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MODELLING OF MICROPOROUS MEMBRANE CLEANING USING SUPERCRITICAL FLUIDS

MODELOWANIE OCZYSZCZANIA MEMBRAN MIKROPOROWATYCH PRZY UŻYCIU PŁYNÓW W STANIE NADKRYTYCZNYM

Abstract

In this paper, a method for CFD modelling of microporous membrane cleaning by supercritical fluid extraction (SFE) is presented. Results of CFD simulations results are shown and compared with experimental data for the process of microporous polypropylene membrane cleaning by SFE in a continuous-flow lab-scale SFE module.

Keywords: *microporous membrane*, *supercritical fluid extraction*, *cleaning*, *CFD*

Streszczenie

W artykule przedstawiono sposób modelowania CFD oczyszczania membran mikroporowatych metodą ekstrakcji nadkrytycznej. Zaprezentowano wyniki symulacji CFD i porównano je z danymi doświadczalnymi dla procesu oczyszczania mikroporowatych membran polipropylenowych metodą ekstrakcji nadkrytycznej w module przepływowym w skali laboratoryjnej.

Słowa kluczowe: *membrana mikroporowata*, *ekstrakcja nadkrytyczna*, *oczyszczanie*, *CFD*

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1. Introduction

In many processes related to production and maintenance of polymer membranes, large amounts of organic solvents are used. This concept has significant drawbacks, such as environmental load, high costs due to the lack of possibility of solvent regeneration, as well as various concerns related to process safety due to flammability of organic solvents. A promising alternative is the replacement of organic solvents by supercritical fluids, especially supercritical carbon dioxide (scCO_2). An example of such a process, in which organic solvents could be replaced by supercritical fluids, is porous microfiltration membrane production using the Temperature Induced Phase Separation method (TIPS). In this method, oils are present in the membrane pores after phase separation and they must be removed in order to prepare the membrane for normal usage in separation processes. Previously, the course of supercritical fluid extraction (SFE) used for cleaning of microporous polypropylene membranes containing organic oils was investigated experimentally [1, 2] and the influence of supercritical carbon dioxide on structure and mechanical properties of the membranes was studied [3]. The hydrodynamics of membrane cleaning in a lab-scale SFE module was also modelled [4]. The development of a method for CFD modelling of the process of microporous membrane cleaning by SFE, which takes into account both hydrodynamics and mass transfer in the multiphase system, would be beneficial for many reasons. It would help to investigate the course of the process and to determine the mass transfer mechanisms, the factors limiting the process rate and ways to perform process intensification. On the other hand, it would enable to perform process optimisation without carrying out expensive experiments. Moreover, it would be a helpful tool for the design of supercritical extraction equipment for processes involving microporous media.

The aim of this work is to present a method for modelling of microporous membrane cleaning by supercritical fluid extraction, which is suitable for CFD simulations. Exemplary results of such simulations are presented in this work as well. The cleaning process of a microporous polypropylene membrane in a lab-scale supercritical fluid extraction module, was considered. An ACCUREL® hollow-fibre membrane type PP S6/2 (Membrana GmbH, Germany) was used during the simulations and experiments (membrane length L = 100 mm, outer diameter d_m = 2.7 mm, wall thickness δ = 0.45 mm, porosity ε = 0.7). The pores of the membrane were filled with soybean oil (an oil used in the TIPS method) and this oil had to be removed during the cleaning process using pure scCO_2 as solvent. The membrane was placed centrally in a cylinder-shaped extraction module having a diameter of 4.6 mm and the same length as the membrane (L = 100 mm). The lumen of the membrane was filled by a solid (e.g. a steel bar), in order to stabilise the membrane in the module and to simulate mass transfer of the oil in only one direction, namely to the outer surface of the membrane. The flow of scCO_2 occurred in the annular region between the outer surface of the membrane and the extraction module wall (see Figure 1).

2. Mathematical model

Supercritical fluids are compressible and this feature should generally be taken into account in simulations, e.g. by using cubic equations of state, especially the Peng-

-Robinson EOS. However, if pressure changes in a system are low (as in the presented case), compressibility effects can be neglected [4]. In these simulations, scCO$_2$ density data published by Gupta and Shim were used [5].

