USING THIN FILM NANOCOMPOSITE BRACKISH WATER REVERSE OSMOSIS MEMBRANES TO PROVIDE GREATER CONFIDENCE FOR NDMA REMOVAL

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Introduction

Nitrosamines are a chemical carcinogen family, the most prevalent being N-Nitrosodimethylamine (NDMA). Nitrosamines form in water sources by several methods including leaching from polyethylene pipe, as a byproduct of the chloramination process and from incorrect dosing of polymer coagulant, polyDADMAC. This problem chemical is prevalent in drinking waters across Europe and, in particular, the Netherlands due to its position at the end of the European water catchment. Nitrosamines are also a chemical of concern in the United States (US). In the US, NDMA is an unintended byproduct from the disinfection of wastewater and drinking water. NDMA has been reported to be present in foods such as bacon, beverages such as beer, and tobacco smoke. The California Department of Public Health (CDPH) has established a notification level (NL) for NDMA of 10 ng/L. Based on a CDPH data query dated June 2010, 30 public drinking water wells of 886 sampled had concentrations of NDMA above the NL of 10 ng/L. Most NDMA detections exceeding the NL (26 of 30) have occurred in Los Angeles County.

In addition to NDMA, other N-nitrosamines known to occur in secondary effluent include N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR) N-nitrosodiethylamine (NDEA), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR), N-nitrosodipropylamine (NDPA) and N-nitrosodi-n-butylamine (NDBA) (Fujioka et al., 2012). The chemical structure of N-nitrosamines is generally described as $R_1R_2N\text{-}N\text{=}O$ with molecular weight from 74 to 198g/mol and usually are uncharged.

Many technologies exist for the removal of nitrosamines. While activated carbon is one of the leading technologies for complete removal of nitrosamine, in many instances this would represent another process step and the expense of further capital costs. Across the Netherlands and the USA, many well waters and wastewaters already incorporate a reverse osmosis (RO) process that can remove some of the nitrosamine. However, NDMA is not completely removed by standard thin film composite (TFC) RO membranes, with average rejections of 40-60%. According to membrane theory, this is because of the NDMA's small molecular size and lack of charge. Bellona et al, (2005) reported that estimating the rejection of an organic micropollutant by a TFC membrane depended on the properties of the membrane such as its molecular weight cut-off (MWCO), salt rejection, porosity, membrane morphology and hydrophobicity. Organic micropollutant removal also depends on the solute's molecular weight, molecular size, charge and hydrophobicity in relation to the feedwater chemistry.

Thin-film nanocomposite (TFN) membranes represent a new opportunity as they feature the highest rejection on the market. This study aims to make an assessment of nitrosamine removal using TFN membranes versus TFC membranes in a like-for-like comparison by flux basis. Successful removal of NDMA of greater than 60% through the use of TFN membranes will aid customers in designing smaller post-RO treatment systems (activated carbon).

Method

Two membranes were selected for comparison, a brackish water 'Qfx BW' TFN membrane from LG NanoH_2O (26.25 GFD and 99.7% NaCl rejection at 2,000 ppm NaCl, 225 psi and 25°C) and an industry standard brackish water membrane 'TFC' (26.25 GFD and 99.5% NaCl rejection at the same test conditions). Three small coupons of each membrane were sampled and loaded on standard testing benches and tested for integrity at 1-hour and 24-hours. The Qfx BW membrane was cut straight from the coating line and used in the bench, while the TFC membrane was sampled from an element. To minimize any damage to the TFC membrane, the sample was taken from the very middle of the sheet, where damage is usually minimized. As expected, membrane flux was very similar for both membranes after stabilization. Both 8-inch membrane elements have a flux of 10,500 GPD at 2,000ppm NaCl, 225 psi and 25°C. Qfx BW rejection stabilized to 99.72% over 6 days, while TFC stabilized to 99.20%. While the TFC membrane stabilized under the normal published specification (99.5%), this rejection value is typical for small coupons tests. It is well above the minimum salt rejection value of 99.0% removal for this membrane as quoted on the TFC's specification sheet.

Results

Figure 1 shows Nitrosamine removal at the 150-hour stabilization point. For confidence, two samples of feed and permeate water were taken at this point. The TFN membrane (average 78%) removed NDMA better than the TFC membrane (average 62%). This 16% increase in removal efficiency for NDMA would mean that a treatment plant would be able to mitigate a raw water NDMA concentration of around 50 ng/L when using a TFN membrane whereas when using a TFC membrane, this amount is around 25 ng/L. Some differentiation was also seen for the Qfx BW membrane for NMEA removal (~5% better) and for NPYR (~4%). All other nitrosamines were evenly removed by both membranes. This is to be expected as the molecular weights of most nitrosamines are much larger than the theoretical MWCO of both membranes.

