramic Membrane

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Abstract: Suspensions of a microparticulate Lewatit ion-exchanger can be effectively concentrated by microfiltration (MF) to relatively high concentrations of about 25% of dry particles. This is important for formation of a hybrid process combining ion-exchange and MF. A tubular ceramic membrane with the mean pore size of 0.1 μm and the ground ion-exchanger Lewatit S100 with the mean particle size 5.25 μm have been used. Analysis of the flux decline revealed that the dominant membrane fouling mechanism is cake formation. With increasing suspension velocity the permeate flux significantly increases. The velocity of suspension above 2 $\text{m} \cdot \text{s}^{-1}$ should be used to achieve a reasonable flux. The limiting flux was reached at a pressure of about 100 kPa, but at higher suspension concentrations even at about 60 kPa. Surprisingly, the dependence of the permeate flux vs. suspension concentration goes through a flat maximum at the mass fraction of the dry resin of about 0.13. This can be interpreted as a result of inertial lift of larger particles in the suspension. At higher ion-exchanger concentrations further accumulation of particles in the cake increases its resistance and decreases the

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flux. Even at concentrations as high as 37.5 mass% of wet (25% of dry) particles in the suspension the permeate flux of about $72 \text{ dm}^{-3} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ can be achieved.

Keywords: Microfiltration, suspensions, ion-exchange, concentration

INTRODUCTION

Removal of xenobiotics present at low concentrations in water and wastewaters is frequent and sometimes not an easy task. This can be solved in many cases by application of adsorption techniques. Adsorption or ion-exchange is carried out mostly with adsorbent particles with a size larger than 0.3 mm in adsorption columns. Diffusion resistance in ion-exchanger particle is in most cases the dominant resistance and results in the need to have low liquid velocity in a columns and in a higher amount of ion-exchanger required for the desired feed throughput. Application of microparticulate ion-exchangers can be an effective way of intensification of the kinetics of an adsorption or ion-exchange process. This approach is widely used in analytical HPLC columns, but requires high pressure to achieve reasonable flow rate through a column. An alternative approach can be the application of microparticulate ion-exchangers suspended in the treated solution combined with the separation of adsorbent by microfiltration or ultrafiltration (1–6). Simulation of the influence of the particle size on kinetics of adsorption, based on the experimental data of the diffusion coefficient, was done for both Lewatit S100 and ground Lewatit S100-G particles swollen in water with a mean diameter of 324 and $5.25 \mu\text{m}$, respectively. For these ion-exchangers the estimated time of adsorption needed to achieve 90% of equilibrium copper concentration was about 31 min and 30 s, respectively (4). In the recirculation loop several steps as pre-concentration of the suspension, desorption of the adsorbate and final concentration of the suspension, are required (3–7). Microfiltration of relatively concentrated suspensions of more than 10 mass% of particles, for which practically no data are available, is necessary. The suspension from a solute desorption has low pH when the acid is used for stripping. Ceramic membranes can be used with an advantage in this application. They also have a good resistance to surface abrasion.

The aim of this work was to study microfiltration characteristics of microparticulate ion-exchanger suspensions in a wider concentration interval.

EXPERIMENTAL

Materials and Chemicals

Lewatit S100 is a strongly acidic, gel-like cation exchange resin (Lanxess, D) with beads of uniform size (about $324 \mu\text{m}$) based on a styrene-divinylbenzene

copolymer. The monodisperse beads are chemically and osmotically highly stable. The ground sample of Lewatit S100, designated as Lewatit S100-G, was used for the preparation of suspensions. Lewatit S100 swells in water. The water content of resin swollen at $\text{pH} = 6.0$ and 25°C was of 33.3 mass%. This was estimated from the weight difference of a certain amount of original particles dried to a constant weight in a desiccator and their weight after swelling in water at $\text{pH} = 6$, repeated for three times. A relatively wide interval of particle diameters from particles smaller than $0.4\text{ }\mu\text{m}$ up to about $65\text{ }\mu\text{m}$ was found in ground Lewatit. The size distribution of particles swollen in water was estimated by the particle sizer Analysette 22 (Fritsch, D) and is presented in Fig. 1. The Sauter mean diameter of swollen particles was $5.25\text{ }\mu\text{m}$. 0.1% and 1% of particles have a diameter below 0.4 and $0.8\text{ }\mu\text{m}$, respectively.