In general, there are two approaches to model the solubility of a substance in supercritical media: either by determination of phase equilibrium using an appropriate equation of state, or by employing empirical correlations. In this work, an empirical correlation proposed and fitted to experimental data by Jokić et al. was used [6]:

$$S = \rho^{(a_1 + a_2 \rho)} \exp\left(\frac{a_3}{T}\right) \tag{1}$$

where:

S – the solubility of soybean oil in supercritical carbon dioxide [g/L],
ρ – the density of supercritical carbon dioxide [kg/m^3],
T – the temperature of supercritical carbon dioxide [K],
a_1, a_2, a_3 – constants.

Viscosity of supercritical fluids depends significantly on temperature and pressure. In this work, a correlation by Heidaryan et al., which covers a wide temperature and pressure, was used to calculate the viscosity of supercritical carbon dioxide [7]:

$$\mu = \frac{A_1 + A_2 p + A_3 p^2 + A_4 \ln(T) + A_5 (\ln(T))^2 + A_6 (\ln(T))^3}{1 + A_7 p + A_8 \ln(T) + A_9 (\ln(T))^2} \tag{2}$$

where:

μ – the viscosity of supercritical carbon dioxide [cP],
p – the pressure of supercritical carbon dioxide [bar],
T – the temperature of supercritical carbon dioxide [K],
$A_1, \dots, A_9$ – constants.

In order to simulate the mass transfer in the system, the diffusivity of soybean oil in scCO$_2$ has to be determined. Sassiat et al. recommended to use the Wilke-Chang equation to calculate the diffusivity of a substance in supercritical carbon dioxide [8]:

$$D = 7.4 \cdot 10^{-8} \frac{TM^{0.5}}{\mu V^{0.6}} \tag{3}$$

where:

D – the diffusivity [cm^2/s],
T – the temperature [K],
M – the molar mass of the solvent [g/mol],
μ – the dynamic viscosity of the solvent [cP],
V – the molar volume of solute at the ebullition temperature and under atmospheric pressure [cm^3/mol].

However, in porous media the effective diffusivity D_e depends also on the morphology of the porous structure and can be calculated as follows [8]:

$$D_e = D \frac{\varepsilon}{\tau} \tag{4}$$

where:

D – the diffusivity,

ε – the porosity coefficient of the porous structure of the membrane,

τ – the tortuosity of the porous structure of the membrane.

For the investigated membranes, porosity ε is equal to 0.7 and tortuosity τ is assumed to be 2, as most porous membranes produced in a phase inversion process have tortuosity values in the range of 1.5–2.5, as reported by Sagle and Freeman [9].

3. CFD simulations

The geometry of the membrane module used for CFD simulations is depicted schematically in Figure 1, while in Table 1 process parameters and extraction module dimensions are summarised. $scCO_2$ flows from the left to the right and there is a constant velocity profile at the inlet of the extraction module. The $scCO_2$ flow is perpendicular to the outer surface of the membrane. On the other hand, diffusion in the porous structure occurs generally in radial direction. Simulations were carried out using the ANSYS Fluent 14.0 CFD package. Due to symmetry of the system, the geometry was designed as a 2D axisymmetric geometry with a computational mesh consisting of 22,000 square elements. Computations were carried out for steady-state, laminar, incompressible flows. $scCO_2$ velocity was set to zero inside the porous membrane, because high flow resistance inside the membrane promotes the flow outside the membrane, as we showed in to our previous studies [4]. Hence, only diffusion occurs inside the membrane. A scalar transport equation was used for simulation of soybean oil transport, and the diffusivity value was set to D_e inside the membrane and to D outside the membrane.

