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The influence of solute polarizability and molecular volume on the rejection of trace organics in loose nanofiltration membrane processes

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ABSTRACT

The removal of trace organic compounds of emerging concern (TrOC) from ground water was evaluated using a split-feed, center exit, nanofiltration (NF) pilot process. Ground water was dosed with varying amounts of bisphenol-A, caffeine, carbamazepine, N,N-diethyl-meta-toluamide, estrone, gemfibrozil, naproxen, sucralose, and sulfamethoxazole between 150 ng/L and 4.5 mg/L, and processed with NF membranes operating at a feed flow rate of 60,636 L/h (267 gpm), a flux rate of 25.6 L m^{-2} h^{-1} (15.1 gsfd), and 85% water recovery. TrOC rejection by the NF process ranged from 68% for caffeine to below detection for gemfibrozil and sucralose. Correlations between rejection and various chemical and physical compound properties were investigated. It was found that TrOC rejection correlated well with polarizability (0.94 R^2) and molecular volume (0.94 R^2), and to a lesser extent hydrophobicity/hydrophilicity (0.87 R^2). However, in this work, molecular weight and log D were not well correlated with solute rejection. Analysis of TrOC rejection data collected from five prior independent loose NF research studies representing 61 different TrOCs were found to correlate well with polarizability (0.71 R^2) and molecular volume (0.72 R^2), suggesting that polarizability and molecular volume are useful in estimating TrOC removal from fresh ground water using loose NF membrane processes.

Keywords: Pharmaceuticals; Compound of emerging concern; Pilot plant; Polarizability; Endocrine disrupting compound

1. Introduction

Trace organic compounds (TrOCs) continue to receive widespread attention due to their presence in wastewater treatment facilities and the aquatic environment. Research related to the removal of TrOCs in water treatment processes has been ongoing since the discovery of pesticides in water supplies in the 1980’s [1]. Understandably, the presence of pesticides and other TrOCs of emerging concern in drinking water are highly undesirable in the eyes of the consuming public. Membranes represent a technology that can cost-effectively deal with many of these emerging TrOCs. Although prior work has historically demonstrated the effectiveness of diffusion-controlled membrane technologies for pesticide removal [1–5], these efforts did not include newly observed pharmaceuticals, health care products, and plasticizer compounds. In more recent work, experiments are typically

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conducted using flat sheet or bench-scale membrane units in a laboratory, with few studies having examined TrOC removal using pilot- or full-scale processes [6–10]. While laboratory studies allowed the membrane industry to investigate TrOC behavior under controlled settings, including various feed water chemistries and operating conditions (i.e. flux, pressure, flow rate), this type of operation does not necessarily simulate a full-scale membrane treatment processes [7–10]. Alternatively, while investigations using full-scale membrane processes provide utilities with actual data, these experiments are limited since feed water chemistry cannot be altered.

It is generally understood that TrOCs can be removed from a diffusion-controlled process by one of three primary removal mechanisms: size exclusion, electrostatic repulsion, and adsorption [7–9]. These solute–membrane interactions are determined by TrOC properties, (molecular weight, molecular size (length and width), charge (determined using the acid dissociation constant, and the solution pH), diffusion coefficient, and hydrophobicity (expressed by the octanol–water partition coefficient, log K_{ow}, and the octanol–water partition coefficient at any pH value, log D)), membrane properties (molecular weight cut-off (MWCO), pore size, hydrophobicity (contact angle), surface charge (zeta-potential), surface morphology (roughness)), operating conditions (pressure, flux, and recovery), and solution chemistry (pH, temperature, conductivity, alkalinity, and organic content) [11–19]. This prior research indicated that the removal mechanism responsible for TrOC rejection is largely dependent on whether or not a compound is hydrophobic or hydrophilic, as well as if the TrOC is ionic or neutrally charged. Others have shown that the organic and charged ionic content of the feed water can impact TrOC rejection by NF membranes [10,16], which agrees with prior work performed studying pesticides [1,3]. However, correlations between the compound properties and rejection by the loose NF membranes studied were not statistically significant, indicating that loose NF did not reject lower molecular weight TrOCs due to the large MWCO of the NF membrane [16].

Despite the significant amount of research performed as described herein, polarizability was one solute chemical property that has not been investigated when examining solute–membrane interactions. It appears that little to no research has investigated membrane solute rejection as a function of the TrOC's polarizability within any diffusion-controlled membrane process. Polarizability describes how easily electrons are able to move within a compound, and is related to the dipole moments within a molecule, and increases with molecular volume. While this parameter has been eluded to as an influence on compound adsorption to membranes [20], as well as for its relationship with solvent and lipid bilayer interfaces [21], this chemical property has not been extensively examined for its influence on TrOC removal.

The main objective of this work is to investigate solute-NF membrane interactions as determined by TrOC polarizability and molecular volume, and evaluate multiple independent literature sources (100 data points) to investigate the relationship between TrOC properties and rejection. Several physical and chemical properties suspected to influence TrOC rejection were evaluated using a pilot unit housing NF270 membranes operating at full-scale plant conditions.

