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**Gas Responsive Microgels as Novel Draw Agents
for Forward Osmosis Desalination**

By

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Declaration

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Abstract

Forward Osmosis (FO) process is a low-energy membrane separation technique, which has attracted increasing attention recently for desalination applications. Unlike Reverse Osmosis, which needs a high-pressure pump; FO works via natural osmotic pressure provided by a draw solution. Therefore, development of efficient draw solutions is quite important. Polymeric stimuli-responsive microgels/hydrogels are promising options as they can be recovered by applying the proper stimulus heating or gassing processes. The temperature-responsive microgels/hydrogels have been developed for FO application in recent years. This thesis study was aimed to the development of gas-responsive microgels as draw solutions for FO desalination. Two main series of microgels: CO₂-responsive and O₂-responsive microgels are for the first time fabricated and evaluated for FO desalination throughout the thesis. The feed saline water used here is 2000 ppm NaCl, which is considered as brackish water.

A few of polymer monomers with tertiary amine moieties are selected for synthesizing CO₂-responsive microgels. Water flux of the microgels was measured by monitoring conductivity of the saline feed water and interpreting it to the water flux through the membrane. The microgels are active and protonated as a draw solution after CO₂ purging, and can be recovered after CO₂ stripping by N₂ purging. Microgels synthesised with diethylaminoethyl methacrylate (DEAEMA) can provide water flux as high as 56 LMH. Characterization tests are carried out to explore the most-effective microgels with respect to cationic monomers: DEAEMA and dimethylamino ethyl methacrylate (DMAEMA), and the type and concentration of crosslinkers:

poly (ethylene glycol diacrylate) (PEGDA), N,N'-methylene-bisacrylamide (BIS) and ethylene glycol dimethacrylate (EGDMA). The microgels are recovered at their isoelectric point, where microgels are not charged and release water easily.

O₂-responsive microgels are synthesised and their FO desalination performance is studied systematically. Two Fluoro-containing monomers (2,3,4,5,6 pentafluorostyrene (FS), 2,2,2-trifluoroethyl methacrylate (FM)), which are responsive to oxygen, are selected to copolymerize with four suitable ionic and non-ionic monomers: DEAEMA, Hydroxyethyl methacrylate (HEMA), DMAEMA and N-isopropylacrylamide (NIPAM). The results show that the water recovery ratio can be enhanced if a proper non-ionic monomer like NIPAM is used. The O₂-responsive microgels synthesised by DMAEMA and 5wt% FM monomer can perform the highest water flux up to 29 LMH. The experimental data reveal that HEMA is not a suitable non-ionic monomer to synthesise O₂-responsive microgels as HEMA has –OH groups, which lead to high negative surface charges and affect the water recovery. FO desalination data show that O₂-responsive microgels perform comparable water flux and water recovery capability.

Dynamic light scattering (DLS) as the main characterization test for microgels is done. The microgels show larger hydrodynamic diameter after CO₂ or O₂ purging and they become smaller after removing these gases via N₂ purging. The swelling ratio for the microgels is up to 14 and 6.5 for CO₂ responsive and O₂-responsive microgels, respectively.

As new polymer draw agents, CO₂- and O₂-responsive microgels demonstrate high water flux and water recovery capabilities as promising

draw solutes for energy-effective FO desalination. CO₂-responsive DEAEMA microgels with 1wt% PEGDA crosslinker performed water flux of 56 LMH with 50 % water recovery ratio. DMAEMA CO₂-responsive microgels perform smaller water flux due to lower pK_a of DMAEMA than DEAEMA. O₂-responsive microgels show relatively lower water flux than CO₂-responsive microgels. The best water flux performance is observed for DEAEMA/DMAEMA-5wt% FM microgels with 26-29 LMH, while the highest water recovery is given by NIPAM-5wt% FM microgels with 56%.

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