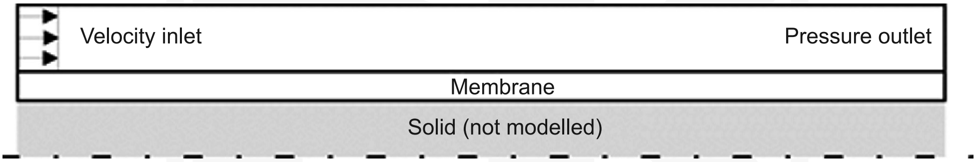

Fig. 1. Scheme of the extraction module geometry (not to scale)

The CFD simulations were performed for one process temperature (313 K), one process pressure (20 M Pa) and four different $scCO_2$ mass flow rates (0.5, 1, 2, and 4 g/min). Additionally, for every set of process parameters, four different cases were analyzed:

- Case A (“begin”) represented the state at the begin of the cleaning process, when the membrane is totally filled with the oil. Hence, concentration at the outer surface of the membrane was set to the value of solubility of soybean oil in $scCO_2$.
- Case D (“end”) represented the state, when the cleaning process is almost finished – residues of oil are present on the inner surface of the membrane only and on this surface the concentration of soybean oil was set to the value of solubility of soybean oil in $scCO_2$.

– Cases B and C (“intermediate states”), in which the oil-scCO$_2$ phase boundary reached 33.33% and 66.67% of the membrane’s thickness, respectively, which corresponds to 37.78% and 71.11% of the oil removed from the membrane pores.

In these simulations, a idealized system was considered, during which the oil-scCO$_2$ phase boundary is parallel to the inner and outer surface of the membrane during the whole process. This situation may occur, when the solvent flow is sufficiently high and the saturation of scCO$_2$ with oil at the outlet of the extraction vessel is relatively low.

Concentration of the oil was calculated using the User Defined Scalar approach, in the form of dimensionless concentration:

$$C = \frac{c}{s} \tag{5}$$

where:

c – the local concentration of soybean oil in scCO$_2$,
S – the solubility of soybean oil in scCO$_2$.

According to the definition above, one gets $C = 0$ for pure scCO$_2$ and $C = 1$ for scCO$_2$ saturated with soybean oil.

For comparison of convection rate and diffusion rate, two time constants were defined, namely the convection time t_c (which is equal to the residence time of the solvent in the extraction module) and the diffusion time t_d:

$$t_c = \frac{L}{u} \tag{6}$$

$$t_d = \frac{\delta^2}{D_e} \tag{7}$$

where:

L – the length of the extraction module,
u – the velocity of scCO$_2$ at the inlet of the extraction module,
δ – the thickness of the membrane,
D_e – the effective diffusivity.

Table 1

Process parameters and extraction module dimensions

Parameter	Value	Parameter	Value
Temperature T [K]	313	Module length L [m]	0.1
Pressure p [MPa]	20	Module diameter d [m]	0.0046
scCO$_2$ density ρ [kg/m^3]	839	Membrane diameter d_m [m]	0.0027
scCO$_2$ viscosity μ [Pa·s]	$7.812 \cdot 10^{-5}$	Membrane thickness δ [m]	0.00045
Diffusivity D [m^2/s]	$3.15 \cdot 10^{-9}$	Porosity ε [–]	0.7
Effective diffusivity D [m^2/s]	$1.10 \cdot 10^{-9}$	Solvent mass flow rate [g/min]	0.5; 1; 2; 4
Diffusion time t_d [s]	183.64	Soybean oil solubility [g/kg]	4.811

4. Experimental data

In order to validate the mathematical model, experimental data from a lab-scale supercritical fluid extraction systems were used [10, 11]. Membrane cleaning was conducted in a extraction module with the same geometry as in the CFD simulations. The process was carried out for two solvent mass flow rates (1 and 2 g/min) and various process times. The cleaning efficiency obtained during the experiments was calculated as follows:

$$\eta = \frac{\Delta m}{m} \tag{8}$$

where:

Δm – the mass of oil removed by the cleaning process,
m – the initial mass of the oil inside the membrane pores.