Equipment and Methods

A laboratory microfiltration unit with a circulation loop of feed was used. Its scheme is shown in paper (8). The suspension was pumped by a volumetric lobe pump, with an adjustable flow rate, from the feed tank through heat exchangers to the membrane module with a tubular ceramic membrane. The volumetric flow of suspension was measured by a magnetic flowmeter. The values of the input and the output trans-membrane pressures were measured by tensiometric sensors. The permeate flowed to the collecting beaker placed on an electronic balance. In regular time intervals the actual weight of the permeate, the temperature, and the flow rate of the suspension

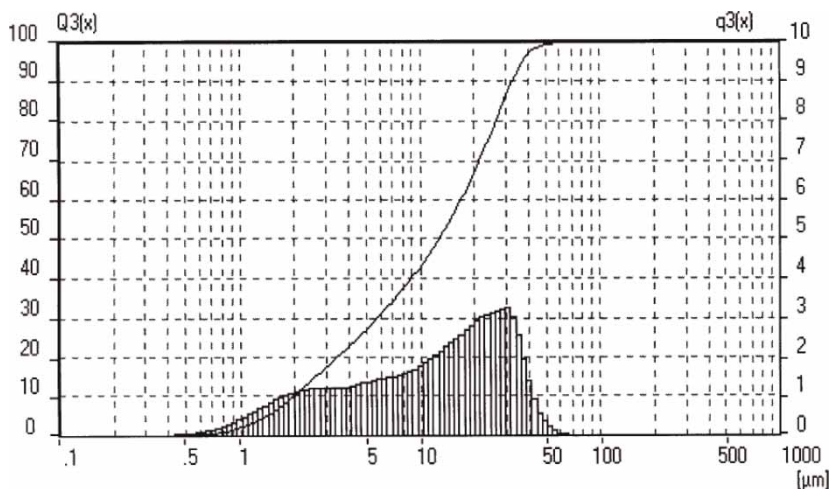


Figure 1. Particle size distribution of the Lewatit S100-G particles swollen in water with the Sauter mean diameter of particle of $d_{32} = 5.25\text{ }\mu\text{m}$.

and pressures were logged into a computer. The permeate was periodically returned to the feed container to prevent change in the feed concentration.

The tubular ceramic microfiltration membrane Membralox (Pall) was an asymmetric membrane with an inner diameter of 7 mm and a length of 0.25 m. The mean pore size of the membrane active layer was 0.1 μm and the effective area of the membrane 50 cm^2 . The active layer was made of $\alpha\text{-Al}_2\text{O}_3$, which was deposited on a durable porous alumina support. The membrane was resistant against mechanical strain, and temperatures up to 150°C. The working range of pH was from 0.5 to 13.5 what enabled cleaning of the membrane by aggressive chemicals. The permeate fluxes of distilled water and an aqueous solution with 0.05 $\text{kmol} \cdot \text{m}^{-3}$ of NaCl at 44.5 kPa were found similar. Suspensions were prepared from a concentrated suspension with swollen resin particles mixed into an NaCl solution with 0.05 $\text{kmol} \cdot \text{m}^{-3}$ and adjusted to pH = 6 or by adding a concentrated suspension to the less concentrated suspension. The permeate was periodically returned to the feed container with minimum suspension volume of 3 dm^3 , to prevent change in the feed concentration.

In measurements of flux decline with time when a steady flux of distilled water was achieved, a concentrated suspension of swollen Lewatit S100G was added to the feed container in an amount to yield a suspension with dry ion-exchanger concentration of 1 or 6 mass%.

RESULTS AND DISCUSSION

The volumetric flux of the permeate through a membrane is related, at least in a limited lower flux interval, to the trans-membrane pressure difference, Δp , by a linear relation

$$J_v = \Delta p / R \quad (1)$$

where R is the overall mass-transfer resistance of membrane and adjacent filtration cake and its reciprocal value, $1/R$, is the permeability of this system. In the case of flux of pure solvent (no suspended particles) $1/R$ represents the permeability of the membrane.

