Development and characterization of Silicon Carbide membranes for innovative applications

Institute for Sustainable Process Technology

Final report

(public summary)

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PUBLIC Summary

The separation of oil from stable oil in water emulsions is a challenge, especially if low limits for oil in water are required as in the case of produced water (< 30 ppm dispersed oil). Many technologies have been studied, but proved to be technically or economic challenging (energy demand, need for additional materials,etc.) Ceramic membrane filtration proved to be an interesting option. Boundary condition is that the membranes can be operated and cleaned at rather extreme pH and temperature conditions. The existing zirconia or alumina membranes have a limited pH resistance and exhibit extensive fouling tendency under certain conditions. Silicon Carbide (SiC) does not have these limitations. In previous projects (e.g. CombiClear) it is shown that the SiC membranes show a good performance for the treatment of oil in water emulsions. Still missing is the behavior of these membranes at duration tests and in particular cleaning possibilities of these membranes. This has been studied in this project during a pilot trial. At ESD a pilot trial is executed with a SiC membrane module of 8 m^2 from Liqtech on gas condensate, containing PAH. The reference for this pilot trial is the existing membrane unit at ESD with Al_2O_3 membranes. During the pilot trial the same cleaning procedure and frequency is applied as for the Al_2O_3 membranes. The pilot unit (Semco) is controlled on flux, while turbidity and PAH concentration in the permeate are monitored. Results show that the turbidity of the permeate of the SiC membranes is in average higher than the turbidity of the permeate of the Al_2O_3 membranes, but that the more important PAH concentrations in both permeates are similar. The cleaning operation is sufficient to keep the installation running during the pilot trial, which proves the cleanability of these membranes. More specific conclusions on the effect of the cleaning are hard to draw, because the quality of the feed changes continuously during the pilot run, having a large effect on the performance of the membrane. Based on the results obtained in the pilot trial, ESD has decided to replace a part of their existing Al_2O_3 membranes by SiC membranes to monitor the performance of these membranes for a longer period. The pilot trials have been executed with the native SiC-UF membrane. In order to determine if grafting this membrane would lead to a better membrane performance (fouling, retention), laboratory experiments have been executed with the grafted membrane with the same type of water as used in the pilot trials. The ESD Clean Water permeability (CWP) values found in this study (142-202 L/m^2.h.bar) were comparable to the CWP values during the on-site pilot test at ESD. This despite of the fact that during pilot testing at ESD periodical backwash (and backpulsing) was applied during 5 weeks. A periodical backwash was not possible during the lab-scale tests and of course the testing period was much shorter. TOC removal was high (85%) and moderate (40%) at the start of the labscale filtration experiment with ESD water for respectively the unmodified and grafted SiC membrane. At the end of the experiment, however, the TOC removal was extremely low (7%). This could be explained by damage which occurred during the labscale experiment. However, this was not corroborated by the PAH removal values which remained relatively high for both SiC membranes during the complete labscale filtration test (76-99%). PAH are more hydrophobic compounds which might be removed due to adsorption on the membrane, which might be the dominating mechanism during the relatively short labscale filtration experiment.

Because SiC membranes are very robust, it is interesting to extend their applicability to other domains, e.g. food, dairy, pharmaceuticals, chemistry. In this project the potential of the SiC membranes for several of these applications have been studied on small scale (TRL 3-5) and will provide the performance of these membranes for these applications (flux, separation factor, fouling, etc.).

For **dairy applications** two separations have been studied:

- Separation of casein from serum proteins in skimmed milk
- Separation of fat from proteins in raw milk

For the casein/protein separation UF-SiC membranes are applied. For one experiment a native membrane is used, while for the other experiment a grafted (surface treatment aiming at reduced fouling) membrane is used. Results of the tests are compared with known results of other types of ceramic membranes. Preliminary results show that the separation and flux performance of the native membrane show similar results compared to the known ceramic membranes like Al_2O_3 membranes, The grafted membrane shows a more stable flux during concentration, but seems to be more dense resulting in a poorer separation performance (too high rejection for serum proteins).

For the fat/protein separation both a native and a grafted MF-SiC membranes is used with a poresize of ca. 1 µm. Separation results with the native show a high loss of fat at low dry weight content, improving at higher dry weight content. The results with the grafted membrane show less loss at low dry weight content, but the loss is still too high to get an economic feasible separation process.

For a **pharmaceutical application**, the purification of wool grease (removal of colloidal material)has been studied with SiC membranes with different pore size. Both membranes have been applied in the native form, but also after grafting (in two different ways). The experiments are executed at a temperature between 90 and 100 °C. The results show that the smallest available poresize (ca 46 nm) was not small enough to reject the colloidal material sufficiently. This was the case for both the native and grafted membranes.

Besides the research on the application of existing MF and UF SiC membranes, the filtration range of SiC membranes has extended to nanofiltration. Nanofiltration (NF) is widely applied in the food processing and dairy industry and cleaning and disinfection possibilities at rather high/low pH and high temperatures are often demanded. SiC nanofiltration membranes might be an answer to that demand. First, SiC layers were deposited on silicon wafers via chemical vapor deposition (CVD) at two different temperatures, 750°C, and 860°C. The reaction kinetics at 860°C were higher than at 750°C, leading to rapid layer growth in shorter period of times. X-ray diffraction analysis demonstrated that the SiC layer deposited at 750°C was amorphous and the SiC film deposited at 860°C was polycrystalline. The next step was to deposit SiC with Atomic Layer Deposition (ALD) to decrease the pore size to the nanofiltration range. After a several experiments we had to conclude that, with available ALD set-up, the deposited layers were not uniform and also not reproducible. Recent literature shows that the precursors react with the 3C-SiC surface, but passivate it. Adding an additional plasma activation step to sustain an ALD process resulted in Si growth by forming Si-Si bonds, however, none of these reactions are self-limiting. Therefore, new precursors and reaction chemistries need to be identified in order to deposit SiC by ALD, otherwise, the SiC growth will proceed in a CVD-type growth. Alternatives could be sought, for instance, in doping of carbon in silicon dioxide or deposition of Silicon Oxycarbide via Molecular Layer Deposition.