Effective methods for nanofiltration of small volume samples

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Motivation

- Concentration of small volume samples is necessary, for instance, in the research and production of high value chemical compounds or in the analysis of environmental and biological media.
- Devices for microfiltration and ultrafiltration of small samples are available commercially, usually in the form of centrifugal devices.
- Available centrifugal devices are not suitable for the concentration/fractionation of low molecular weight substances (MW < 1000 g/mol).
- The application and evaluation of nanofiltration membranes for small volume sample filtration using centrifugal devices is needed.

Background

A membrane is any material that controls the partition of substances [1]. The two basic setups in pressure-driven membrane technologies are: batch dead-end (Fig. 1A), and continuous tangential-flow filtration (TFF) (Fig. 1B).

The quantification of membrane processes is based on the permeate flux, Jp, and on the apparent rejection of the component, the relation between feed and permeate concentrations, Rj = (c - c)/c.

Depending on the characteristics of the membrane, distinct applied pressure are necessary and different separations are obtained, which are classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). For instance, MF membranes retain bacteria and cells, UF membranes retain virus and large proteins, NF membranes retain divalent salts, peptides and other small molecules, while RO membranes retain monovalent salts.

The analysis of molecules in dilute samples or at a concentration several orders below the main components are challenging. Examples are the study of peptide in body fluids or of toxic compounds in the environment. Chromatography can be used for fractionating and concentrate small volume samples, but is expensive and time consuming. Conventional membrane processes are an alternative but leads to concentration polarization (CP) [2]. A faster, cheaper and simpler technique is Centrifugal Filtration (CF).

The fundamentals of CF rely on Fig. 2, on the one hand, on the pressure Δp created on fluid elements (of mass m) rotating (at angular velocity ω) at a certain distance, r, from the axis of rotation and, on the other hand, on its self-cleaning mechanism that drag away the heavier fluid elements. The advantages of CF are: 1) pumps are not necessary, 2) self-cleaning of the membrane, 3) easily scalable (depending on the available centrifuges). Up to date, CF of small samples was performed only with MF/UF membranes and several commercial devices are available [3] for MF/UF. It is then of significant importance to assess the use of nanofiltration in CF devices.

Figure 2 – Fundamentals of centrifugal filtration.

The purpose of this work is two-fold. First, the limitations of TFF are shown and, second, the feasibility of Centrifugal Nanofiltration (CNF) will be demonstrated.

Methodology

Real time TFF of K2SO4 water solutions were evaluated using a flat NF device, which channel height was 2 mm. Visualization of the concentration distribution was obtained by Holographic Interferometry technique and the results were compared with the ones from computational simulations [4].

CNF efficiency was evaluated using a hollow tube with a NF membrane in between feed and permeate reservoirs. K2SO4 (MW = 174.3 g/mol), sucrose (MW = 342.3 g/mol) and polyethylene glycol (MW = 1000 g/mol) were used as model molecules.

Results and Discussion

For TFF processes a CP layer develops near the membrane, as can be seen from the concentration distribution in TFF experimental interferograms (Fig. 3A) and numerical simulations (Fig. 3B).

Figure 3 – Concentration field of K2SO4 in TFF: A) experimental; B) numerical (black iso-concentration lines and white streamlines).

CP layer increases the osmotic pressure in vicinity of the membrane, decreasing the effective driving force and permeate flux. At the same time, it increases the solute concentration gradient across the membrane, inducing solute transport and the decrease of the apparent rejection.

TFF results evidence that the apparent rejection and the permeate flux drop as Re decreases (green dots in Fig. 4). Flows at low Re are relevant since they are common in microfluidic processes used to treat small volume samples. Therefore, new methods must be developed to process tiny fluid volumes, keeping high permeate flux and rejection, being CNF the object of study.

The potential of CNF is clear from Fig. 4 where data obtained from CNF experiments (blue dots) are compared with its TFF counterpart (green dots). For the same K2SO4 solution and average applied pressure the rejection is higher in the CNF. Moreover, one can easily increase the permeate flux (increasing the rotations per minute, rpm) which could be hard to implement in microfluidic TFF devices. Fluxes are shown as the ratio between solution permeate flux and pure water flux, Jp.

Figure 4 – Comparison between TFF and CNF of K2SO4 (2g/L).

CNF proved to be efficient at retaining the three model solutes, unless high concentration and low pressure are applied simultaneously (Fig. 5).

Conclusion

CNF has shown to be a consistent method for the retaining of small solutes (MW 170 – 1000 g/mol), in the retentate, when the concentration factor is small. Permeate flux can be boosted, raising rpm, without loss of permeate quality. Further study should focus on the filtration behavior when high concentration factor is necessary.

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References