The time dependences of the permeate flux can be correlated according to the modified Hermia model [9] by a relation derived in paper (10)

$$-\frac{dJ_v}{dt} = k_2(J_v - J_v^*)J_v^{2-N} \quad (2)$$

where k_2 and N are model parameters, J_v^* is a steady state flux and t is time. The value of N indicates the fouling mechanism. For $N = 1$ intermediate pore blocking is supposed with partial blocking of pores with particles. Basic characteristics of the ceramic membrane Membralox were estimated for distilled water and diluted NaCl solutions as model permeate. The value of

the membrane permeability (reciprocal resistance) was practically independent of salt concentration and was about $1/R = 1.5 \cdot 10^{-6} \text{ m} \cdot \text{s}^{-1} \cdot \text{kPa}^{-1}$. The membrane permeability slightly decreases with increasing salt concentration. The influence of pH on the membrane permeability was also found less important in an interval from 6 to 8.2.

The analysis of the flux decline with time for the 1 and 6 mass% of dry Lewatit S100-G suspensions was done according to the modified model of Hermia (10). This analysis revealed that the dominant membrane fouling mechanism is cake formation. The time dependences of the permeate flux are shown in Fig. 2. A quick flux decline has been observed after the addition of a suspension into distilled water. Thus, the permeate flux dropped, for example from $82 \cdot 10^{-6}$ to $23.3 \cdot 10^{-6} \text{ m} \cdot \text{s}^{-1}$ for a suspension with a concentration of 6 mass% (Fig. 2b).

The feed velocity in the tubular ceramic membrane is an important parameter influencing the permeate flux. With increasing velocity, the permeate flux significantly increases (Fig. 3). Velocity above $2 \text{ m} \cdot \text{s}^{-1}$ should be used in MF of concentrated suspensions to achieve a reasonable flux. Its value will result from optimization of the process economy.

With increasing trans-membrane pressure, Δp , the permeate flux increases greatly at lower suspension concentrations, w_a , but at the mass fraction higher than about 0.2 the flux is nearly independent of Δp (Fig. 4). At a relatively low Δp , below about 60 kPa, a critical permeate flux (end of the linear part of the pressure dependence) is achieved. The limiting flux was reached at Δp of about 100 kPa, but at higher concentrations even at about 60 kPa. A further increase of Δp did not increase the permeate flux.

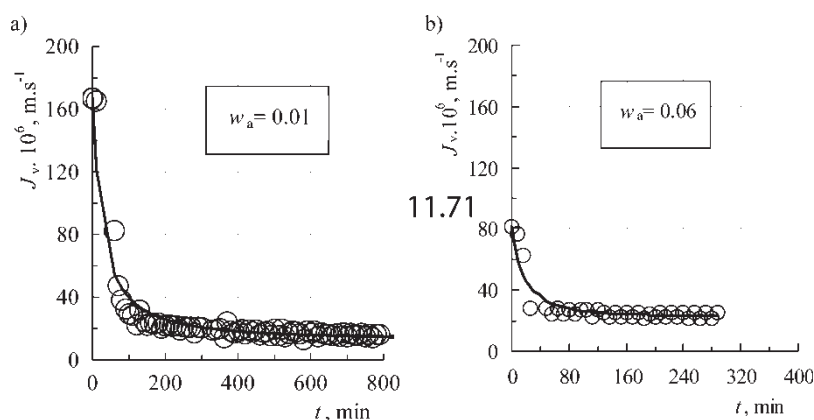


Figure 2. Time dependence of the permeate flux for Lewatit S100-G at a) $w_s = 0.01$, $v = 1.1 \text{ m} \cdot \text{s}^{-1}$, $\Delta p = 68.4 \text{ kPa}$ and b) $w_s = 0.06$, $v = 2 \text{ m} \cdot \text{s}^{-1}$, $\Delta p = 50.3 \text{ kPa}$. Lines are correlated according to Eq. (2) for $N = 1$.