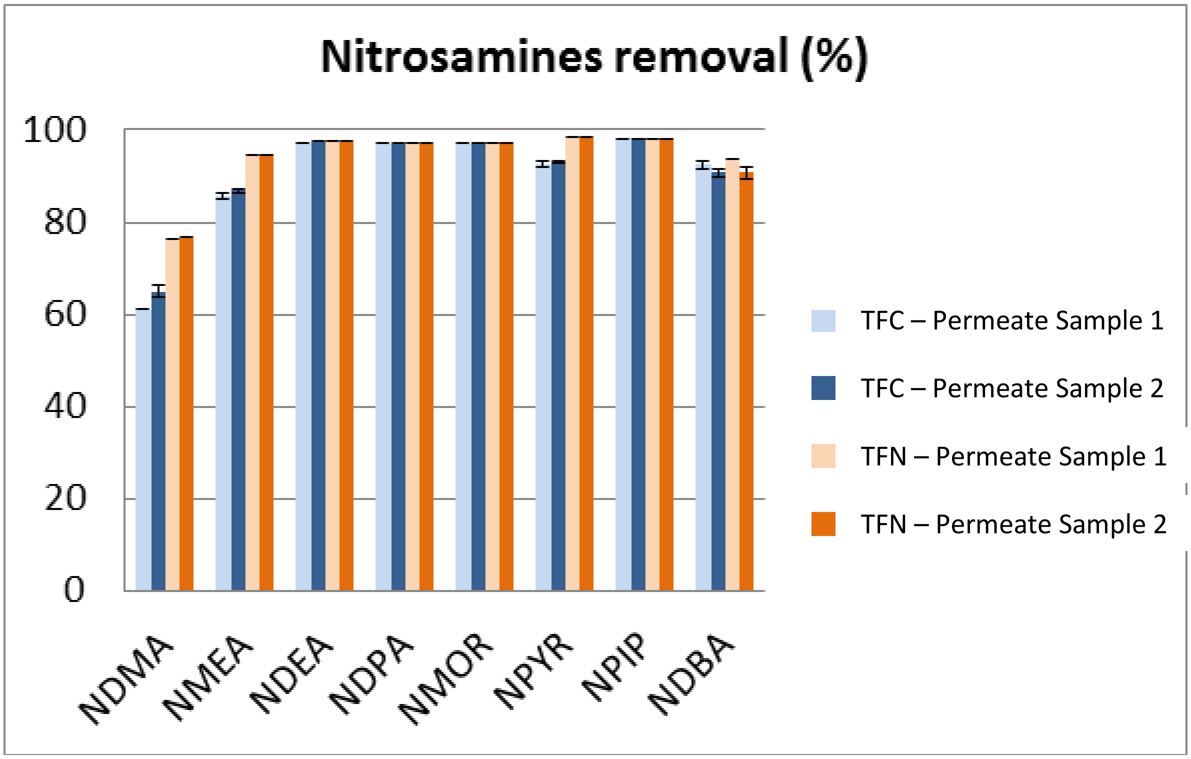

Figure 1. Nitrosamine removal as a grab sample after a 150-hour stabilization of membrane performance.

Discussion

In a comparable laboratory scale study, a set of RO TFC membranes including the TFC membrane used in the current study were tested for NDMA removal. The study found that NDMA was removed at a range of different removal rates from 45-70% (Fujioka et al., 2012). The TFC membrane used in the current study matched the removal rate achieved by Fujioka et al. (2012). Across several full scale plant studies, including at El Segundo West Basin Water Recycling Plant (USA), Scottsdale Water Campus (USA), Bundamba Advanced Water Treatment Plant (Australia), Interim Water Factory 21 (USA), NDMA removal was 10-70% and therefore well correlated with the maximum removals attainable on the bench scale trial undertaken by Fujioka et al, (2012). These trials were undertaken at very similar fluxes and recoveries. To this end, the TFN membrane removed 8% more NDMA than regular TFC membranes when comparing the current study with previous field results. Miyashita et al. (2009) reported less than 5% variation in NDMA rejection on the same membrane type when the feed concentration of NDMA varied from 0.4 to 900ug/L, therefore NDMA concentration is less important than the membrane properties themselves in affecting removal efficiency. Therefore it can be expected that the TFN membrane would outperform other TFC membranes in the field.

Interestingly, in another study, a strong linear correlation ($R^2 = 0.95$) between the rejections of boron and N-nitrosodimethylamine (NDMA) by six different reverse osmosis (RO) membranes, suggesting that boron can be used as a surrogate for NDMA rejection (Tu et al., 2013).

Conclusion

These results show that TFN membranes have the potential to increase NDMA removal capacity of water and wastewater treatment plants that incorporate RO technology. TFN membranes can provide a technology to give managers and operators greater confidence in the RO stage of a multiple barrier approach to nitrosamine removal.

References

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