Influence of operating parameters and membrane materials on fouling of ceramic hollow fibre membranes

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ABSTRACT

Fouling is one of the critical issues in membrane filtration, especially in the field of wastewater treatment. In this study sodium alginate was used as model compound for extracellular polymeric substances (EPS) in order to investigate the filtration and fouling characteristics of two newly developed ceramic hollow fibre membranes. The membranes studied have an asymmetrical structure consisting of an Al_2O_3 support layer, which is covered by an active layer. Two different active layers (Al_2O_3 and SiC) were studied under various operating conditions (dead-end and cross-flow filtration) by filtering sodium alginate solutions in the presence and absence of calcium ions. Fouling mechanisms taking place in dead-end mode were evaluated according to the cake filtration model. Dead-end filtration experiments revealed a change in fouling mechanisms from pore blocking and cake filtration in the absence of calcium ions to cake filtration only in the presence of calcium ions. Furthermore, cross-flow filtration experiments showed a big influence of calcium ions on the removal of the resulting alginate layer from the membrane surface due to shear forces induced by cross-flow. In the absence of calcium ions, the filtrate flux was found to depend strongly on transmembrane pressure (TMP) and cross-flow velocity, whereas in the presence of calcium ions, the chosen cross-flow velocities (1–3 m/s) were not sufficient to control alginate fouling. Cross-flow experiments without calcium addition revealed a higher flux for SiC membranes compared to Al_2O_3 membranes. For dead-end filtration experiments, no significant difference was found.

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1. Introduction

Membrane fouling is one of the critical issues, as it affects productivity, plant operation and maintenance costs in membrane filtration processes [1]. This is especially true for membrane applications in membrane bioreactors (MBR) and other treatment processes of water with high organic loads. Membrane fouling is the unwanted accumulation of materials on the membrane surface, leading to an enhanced filtration resistance [2]. It was reported that one of the main causes of membrane fouling in MBR are the extracellular polymeric substances (EPS) [1,3,4]. Among proteins and humic substances, polysaccharides have been identified to be main constituents of EPS [5]. In membrane filtration research, sodium alginate often serves as a model compound for EPS [3,4,6–9]. Sodium alginate is a polysaccharide, which is negatively charged near the neutral pH and very sensitive to changes in ionic strength. Alginates form gels in the presence of divalent cations, such as Ca^{2+}, which are also discussed to affect membrane fouling

in MBR due to a promotion of molecular binding [7,10]. The Ca^{2+} ions preferably bind to the carboxylic groups of alginates, leading to a highly organised network which can be explained by the "egg-box" model [4,6]. This phenomenon is well-known in literature, but leads to different conclusions in terms of permeate flux decline [6]. Some studies show that the addition of Ca^{2+} cause an increase in fouling behaviour of the system [11], while other groups found that the addition of Ca^{2+} improved permeate flux and reduced fouling resistances [6]. It has to be taken into account that the fouling behaviour of a system can be affected by operating and hydrodynamic conditions, membrane material and its pore size distribution, as well as by the feed composition. Hence, these contradictory results may be due to different feed and operation conditions.

The aim of this work is to improve the understanding of ultrafiltration fouling phenomena using alginate as model compound for EPS. In particular, the influence of hydrodynamic parameters (TMP and cross-flow velocity), feed solution characteristics in terms of Ca^{2+} concentration, as well as the influence of different membrane materials (Al_2O_3-coated and SiC-coated membranes) on membrane fouling characteristics is studied. We use ceramic

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Nomenclature

A	active filtration area of the membrane [m^2]
a	parameter in Eq. (9) [–]
b	parameter in Eq. (9) [–]
c$_b$	bulk concentration of organic foulant [kg/m^3]
J	permeate flux [l/(m^2 h)]
N$_f$	resistance number [–]
N$_S$	shear stress number [–]
TMP	transmembrane pressure [kPa]
PWP	Pure water permeability [l/(m^2 h bar)]
R$_f$	fouling resistance [1/m]

R$_m$	membrane hydraulic resistance [1/m]
R_t	total resistance [1/m]
V	filtrate volume [ml]
v_{CF}	crossflow velocity [m/s]

Greek letters

α	specific cake resistance [m/kg]
ρ	density of the feed solution [kg/m^3]
η	dynamic viscosity [Pa s]
ΔP	transtubular pressure drop [kPa]

hollow fibre membranes, because these membranes are characterised by high chemical and thermal stability as well as by a large specific membrane filter surface area.