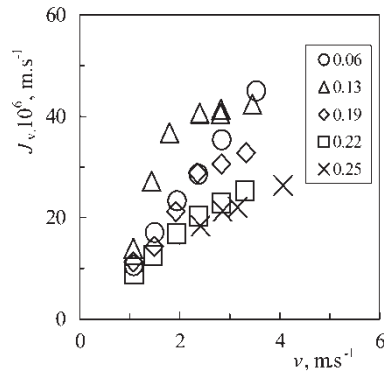


Figure 3. Influence of the suspension velocity in the tubular ceramic membrane on the permeate flux in MF of the Lewatit S100-G suspension in a solution with $0.05 \text{ kmol} \cdot \text{m}^{-3}$ of NaCl at pH = 6. The transmembrane pressure difference was 40 kPa. The parameter of dependences is the mass fraction of a dry sorbent in the suspension.

Concentration of the suspension influenced the permeate flux, but there is no significant concentration dependence of the permeate flux at low suspension velocities of about $1.2 \text{ m} \cdot \text{s}^{-1}$ (Fig. 5). Surprisingly, at higher suspension velocities the plot of the permeate flux vs. suspension concentration goes through a maximum at a mass fraction of dry sorbent of about 0.13 (Fig. 5). This can be interpreted by an inertial lift of larger particles, with a diameter

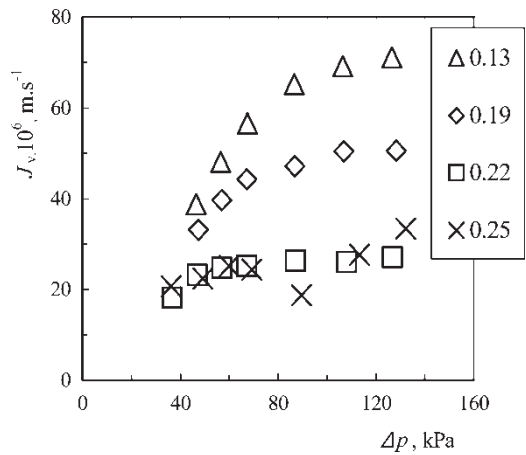


Figure 4. Permeate flux through the tubular ceramic membrane vs. transmembrane pressure difference in MF of Lewatit S100-G suspensions in a solution with $0.05 \text{ kmol} \cdot \text{m}^{-3}$ of NaCl at pH = 6. The parameter of dependences is the mass fraction of a dry sorbent in the suspension. The suspension velocity in the membrane tube was $2.8 \text{ m} \cdot \text{s}^{-1}$.

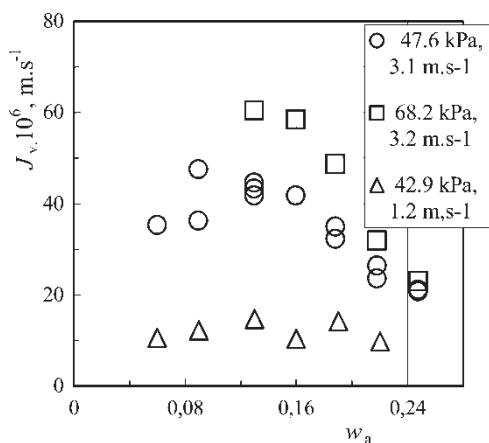


Figure 5. Permeate flux through the tubular ceramic membrane vs. mass fraction of dry ion-exchanger in the suspension of Lewatit S100-G in a solution with $0.05 \text{ kmol} \cdot \text{m}^{-3}$ of NaCl at pH = 6. Parameters of dependences are the mean trans-membrane pressure difference and the velocity of the suspension in the membrane tube.

above about 20–30 μm , as discussed in papers (11, 12). Percentage of swollen particles of Lewatit S100-G larger than 20 and 30 μm was about 32.9 and 14 vol%, respectively. At higher ion-exchanger concentrations a further accumulation of particles in the cake increasing its thickness starts to be dominant. These results show that the resistance of the particle cake is high at low velocities and high concentrations. Even at higher concentrations, for example at about 25 mass% of dry particles (37.5 mass% of swollen particles) in the suspension at a velocity of $3.1 \text{ m} \cdot \text{s}^{-1}$ and $\Delta p = 47 \text{ kPa}$ the permeate flux has a reasonable value of about $20 \cdot 10^{-6} \text{ m} \cdot \text{s}^{-1}$ ($72 \text{ dm}^{-3} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$).