5. Results and discussion

In Table 2, the CFD simulation results for four different inlet velocities are summarised. The Reynolds number was determined using the hydraulic diameter calculated for the annular cross-section of the extraction module. The flow was laminar for all investigated inlet velocities and resulted in the development of a typical laminar flow velocity profile in the CFD simulations. Diffusion time is constant, but convection time decreases with increasing inlet velocity as the mean residence time decreases. This results in the decrease of the t_c/t_d ratio – convection becomes faster than diffusion. In turn, this results in a decrease in the mean soybean oil concentration C at the outlet of the extraction module. Hence, the t_c/t_d ratio is an important parameter describing the course of the process, because it shows whether the process is controlled by convection (high t_c/t_d ratio values) or diffusion (low t_c/t_d ratio values).

Table 2

CFD simulation results

Solvent mass flow rate [g/min]	**0.5**	**1**	**2**	**4**
Inlet velocity u [m/s]	0.000912	0.001824	0.003647	0.007294
Reynolds number Re [–]	18.6	37.3	74.5	149.0
Convection time t_c [s]	109.64	54.82	27.42	13.71
Diffusion time t_d [s]	183.64	183.64	183.64	183.64
t_c/t_d [–]	0.597	0.299	0.149	0.075
Soybean oil concentration C at the outlet of the exctraction module[%]				
Case A (begin of cleaning)	47.81	29.57	17.77	10.52
Case B (37.78% of oil removed)	30.55	17.29	9.55	5.20
Case C (71.11% of oil removed)	19.37	10.43	5.53	2.90
Case D (end of cleaning)	13.61	7.16	3.73	1.92

One can also notice that there is a significant difference in outlet concentrations *C* between case A, when the membrane is filled with soybean oil (begin of cleaning) and the cases B, C, and D when the membrane is being gradually cleaned with $scCO_2$. At the beginning, no diffusion through the pores occurs as soybean oil is still present at the outer surface of the membrane, which contacts with $scCO_2$. Hence, the mass transfer resistance is lower and more oil can be removed. As the cleaning process advances, the soybean oil-$scCO_2$ phase boundary moves inside the membrane. The dissolved soybean oil molecules are transported outside the membrane by molecular diffusion (as stated before, no convection occurs inside the membrane). The longer the diffusion distance through the membrane, the lower the driving force and the lower the mass flux – the cleaning process becomes significantly slower. A further increase of the flow rate is pointless as it does not affect the mass transfer resistance in the membrane pores, which is the main factor limiting the overall process rate. On the other hand, it implies that the volume flow rate should not be constant during the cleaning process in order to keep the cleaning rate (defined as dimensionless concentration *C* at the outlet of the extraction module) on an appropriate level. However, mass transfer can be enhanced when the geometry of the system will be changed, i.e. when the solid will be removed from the lumen of the membrane, which will allow to swill the membrane from both sides (inner surface and outer surface), not only from outside. This variant will be further investigated in CFD simulations and in laboratory scale experiments.

Fig. 2. Dimensionless concentration *C* of soybean oil in $scCO_2$ in the extraction module (solvent mass flow 0.5 g/min)

In Figure 2, dimensionless concentration *C* profiles for one flow rate and for the four cases A, B, C, and D of the extraction process (showing the progress of the cleaning process) are depicted (not to scale). As mentioned before, the saturation decreases significantly as the cleaning process advances. Moreover, as can be noticed in Figure 2, soybean oil concentration at the membrane surface changes in axial direction and mass transfer rate depends on the axial coordinate ($scCO_2$ is being saturated while flowing through the module). The membrane is cleaned unequally and will already be clean near the extraction module inlet while it will still contain soybean oil in other regions. Hence, the process will be described more accurately, if the assumption of parallel movement of the oil-SCF phase boundary will be rejected and a dynamic phase boundary capturing approach using the volume of fluid method will be used instead.

In Figure 3, the results of the CFD simulations are compared with the experimental data for validation of the proposed modelling method. The CFD simulation results are those presented in Table 2. The curves presenting the experimental data were determined as follows: The experimental data were presented as (time; cleaning efficiency) data points and theoretic curves were fitted to these data. The curves were defined by the following differential equation:

$$\frac{d\eta}{dt} = \frac{1}{\alpha\eta + \beta} \tag{9}$$

where:

η – the cleaning efficiency of the process,

α – the constant describing the influence of the progress of the cleaning procedure on the increase of mass transfer resistance,

β – the constant describing the initial mass transfer resistance.