2. Materials and methods

2.1. Resistance determination

A number of mechanisms may lead to flux decline in the cross-flow and dead-end modes. Filtrate flux can be calculated using Darcy's law for constant TMP according to the resistance in series model [5,12]:

$$J = \frac{1}{A} \cdot \frac{dV}{dt} = \frac{TMP}{\eta(R_m + R_f)} = \frac{TMP}{\eta \cdot R_t} \tag{1}$$

where *J* is the permeate flux, *TMP* is the transmembrane pressure, η is the dynamic viscosity, R_m is the membrane resistance, R_f is the fouling layer resistance, and R_t the total resistance at the end of the filtration experiment.

TMP was calculated from the pressure data taking the pressure drop along the hollow fibre feed channel into account:

$$TMP = \left(P_{Feed} - \frac{\Delta P}{2} \right) - P_{Perm} \tag{2}$$

where P_{Feed} is the pressure of the feed stream, P_{Perm} the pressure of the permeate stream (ambient pressure) and ΔP is the pressure drop along the hollow fibre membrane.

Membrane resistance R_m was determined by filtering ultrapure water for 30 min at a TMP of 100 kPa in the dead-end mode through the unused membrane before every fouling experiment. R_m was calculated from the clean water fluxes J_0 according to following equation:

$$R_m = \frac{TMP}{\eta \cdot J_0} \tag{3}$$

The total resistance R_t was calculated from the resulting filtration flux at the end of the filtration experiment:

$$R_t = \frac{TMP}{\eta \cdot J_{120}} \tag{4}$$

J_{120} is the flux after 120 min of dead-end filtration. Knowing R_t and R_m, the fouling layer resistance R_f can be calculated.

Fouling mechanisms for dead-end filtration can be visualised by plotting the flux data in an appropriate linearised form according to the following model [3]:

$$\frac{t}{V} = \frac{\eta R_m}{TMP \cdot A} + \left(\frac{\eta \alpha c_b}{2 \cdot TMP \cdot A^2} \right) V \tag{5}$$

Here, R_m is membrane resistance, *A* is the active filtration area of the membrane, *V* is the filtrate volume at time *t*, α is specific cake

resistance, and c_b is the bulk concentration of organic foulant (e.g. alginate). If a linear relationship is the result of plotting t/V = f (V), this means that cake formation is the only fouling mechanism taking place.

2.2. Ceramic hollow fibre membranes

Ceramic hollow fibre membranes combine the advantages of both inorganic membrane material and hollow fibre geometry [13]. The main advantages resulting from this combination are high chemical and thermal stability associated with a high specific packing density [13]. Further advantages of ceramic membranes are their abrasion resistance as well as the possibility to backflush the membranes. Major drawbacks which have limited the widespread application of ceramic membranes are high capital costs as well as the brittleness of the membranes [14].

The ceramic hollow fibre membranes studied have an asymmetrical two-layer structure. The α-Al$_2$O$_3$ microfiltration support layer has open pores and determines the stability of the fibre. The support layer can be covered by different ceramic coating layers for ultrafiltration (active layers). Fig. 1 shows a cross-section of a ceramic hollow fibre membrane and a detailed representation of the active layer on the inner lumen of the membrane. In this study ceramic hollow fibre membranes with two different inorganic active layers (Al$_2$O$_3$ and SiC) are used. The membranes are manufactured by a simultaneous spinning and phase inversion process. After the spinning process the fibre is washed and sintered at high temperatures. During this sintering process the polymer, which was besides ceramic powder, a number of additives and a corresponding solvent system, one compound of the spinning mass, is burned completely out of the fibre structure. After sintering, the support layer is covered by the functional ultrafiltration ceramic coating layer and sintered a second time. Further information on the manufacturing process of the membranes used in this study is given by Ebrahimi et al. [13].

Fig. 2 shows SEM images of the Al$_2$O$_3$ and SiC active layers investigated. The active layer is located on the feed side of the membrane. Depending on the filtration mode, the coating is applied on the inside of the hollow fibre membrane (in-out mode) or on the outer surface of the hollow fibre (out-in mode). Membranes operated in the in-out filtration mode allow an operation in the cross-flow mode. Membranes coated on the outside of the hollow fibre are used for the treatment of higher concentrated feed solutions, which are difficult to pump through the inner lumen of the hollow fibre membrane and preferably operated in dead-end mode.

Different combinations of the Al$_2$O$_3$ support layer with the two different active layers result in different pure water permeabilities (PWP) due to differences in the particle size distributions of the active layer starting material. Pore size distributions are measured