CONCLUSIONS

Suspensions of a microparticulate Lewatit ion-exchanger can be effectively concentrated by microfiltration to relatively high concentrations of about 25%. From an analysis by the modified Hermia model follows that the dominant membrane fouling mechanism is a cake formation. The permeate flux significantly increases with increasing feed velocity. Velocity of about $2 \text{ m} \cdot \text{s}^{-1}$ should be used in MF. With increasing pressure the permeate flux increases greatly at lower suspension concentrations, but at the mass fraction higher than about 0.2 the flux is nearly independent of pressure. The limiting flux was reached at a pressure difference of about 100 kPa, but at higher concentrations even at about 60 kPa, while the critical permeate flux was achieved at a relatively low pressure below about 60 kPa. At higher suspension velocities the

plot of the permeate flux vs. suspension concentration goes through a flat maximum at a mass fraction of dry sorbent of about 0.13. Even at concentrations as high as 25 mass% of dry particles in the suspension the permeate flux of about $72 \text{ dm}^{-3} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ can be achieved.

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REFERENCES

1. Sluys, J.T.M., Bakkenes, H.W., Creusen, R.J.M., Schneiders, L.H.J.M., and Hanemaaijer, J.H. (1994) Membrane assisted affinity separations: Some techniques and applications. Crespo, J.G. and Boedekker, K.W. (Eds.), In *Membrane Processes in Separation and Purification*; Kluwer Acad. Publ, 395–414.
2. Flores, V. and Cabassud, C. (1999) Cu^{2+} removal by ion-exchange in a membrane reactor-Comparison with a packed-bed reactor. *J. Membrane Sci.*, 162: 257.
3. Bakalár, T., Schlosser, Š, and Búgel, M. (2003) *Hybrid Process for Removal of Copper from Aqueous Solutions by Adsorption on Microparticles Combined with Microfiltration*, Schlosser, Š and Kertész, R. (Eds.), Proc. PERMEA 2003, full text of lecture on CD ROM, 15 p., Tatranské Matliare, (SK), Sept. 7–11.
4. Bakalár, T., Schlosser, Š, and Búgel, M. (Eds.), (2004) *Hybrid Adsorption and Microfiltration Process for Removal of Metals from Aqueous Solutions*, Proc. CHISA 2004, full text on CD ROM, 15 p., Praha, (CZ), Aug. 22–26.
5. Kabay, N., Yilmaz, I., Bryjak, M., and Yuksel, M. (2006) Removal of boron from aqueous solutions by a hybrid ion exchange-membrane process. *Desalination*, 198: 158.
6. Yilmaz, I., Kabay, N., Bryjak, M., Yuksel, M., Wolska, J., and Koltuniewicz, A. (2006) A submerged membrane-ion-exchange hybrid process for boron removal. *Desalination*, 198: 310.
7. Blahušiak, M. and Schlosser, Š. (2006) Simulation of the adsorption-MF process for boron removal from seawater, Proc. Int. Workshop On Frontiers and Interfaces of Ion Exchange, Antalya, (TR), June 11–15, Abstract of poster P.18 74.
8. Stopka, J., Bugan, S.G., Broussous, L., Schlosser, S., and Larbot, A. (2001) Microfiltration of beer yeast suspensions through stamped ceramic membranes. *Separation and Purification Technology*, 25: 535.
9. Hermia, J. (1982) Constant pressure blocking filtration laws—Application to power-law non-Newtonian fluids. *Trans. Inst. Chem. Eng.*, : 60.
10. Field, R.W., Wu, D., Howell, J.A., and Gupta, B.B. (1995) Critical flux concept for microfiltration fouling. *J. Membrane Sci.*, 100: 259.
11. Belfort, G., Davis, R.H., and Zydney, A.L. (1994) The Behavior of Suspensions and Macromolecular Solutions in Crossflow Microfiltration. *J. Membrane Sci.*, 96: 1.
12. van Reis, R. and Zydney, A. Bioprocess membrane technology. *J. Membrane Sci.* in Press, Accepted Manuscript doi:10.1016/j.memsci.2007.02.045.