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Multistage counter-current solvent extraction in a flat membrane microcontactor

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HIGHLIGHTS

- In situ and multistage counter-current extraction in a membrane microcontactor were shown.
- An analytical model to describe the mass transfer kinetics was presented.
- The Sherwood number was determined for pillar filled channels.
- A semi-numerical model involving varying partition coefficients was presented.

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ABSTRACT

Co-current, multistage counter-current and in situ counter-current extraction is demonstrated in a membrane microcontactor, by extracting benzyl alcohol from *n*-heptane with water as extractant, without the need for active pressure control or additional pumps in between stages. An analytical model to describe the concentration profile as a function of the residence time is presented for the different configurations. From the obtained experimental results the Sherwood number is determined for a channel filled with diamond shaped pillars having an aspect ratio of 3. This allows to calculate the local mass transfer coefficients and to determine the mass transfer kinetics. The obtained model can be used for the prediction of purity levels and allows to optimize the set-up configuration.

1. Introduction

Solvent extraction (SX) is extensively used for the purification of metals, wastewater recycling, recovery of spent nuclear fuels as well as purification and concentration of many solutes of biological importance such as DNA and pharmaceuticals [1]. Traditionally SX is performed in mixer-settlers, batch vessels, extraction columns or centrifugal extractors. In all of these devices the feed liquid is dispersed into the extraction solvent or vice versa. By doing so, a range of possible problems can arise: formation of a stable emulsion, foaming, unloading or flooding [2]. Furthermore, intensive mixing is needed to achieve good dispersion (small droplets) to reduce the residence time and to achieve fast mass transfer kinetics. However, smaller droplets make it more difficult to obtain complete phase separation afterwards. Microreactor technology allows to avoid this phase separation step. By fabricating microdevices that ensure a stable parallel flow profile between both phases, each phase can be collected individually at the outlets. As the parallel flow profile is easily disrupted [3–4], different strategies to stabilize the interface have been demonstrated [5]. Aota et al. [6] coated the lower half of the microchannel wall with hydrophobic molecules, while the upper half of the microchannel wall was kept hydrophilic. This allowed, within a certain flow rate range, to compensate for the shear stress at the interface. Tokeshi et al. [7] placed two guide structures of 5 μm high at the bottom of the channel, allowing to form a stable tri-layered parallel flow profile and Maruyama et al. [8] constructed intermittent partition walls (50 or 100 μm long, 20 μm high and 5 μm wide) in the center of the channels. These pillars were placed apart, with the same distance as their length (50 or 100 μm) in between them, resulting in a stable parallel flow profile with a complete phase separation at the end of the channel. The disadvantage of these devices is that the parallel flow is only stable in a narrow operating range. A

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List of symbols

P	pressure (Pa)
Q	flow rate (m^3/s)
n	number of pores (–)
r	pore radius (m)
D	diffusion coefficient (m^2/s)
t	time (s)
u	velocity (m/s)
N	number of theoretical plates (–)
h	channel depth (m)
K	global mass transfer coefficient (m/s)
L	length of the MMC (m)
H	partition coefficient (–)
C	concentration (mol/m^3)
Sh	Sherwood number (–)

Greek symbols

μ	dynamic viscosity (Pa s)
δ	thickness of the membrane (m)
$\Delta\sigma_x^2$	peak spatial variance (m^2)
$\Delta\sigma_t^2$	time based peak variance (s^2)
γ	correction factor (–)
ε	porosity of the membrane (–)
τ	tortuosity (–)

Subscripts

per	permeate
f	feed
s	extraction solvent
R	raffinate
E	extract
i	stage number
j	cell number
m	membrane
eff	effective

change in viscosity or pump fluctuations for instance, quickly results in a disruption of the interface. To extend the operation range, the capillary force that pins the interface needs to be increased. An improved stability can be achieved by equipping the device with a membrane at the interface.

In so-called *membrane contactors*, the liquids flow along both sides of this membrane. The membrane acts as a barrier to stabilize the liquid–liquid interface [9–11]. The pores of the membrane are filled with the liquid wetting the membrane and the interface is pinned by capillary action. A certain critical pressure difference across the membrane, the breakthrough pressure, is needed to disrupt this interface. A stable interface is obtained when operating beneath this breakthrough pressure and as long as the pressure of the wetting liquid remains below the pressure of the non-wetting liquid.

In a different approach, the liquids are first mixed and subsequently separated based on the difference in wetting properties. As the mixture flows along the membrane, only the wetting phase enters the pores and leaves the device at the other side of the membrane. This *membrane separator* technology was developed by the group of Klavs Jenssen [12–13] and is currently being marketed by the company Zaiput. Like the membrane contactor, the pressure difference across the membrane is critical for a proper operation of this device [12,14]. For a complete separation only the wetting liquid is intended to enter the pores, meaning breakthrough has to be avoided and thus the pressure difference across the membrane needs to be lower than the breakthrough pressure. On the other hand the entire wetting phase has to pass through the pores to achieve a complete phase separation. This implies that the pressure difference across the membrane has to be larger than the permeate pressure (Eq. (1)), which can be calculated with:

$$P_{per} = \frac{8\mu Q\delta}{n\pi r^4} \tag{1}$$

where P_{per} represents the permeate pressure, μ the dynamic viscosity of the permeate phase, Q the flow rate, δ the membrane thickness, n the number of pores and r the pore radius. This constitutes a drawback as the needed permeate pressure for full separation increases with the power of 4 with a decreasing pore radius while the breakthrough pressure only increases linearly with a decreasing pore radius [11]. This rapidly restricts the working range of membrane separators when operating with membranes with a smaller pore radius.

In contrast, for the membrane contactor the operating range only broadens with a smaller pore radius, as there is no needed permeate pressure. Nonetheless, a drawback of the membrane contactor is its relatively slow mass transfer. Whereas other systems also rely on convective mass transfer, the mass transfer with a membrane contactor is only diffusion based. To cope with this drawback, micro-technology can be used to create a so-called membrane microcontactor (MMC) with shallow channels such that the maximal diffusion distance is in the range of 100 μm or less [15]. In this way, equilibrium can be reached within a residence time of only a few minutes.

Two types of membrane contactor configurations exist: the flat sheet configuration, which can also be spiral wounded to minimize space and the hollow fiber (or tubular) configuration [16]. Although the hollow fiber configuration is a frequently used one [17], it comes with some disadvantages. As a single fiber is not satisfactorily in terms of throughput, a bundle of fibers is preferentially being used. However, the occurrence of dead zones, backmixing, bypassing and channeling, especially on the shell side, causes irregular mass transfer along the module [18]. In case of clogging, cleaning is often no longer possible. An advantage of the hollow fiber is that high surface to volume ratios can be created, i.e. 50–300 cm^2/cm^3 [19].

To minimize the needed amount of extraction solvent and maximize the concentration in the extract phase, multistage counter-current extraction is implemented [20]. With continuous micro-devices, where the two liquids are mixed and subsequently separated, this is difficult to achieve. Each stage generates a certain pressure loss, thus when only two pumps are used the wanted flow direction can never be reached. A compensation is then required for this pressure loss, e.g. by using additional pumps after each stage [12] to ensure a stable operation. From a process control point-of-view, this sounds easier than it is, especially with miniaturized devices. For instance, when the two liquids are partially miscible, a change of flow rate will occur along each stage. When the pumps in between the stages do not compensate for this effect, a pressure build-up or under-pressure (sucking liquid from the previous stage) is generated. The apparently easiest solution to this problem is to decouple the different stages by inserting buffering tanks, but again flow rate monitoring should take place to avoid