INVESTIGATING NANOFILTRATION MEMBRANE PROCESSES FOR REMOVING TRACE CHEMICALS OF EMERGING CONCERN

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Abstract

The primary purpose of this document is to present and discuss the findings of experiments evaluating the rejection of compounds of emerging concern (CECs) via nanofiltration membranes. In this work, a split-feed pilot unit designed to replicate a full-scale nanofiltration train was utilized to investigate CEC removal. Experiments were conducted over a range of feed concentrations, from trace levels (parts per billion) to higher concentrations (parts per million). Based on these findings, it appears that CEC removal ranges from 69 to 98%.

Introduction

The Town of Jupiter Utilities (Jupiter) supplies drinking water to over 80,000 people living within a 58 square mile service area. Jupiter’s Water Treatment Facility is capable of producing 30 million gallons per day (MGD) of drinking water from two raw water sources: a fresh surficial aquifer and the brackish Floridan Aquifer. Jupiter currently uses reverse osmosis (RO) to treat the brackish water supply, and anion exchange and nanofiltration (NF) to treat a fresh, surficial water supply.

In 2014, the Town of Jupiter commissioned a 267 gallon per minute (gpm) NF pilot unit, designed to replicate Jupiter’s full-scale NF train, in attempt to evaluate the ability of their process to reject trace chemicals of emerging concern (CEC’s), should they ever be present in Jupiter’s raw water supply.

The primary purpose of this paper is to present the findings of numerous investigations regarding the behavior of CECs after their addition to the pilots’ feed water supply. A background detailing Jupiter’s existing full-scale system and the NF pilot unit will be discussed, followed by a brief literature review, testing methods employed during this research, and the results of several CEC experiments at trace concentrations (parts per billion) and at higher concentrations (parts per million). Finally, conclusions and recommendations regarding future CEC research related to nanofiltration will be discussed.

Literature Review

Studies investigating compounds of emerging concern (CECs) were underway as early as 1965 (Stumm-Zollinger & Fair, 1965), although research did not gain significant attention in wastewater treatment processes until the 1990’s (Snyder, 2008), and research related to CECs and pressure-driven membranes did not take off until later. The number of studies have increased
over the last 25 years, however a majority of this work has been conducted at a bench-scale level using synthetic water, and few experiments utilize natural waters. To date, only a small number of known CEC research has been conducted at realistic operating conditions have been reported (Duranceau, 1990; Radjenovic et al. 2008; Verliefde et al. 2008; Verliefde et al. 2009; Bellona et al. 2008; Bellona et al. 2012; Sadmani et al. 2014a; Sadmani et al. 2014b). These studies have examined pilot-scale CEC rejection operating at more realistic recoveries using natural waters, which is more representative of how an actual full-scale plant would remove CECs.

Although laboratory-scale studies are relatively simple experiments to conduct and using synthetic water allows researchers to easily evaluate water quality impacts on CEC removal, bench-scale units involving flat sheet or single module membranes are not always representative of how full-scale plants operate. Verliefde et al. (2008) found that as water recovery increased, CECs rejection decreased. Since it is known that water recovery impacts constituent removal (AWWA, 2007; Verliefde et al., 2008), it is speculated that a higher water recovery can affect CEC rejection as well, although extensive research has not yet been conducted.

Nanofiltration membranes have proven their ability to reject multivalent ions and organics from drinking water, making them ideal for groundwater softening applications (Blau, Taylor, Morris, & Mulford, 1992; Jacangelo, Trussel, Watson, 1997; Hilal et al., 2004). Compound rejection, $R$, by membranes is calculated using Equation 1, where $C_f$ is the concentration in the feed, and $C_p$ is the concentration in the permeate.

$$R = \left( \frac{C_f - C_p}{C_f} \right) \cdot 100$$  

Equation 1

CECs investigated in this research were selected based on their frequent detection in the aquatic environment and water and wastewater treatment plants. Table 1 presents CECs evaluated in this work, along with their primary use and molecular weights.

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Abbreviation</th>
<th>Primary Use</th>
<th>MW (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bisphenol A</td>
<td>BPA</td>
<td>Plasticizer</td>
<td>228</td>
</tr>
<tr>
<td>Caffeine</td>
<td>CAF</td>
<td>Stimulant</td>
<td>194</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>CBZ</td>
<td>Anti-epileptic</td>
<td>236</td>
</tr>
<tr>
<td>N,N-Diethyl-meta-toluamide</td>
<td>DEET</td>
<td>Insect Repellent</td>
<td>191</td>
</tr>
<tr>
<td>Estrone</td>
<td>EST</td>
<td>Estrogen</td>
<td>270</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>GEM</td>
<td>Lipid Regulator</td>
<td>250</td>
</tr>
<tr>
<td>Naproxen</td>
<td>NPX</td>
<td>Anti-inflammatory</td>
<td>230</td>
</tr>
<tr>
<td>Sucralose</td>
<td>SUC</td>
<td>Artificial Sweetener</td>
<td>398</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>SMX</td>
<td>Antibiotic</td>
<td>253</td>
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Background

The Town’s full-scale nanofiltration plant has a design capacity of 14.5 million gallons per day (MGD) and treats a fresh surficial groundwater supply using various combinations of 51 production wells. The nanofiltration process is depicted as a simplified schematic in Figure 1. NF pretreatment includes sand filtration, followed by sulfuric acid, scale inhibitor addition, and cartridge filtration. Jupiter’s nanofiltration plant is unique in that it is an end-feed, center-exit outlet configuration. In this split-feed configuration, feed water enters each six-element pressure vessel through both ends, while permeate and concentrate exit in the center of the pressure vessel, after only three membranes. In this work, a split-feed pilot unit designed to replicate the full-scale plant was utilized to conduct CEC experiments. The pilot is a 7:2 array design, and operates at an 85% recovery. Feed water after pretreatment is routed to the pilot after full-scale cartridge filtration.

