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Concentrating greywater using hollow fiber thin film composite forward osmosis membranes: Fouling and process optimization

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HIGHLIGHTS

- Greywater was concentrated using TFC forward osmosis membrane up to ten times.
- Casein and Calcium ions caused severe FO membrane fouling.
- Osmotic backwash using caustic water recovered the membrane performance.
- Coagulation using $FeCl_3$ resulted in very stable FO operation.
- High quality water could be extracted using FO based integral treatment process.

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ABSTRACT

Greywater is the main source of municipal wastewater, but lightly polluted. This paper reported a novel forward osmosis (FO) for treating the greywater to obtain pure water. The hollow fiber thin film composite (TFC) FO membrane was synthesized and characterized. For the main organic foulants in greywater, the same FO membrane showed higher rejection in a FO operation than in a hydraulic pressure driven reverse osmosis operation. In a systematic analysis of the FO membrane fouling up to a concentration factor of 10, the protein, casein, was identified as the main factor; conjugation with Ca^{2+} and SDS accelerated the membrane fouling. Osmotic backwash using caustic solution could effectively recover the FO membrane flux. Moreover, the FO membrane fouling was significantly alleviated after using ferric chloride flocculant as the pretreatment. Water analysis showed that nearly 100% of large organic contaminants such as humic acid, casein, and most of the phosphate ions (below detection limit), were removed by the FO membranes but allowed small amount of SDS and NH_4^+ to permeate across. The present results provided a scientific and engineering basis for the potential application of forward osmosis membrane based integral process for treating greywater.

1. Introduction

Water shortage is becoming a challenge to the economic growth and urbanization. Almost two-thirds of municipal water is used by industry, agriculture and construction. Households consume the remaining third (365 million people used 15.3 billion tons of water in 2011) (Tao and Xin, 2014; Chen et al., 2015). Grey water and black water are two important streams of municipal wastewater (Peng et al., 2009). Grey water mainly comes from the laundry, kitchen, and bath, and black water from the toilets (ChristovaBoal et al., 1996). About 75% of the residential water is consumed in grey water production, and 25% household water consumption could be reduced by reusing properly the treated grey water for flushing the toilet (Hocaoglu and Orhon, 2013). In some countries and regions, low precipitation and high evaporation (e.g. Australia, Middle East, northwest China, West Coast of United States) result in shortage of available clean water resources. As an unconventional water resources, grey water is lightly polluted and can be used with high public acceptance (Drouiche et al., 2012).

The selection criteria of a suitable technology in treating grey water lies in water quality, water recovery, operational/capital

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cost, treatment efficiency, generation of secondary waste streams or solid, and footprints (Boyjoo et al., 2013). The high water quality means flexibility for downstream utilization; the high water recovery corresponds to more concentrate and the treatment cost is reduced because of more output per unit capital and time. A large number of studies have been carried out for grey water, testing the whole range of possible technologies from physical treatment such as soil filtration and direct ultrafiltration (Kim et al., 2007; Kadewa et al., 2010) to chemical process such as advanced oxidation (Chin et al., 2009; Sanchez et al., 2010) and biological treatment systems including membrane bioreactor and rotating biological contactor (Lesjean and Gnirss, 2006; Merz et al., 2007). Physical process cannot effectively remove organics, microorganism and ions (Kadewa et al., 2010), chemical processes may cause secondary pollution and increases the cost of processing (Chin et al., 2009), as for biological treatment, large footprint may limit the application to highly inhabited area (Merz et al., 2007).

Membrane filtration as an efficient water treatment has been widely studied. Effluent quality in terms of biochemical oxygen demand (BOD), ammonia and phosphates were studied in ultrafiltration (UF), microfiltration (MF), and nanofiltration (NF) processes; mainly depending on the pore size, UF permeate was generally better than MF permeate; furthermore, the effluent qualities produced by NF was better than those produced by UF and MF (Ramona et al., 2004; Šostar-Turk et al., 2005; Li et al., 2008). Reverse osmosis (RO) and NF could produce high quality water products while the energy consumption of NF and RO is relatively intense compared to MF and NF system.

Membrane fouling is another key issue in treating greywater. Oschmann et al. (2005) found that during hollow fiber filtration of synthetic greywater multivalent ions like calcium played an important role. Depending on concentration of Ca^{2+}, agglomerates of different structures and sizes were formed, which controlled the extent of fouling and retention (Oschmann et al., 2005). A pretreatment using coagulation were practiced to reduced membrane fouling, however, membrane fouling still existed (Šostar-Turk et al., 2005; Oschmann et al., 2005; Choi et al., 2016). Decrease of water recovery and generation of large amount of waste concentrate are the negative points of current membrane processes.

