論文の内容の要旨

Abstract of Dissertation

Characteristics of Seawater Driven Forward Osmosis Process for Concentrating Nutrients in MBR-Treated Municipal Wastewater

(MBR 下水処理水中栄養塩の濃縮における海水駆動正浸透プロセスの特性)

薛　文超

Nutrients recycle is widely accepted as a solution of choice for sustainable treatment of municipal wastewater. For effectively recovering the nutrients from municipal wastewater, appropriate concentration may be required. The emerging forward osmosis (FO) technology is a promising alternative to concentrate nutrients in municipal wastewater with relatively high recovery and low energy cost. FO is a membrane process in which water molecules migrate by natural osmosis through a semi-permeable membrane from a feed solution with lower osmotic pressure to a draw solution with higher osmotic pressure (Cath *et al.*, 2006). As a low-energy input process, FO provides advantages over pressure driven membrane technologies like reverse osmosis (RO) and nanofiltration (NF), such as lower operational cost and equipment investment, lower fouling propensity and higher recovery (Lee *et al.*, 2010; Mi and Elimelech, 2010b). Consequently, the applications of FO in seawater and brackish water desalination (McCutcheon *et al.*, 2005, 2006) and wastewater treatment (Cath *et al.*, 2005a; Cath *et al.*, 2005b; Holloway *et al.*, 2007) are highly promoted in the past decades, and related researches have been drawing increasing interests. In the application of FO, the selection of a suitable draw solution is an important issue. Seawater, containing considerable amount of unexploited osmotic energy, is a potential source of draw solution for FO. In addition, there is no necessity to regenerate the diluted seawater, further reduces to cost for operating FO process. The concept of seawater driven FO combining with membrane bioreactor (MBR) with the function of concentrating nutrients in municipal wastewater as well as discharging purified water into the sea without external fossil-base energy consumption was proposed in this study.

The primary objectives of this study are: i) to select one appropriate membrane for

this seawater driven FO system by comparing the fundamental properties of three available FO membranes, ii) to clarify the influence of various physical and chemical parameters on the performance of FO, in order to find out the optimum operating condition of FO process, iii) to evaluate the feasibility of FO in concentrating nutrients in MBR-treated municipal wastewater by batch filtration tests, iv) to investigate the long-term stability of a FO system for concentrating nutrients in MBR effluent and to characterize FO membrane fouling caused by MBR effluent, and finally v) to develop a mathematical model to simulate and predict the performance of FO in a practical process and further optimize the design parameters of FO membrane module. The major findings derived from this study are summarized as follows.

Among the three candidate FO membranes, the cellulose triacetate FO membrane embedded with polyester screen mesh supporter (CTA-1) achieved 7.4 $L \cdot m^{-2} \cdot h^{-1}$ of water flux, 0.9 $L \cdot cm \cdot mS^{-1}$ of reverse solute selectivity, 90% and 92% of phosphate and ammonia retention, was selected for the seawater driven FO process. On the other hand, the thin-film composite (TFC) membrane made of polyamide active layer with embedded support layer showed very low retention of ammonium. Especially with the active layer facing feed solution (AL-FS) orientation, ammonium was not able to be concentrated in the feed solution. The exchange of counter-ions from different side of membrane enhanced by high negative charge density on membrane surface was hypothesized according to the membrane zeta potential results. This finding may provide a new criterion of membrane selection for FO applications in future.