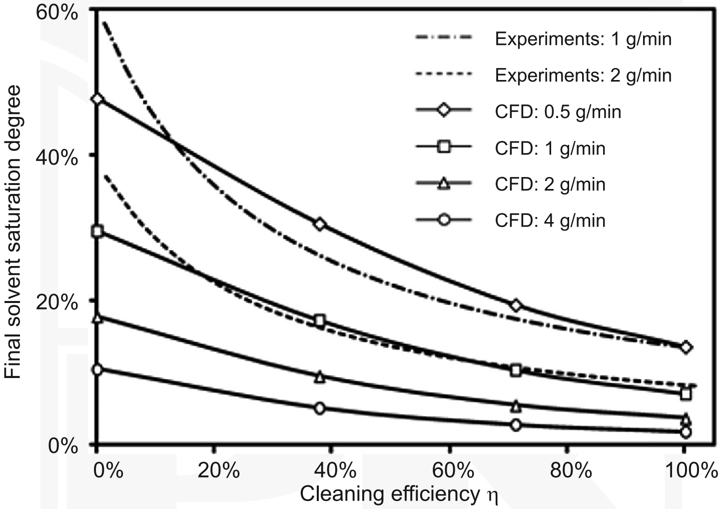

Fig. 3. Final solvent saturation degree – CFD simulations and experimental results

For each of the two mass flow rates of the experimental data, the values of the constants were determined using the least square method (the obtained curves fitted well to the experimental data: R^2 = 99% for 1g/min and R^2 = 97% for 2 g/min). Then, the process rate was determined according to equation 9 and – using the mass flow rate of the solvent and the solubility of soybean oil in the solvent – the solvent saturation at the extraction vessel outlet was determined and plotted in Figure 3.

As can be seen in Figure 3, both results from CFD simulations and experimental data show similar trends, namely the decrease in solvent saturation at the outlet of the extraction module with the progress of membrane cleaning. Moreover, higher solvent mass flow rates result in lower values of solvent saturation for the same stages of the cleaning process (i.e. for the same values of cleaning efficiency). Hence, CFD simulations do reflect the nature of the process in terms of increasing mass transfer resistance caused by the increasing length of the mass transfer path through the porous structure of the membrane. The overall process rate is controlled by diffusion in the porous structure and increasing the mass flow rate of the solvent for process intensification is not a good solution for acceleration of the process, as it does not contribute significantly to better mixing conditions inside the pores and results in decreasing solvent saturation.

However, the results of CFD simulations suggest lower process rates than those achieved in the real lab-scale system (about two times lower). There are several possible causes for this inconsistency:

– The tortuosity τ used for calculation of the effective diffusivity in the porous structure was assumed to be 2; however, the real value may differ from this assumption.
– The correlations for transport properties and especially for the solubility of soybean oil in $scCO_2$ may introduce errors in the calculations.
– During the pressurisation of the experimental system, which takes a while, the process of cleaning already occurs and leads to positive values of cleaning efficiency at the start time $t = 0$.

In order to improve the quality of the CFD model, one has to determine the actual value of the tortuosity. Moreover, the aim is the development of a dynamic process simulation (transient instead of steady-state simulations), which will utilise the Volume of Fluid (VOF) approach and enable to track the actual oil-$scCO_2$ phase boundary inside the porous structure of the membrane.

6. Conclusions

In this work, a method for modelling of microporous membrane cleaning by supercritical fluid extraction, suitable for CFD simulations, was presented. The method enables to predict the course of the extraction process and helps to design experimental systems. The convection time/diffusion time ratio is critical in terms of the saturation of the supercritical fluid at the outlet of the extraction module and it should be a main criterion during process design and scale-up. The presented modelling method was validated using data obtained from the lab scale experimental system. The method will be developed in order to improve the accordance of the simulation results with experimental data and for simulation of a dynamic oil-SCF phase boundary using the volume of fluid approach.

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