A membrane process that suffers the least membrane fouling is the spontaneous forward osmosis that utilizes a draw solution to extract water from the feed. The semipermeable characteristics of the FO membranes can guarantee a high quality permeate across the membrane (Chung et al., 2012). Various membrane processes could be utilized to further extract the clean water from the draw solution: reverse osmosis (Choi et al., 2016), membrane distillation (Li et al., 2014), etc. In a previous report, we have explored the combination of hybrid FO-VMD for water reclamation from shale gas drilling flowback fluids. The hybrid process was able to achieve a water quality higher or comparable to potable water (Li et al., 2014).

Herein, we exploit potential of forward osmosis (FO) process as a pre-treatment of integrated membrane process for reusing greywater. There was no systematic investigation of the fouling and performance of FO membrane in treating greywater available yet. The present work aims at: (1) to produce the highest purity water for wider reuse purpose; (2) to obtain as high as possible water recovery; (3) to explore a highly stable operation. Moreover, we focus on the fouling behavior of a tailored-made hollow fiber thin-film composite FO membrane in concentrating a typical synthetic greywater (Oschmann et al., 2005), where humic acid and calcium are the major contaminants. The rejection for contaminants in the greywater was also analyzed. Our work provides detailed scientific analysis and technical process optimization for treating greywater based on FO. The results will provide basis for understanding the fouling behavior and design of an integrated membrane process for such reuse purpose.

2. Experimental

2.1. Chemicals and membrane materials

Polysulfone (PSF, P-3500N) was kindly supplied from Solvay. *N*, *N*-dimethyl acetamide (DMAc), polyethylene glycol (PEG400), *N*-hexane, sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), humic acid (HA), calcium chloride ($CaCl_2$), ammonium chloride (NH_4Cl), and sodium chloride (NaCl) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Triethylamine (TEA), camphor sulfonic acid (CSA), dimethyl sulfoxide (DMSO), casein, sodium dodecyl sulfate (SDS), *M*-phenylenediamine (MPD) and trimesoyl chloride (TMC) were obtained from Sigma-Aldrich (Shanghai, China). All the chemicals solvents were of reagent grade and used as received.

2.2. Fabrication and characterization of TFC-FO membranes

The PSF hollow fiber support layer was prepared from a mixture of PSF (18 g)/PEG-400 (8 g)/DMAC (74 g) by phase inversion with a two-orifice spinneret. The mixture was stirred at 65 °C until a clear solution was obtained (Xiao et al., 2015; Chen et al., 2015). The polymer solution was maintained at 40 °C, and bore liquid was at 30 °C; the initial solution passed an air gap of 9.5 cm and was immersed in water bath at room temperature. The initial hollow fiber PSF membranes were rinsed with DI water for 48 h (Gang Li et al., 2014).

We followed a literature reported procedure to prepare the hollow fiber FO membranes (Gang Li et al., 2014). The aqueous phase of MPD/CSA/TEA/DMSO/H_2O = 2wt%/0.8wt%/1.1wt%/2 wt% was first introduced and the 0.15 wt% TMC/hexane organic phase was used for a reaction time of 2 min. The membrane was cured in hot water at 95 °C for 5 min, finally the resultant membrane module was stored in deionized (DI) water (Xiao et al., 2015, 2017; Chen et al., 2015, 2016, 2017; Gang Li et al., 2014).

2.3. Membrane characterization

2.3.1. Membrane surface characterization

The membrane morphology was examined by a ZEISS SUPRA™ 55 scanning electron microscope (SEM). Cross-section samples were prepared by cryo-facture using liquid nitrogen, followed by vacuum drying overnight at 30 °C. All samples were coated with a thin gold layer before imaging. Atomic force microscopy (AFM) (MFP-3D -BIO™, Asylum Research Instruments Inc.) measurement was operated with the Silicon probe (NSG10, Shanghai Nano Star Co., Ltd.). Roughness is the mean square root value of the contour line deviation from the average line in the sample length.

2.3.2. Characterization of TFC-FO membranes

The pure water permeability coefficient (A, L/m^2 h bar), solute permeability coefficient (B, L/m^2 h), and salt rejection (Rs, %) of the TFC membranes were determined via RO test based on the method reported in previous work (Xiao et al., 2015). And the membrane structural parameter, S, was determined using the protocol described by Cath et al. (2013).

We selected FO mode by allowing feed water to be directly in contact with the active layer. The flow velocities of the draw and feed were maintained at 0.5 m/s and 1.2 m/s. For charactering the FO membrane properties, DI water and 0.5 mol/L NaCl were used as the feed and draw solutions, respectively.