The effects of physical parameters including cross-flow velocity and membrane orientation, and chemical parameters including feed solution pH, concentration, and composition of feed and draw solution on the performance of FO were systematically investigated with the selected CTA-1 membrane. The cross-flow higher than 6.6 $cm \cdot s^{-1}$ was recommended to improve the water flux in FO filtration. Comparing with the active layer facing draw solution (AL-DS) orientation, the AL-FS orientation showed lower water flux but higher retention of nitrite and nitrate. Critical water flux of 7 $L \cdot m^{-2} \cdot h^{-1}$ was observed for ammonium and phosphate to achieve the asymptotic retentions by FO membrane. Besides, sensitive effects from solution pH on nutrients retention were observed. Neutral pH around 7 was effective for improving ammonia, nitrite and nitrate retention by the FO membrane. On the other hand, the composition of feed solution and draw solution also influenced the retention of nutrients by the FO membrane. Nitrate retention diminished due to the presence of medium components in the feed solution. While, the existence of multivalent solutes in the draw solution was favorable to the retention of co-ions in the feed solution. The investigation of various factors governing the performance of FO gave empirical information for optimizing the operation of FO.

The performance of FO in concentrating nutrients in MBR-treated municipal wastewater was further studied by batch tests together with flux model simulation. Feed solution pH ranged from 6-7 was suggested to ensure the concentration performance of ammonia in MBR effluent, consistent with the results obtained with synthetic feed solution. Batch FO tests showed that, with the water recovery of about 50%, DOC and phosphate were 2.3-fold concentrated, ammonia was 2.1-fold concentrated, and nitrite and nitrate was not well concentrated by FO, being only 1.9 and 1.3 times concentrated, respectively. Furthermore, retentions of higher than 80 % were generally obtained for trace metals, confirmed the reliability of discharging the purified wastewater into the sea by FO membrane. In addition, flux model simulation showed good predictability in comparison with the experimental results obtained in the batch tests. The modeling results showed that ammonia-N, nitrite-N and phosphate-P were able to be respectively concentrated by 4.2-fold, 3.8-fold, and 4.9-fold, in case the water recovery was 80%.

The long-term operational stability of the seawater driven FO in concentrating nutrients in MBR treated municipal wastewater was investigated and the membrane fouling was observed and analyzed to deepen the understanding of the mechanisms and characteristics of membrane fouling of FO process. During the long-term operation, occurrence of nitrification in the retentate dramatically affected the performance of FO on concentrating nitrogen. However, the nitrification in FO retentate was effectively avoided by inhibiting the growth of nitrifying bacteria. 5% of flux decline was observed after 55 days of operation, and little impact of membrane fouling on concentrating nutrients was observed. The mild impact of FO membrane fouling could be well retarded by disinfecting the feed solution. Additionally, the major membrane fouling mechanism of FO by MBR effluents was proposed to explain the experimental results: the AL-DS orientation gave serious water flux decline due to clogging inside the pores of membrane. On the other hand, the AL-FS orientation only formed cake layer on the active layer. Reduction of membrane permeability caused by the cake layer induced the decrease of water flux. And since there was no blocking happening inside the membrane porous structure, the impact of membrane fouling with the AL-FS orientation was much smaller than that with the AL-DS orientation.

Laboratory-scale experiments gave information on the pin-point local performance of FO membrane, which may differ from the overall performance especially in a scaled-up process. Therefore, a mathematical model was developed to simulate and predict the overall performance of FO in a practical process. The model was based on the mass transports including water flux, reverse solute diffusion and forward solute permeation. The variation of hydraulic condition inside the membrane module was also taken into consideration. The distributions of transmembrane osmotic and hydraulic pressure difference were predicted by the input of membrane performance parameters, module design and process operational parameters. Furthermore, the pressure drop in membrane module, and the distribution of water flux and feed solute concentration along the membrane length direction were estimated. According to the simulation results, ammonia was able to be concentrated by 4-fold with the total retention higher than 85% in both plate membrane module and hollow fiber membrane module in case of 80% water recovery. Besides, the model was able to optimize module design and operating parameters to save membrane material and/or to reduce pressure drop in membrane modules, without significant influence on retention performance of FO. Assisted by an ultrafiltration level of pressure (i.e. 0.2~0.4 MPa) 15~27% of required membrane area would be effectively reduced to achieve 80% of water recovery.