Figure 1: Nanofiltration Process Schematic

Testing Methods

A series of experiments carried out on three separate days have been conducted to demonstrate repeatability of CEC results. Compounds evaluated in this research were presented previously in Table 1. With the exception of caffeine, which was used in five experiments, compounds were evaluated in three experiments. CECs were purchased from Sigma-Aldrich as a powder, with the exception of DEET, which was purchased in pure liquid form. CECs were added to a bucket containing feed water routed to the pilot unit after full-scale NF pretreatment, mixed, and continuously injected into the pilot unit using a positive displacement pump at a constant flow rate for at least 15 minutes to allow complete travel time through the pilot prior to sampling.
Samples were collected from the following sample ports:

- Feed
- First Stage Permeate Left
- First Stage Permeate Right
- First Stage Permeate Combined
- Interstage Concentrate (Second Stage Feed)
- Second Stage Permeate Left
- Second Stage Permeate Right
- Second Stage Permeate Combined
- Total Pilot Permeate
- Concentrate

Samples were collected in 1-liter silanized glass amber bottles for analysis. Samples collected during experiments conducted at the parts per trillion (ppt) level were shipped and analyzed by a commercial laboratory (Eurofins Eaton Analytical; 750 Royal Oaks Drive, Suite 100, Monrovia, California, 91016-3629). When experiments were conducted at the ppm level, analysis was conducted by a collaboration between UCF’s Civil, Environmental and Construction Engineering (CECE) and Chemistry Departments.

**Preliminary Results**

*Initial Experimental Results*

Results from multiple experiments indicate at least partial rejection of certain CECs, while others are not detected in any permeate samples. Table 2 presents average rejection of seven CECs via the pilot unit. It appears that caffeine is rejected the least, ranging from 69% in the overall system to 85% in stage 2. Alternatively, gemfibrozil, carbamazepine, and naproxen are generally rejected greater than 90%. It is important to note that with the exception of caffeine, average results were calculated from three experiments, while average caffeine rejection was calculated using results from five experiments. Additionally, when CECs results in permeate samples were below detection limit, the detection limit was used to calculate rejection.

**Table 2:** Average CEC Rejection from Stage 1, Stage 2, and Total System

<table>
<thead>
<tr>
<th>Stage/System</th>
<th>CAF</th>
<th>CBZ</th>
<th>GEM</th>
<th>NPX</th>
<th>SUC</th>
<th>SMX</th>
<th>DEET</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Stage</td>
<td>75</td>
<td>92</td>
<td>98</td>
<td>92</td>
<td>88</td>
<td>86</td>
<td>87</td>
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<tr>
<td>2nd Stage</td>
<td>85</td>
<td>94</td>
<td>99</td>
<td>96</td>
<td>97</td>
<td>95</td>
<td>89</td>
</tr>
<tr>
<td>Total System</td>
<td>69</td>
<td>90</td>
<td>98</td>
<td>91</td>
<td>88</td>
<td>85</td>
<td>83</td>
</tr>
</tbody>
</table>

Figure 2 illustrates CEC concentrations during the first sampling event, and Figure 3 presents CEC concentrations during the second sampling event, both conducted in July 2015. It appears that each of the five CECs evaluated in this study are rejected to some extent. In general, carbamazepine, gemfibrozil, and naproxen are rejected more than caffeine and sulfamethoxazole.
**Figure 2:** CEC Concentrations during Sampling Event 1

Rejection:
1st Stage: 76-96%
2nd Stage: 88-99%
Total Pilot: 68-96%

**Figure 3:** CEC Results from Sampling Event 2

Rejection:
1st Stage: 71-98%
2nd Stage: 83-100%
Total Pilot: 71-98%
Figure 4 illustrates DEET concentrations throughout various pilot sampling ports during experiment 4. Figure 5 presents DEET concentrations in only the permeate samples, to illustrate how left and right sides of the pilot compare to each other.

The concentration of DEET in the feed sample was 1,200 ng/L, and first stage permeate samples had concentrations of 170, 160, and 160 ng/L, in the left, right, and combined sampling ports, indicating 87% rejection during this stage. First stage concentrate, also referred to as interstage concentrate or second stage feed, had a concentration of 4,320 ng/L. Stage 2 permeate samples had DEET concentrations of 360, 400, and 380 ng/L in left, right, and combined sampling ports, indicating 91% rejection. The DEET concentration in the total pilot permeate, which is a combination of first and second stage permeate, was 200 ng/L. The DEET concentration in the final concentrate sampling port was 7,920 ng/L. Duplicate samples were taken from feed and total pilot permeate sampling ports, and had DEET concentrations of 1,300 ng/L and 210 ng/L, respectively, indicating a deviation of 100 ng/L from both original feed and total permeate samples.

**Figure 4: DEET Concentrations during Experiment 3**
Conclusions and Recommendations

The work presented herein describes the ability of a 267 gpm split feed nanofiltration pilot unit to reject various CECs. In general, rejection ranged from 69 to 98%. Rejection was correlated most strongly with compound polarizability, followed by compound molecular volume. These results can be useful to allow future prediction of CECs from this pilot unit. It is recommended that future work be conducted to verify results since experiments are ongoing.

Acknowledgments

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References