2. Materials and methods

2.1. Pilot plant description

A nanofiltration pilot unit (NPU), owned by the Town of Jupiter (Town) water utility, was constructed and placed online in 2014 to investigate trace organic compound removal capabilities of their existing NF process, which utilizes NF270 (DOW) membranes. The NPU is located at the Town's water treatment facility in Jupiter, FL, and is operated by Town staff and University of Central Florida (UCF) researchers. TrOC experiments were conducted using feed water obtained after full-scale plant pretreatment, which includes sand filtration, cartridge filtration (5 μ), and scale inhibitor and sulfuric acid addition, which was then routed to the head of the 60,636 L/h (267 gpm) NPU. This pilot unit was designed and constructed to replicate the Town's existing full-scale, two-stage nanofiltration plant: both systems operate at 85% recovery, with a 7:2 configuration. Additionally, the water flux of the full-scale process is 25.3 $\mathrm{L\,m^{-2}\,h^{-1}}$ (14.9 gsfd), while the flux of the pilot was experimentally determined as 25.6 $\mathrm{L\,m^{-2}\,h^{-1}}$ (15.1 gsfd). The full-scale plant and the pilot operate at constant flux. Furthermore, both processes were designed as split-feed, center-exit configurations. After entering the full-scale NF train or NPU, feed water is split in two, and enters both sides of the six-element pressure vessels. Water passes through three membranes prior to exiting as permeate, at both ends of the vessels, or as concentrate, which is collected in the center of the vessels. A simplified schematic of this configuration is depicted in Fig. 1, and pilot characteristics and typical operating parameters are presented in Table 1.

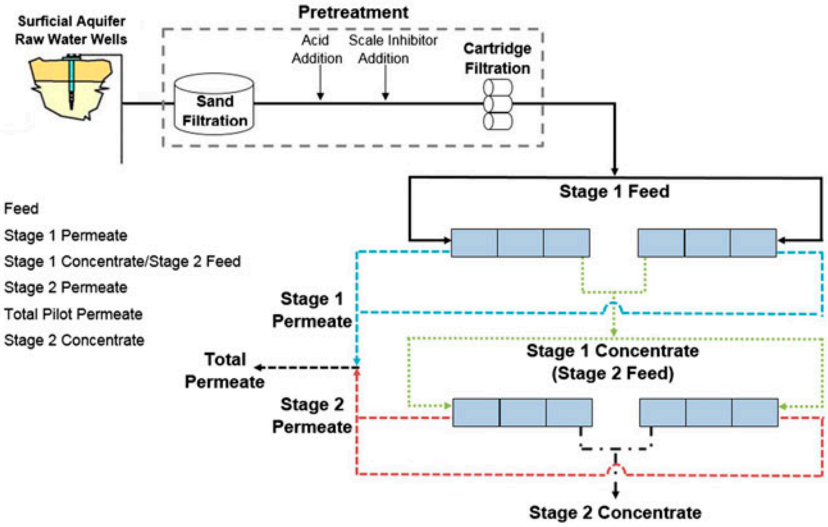

Fig. 1. Simplified schematic of the full-scale nanofiltration process.

Table 1
Membrane and pilot characteristics

Item	Value	
Membrane module	NF270 (DOW Filmtec)	
$MgSO_4$ and $CaCl_2$ rejection (%) [22][a]	97* and 40–60**	
Pilot recovery (%)	85	
Total number of membrane elements	54	
Elements in stage 1	42	
Elements in stage 2	12	
Membranes per pressure vessel	6	
Array	7:2	
Membrane surface area (DOW filmtec)	$37.2\ m^2$/element	$400\ ft^2$/element
Total membrane area in pilot	$2,007\ m^2$	$21,600\ ft^2$
Feed flow rate	60,636 L/h	267 gpm
Total permeate flow rate	51,552 L/h	227 gpm
Concentrate flow rate	9,084 L/h	40 gpm
Feed pressure	3.93 bar	57 psi
Stage 1 concentrate pressure	3.72 bar	54 psi
Stage 1 permeate pressure	1.45 bar	21 psi
Stage 2 concentrate pressure	3.59 bar	52 psi
Stage 2 permeate pressure	1.45 bar	21 psi
Total pilot permeate pressure	1.45 bar	21 psi
Water flux	$25.6\ L\ m^{-2}\ h^{-1}$	15.1 gsfd

[a] Test conditions: 70 psi (0.48 MPa), 77˚F (25˚C), 15% recovery.

*2,000 $MgSO_4$.

**500 mg/L $CaCl_2$.

2.2. Water quality description

Water quality was obtained multiple times over a period of one year and results are presented as averages in Table 2. Feed water pH is maintained at 6.5 using sulfuric acid for scale control and degasification. Alkalinity is 240 mg/L as $CaCO_3$, conductivity of the feed water is typically 750 µS/cm, and the total dissolved solids concentration is 455 mg/L. Feed water consists primarily of multivalent ions, specifically calcium, which has a concentration of 125 mg/L. Organic

Table 2
Nanofiltration pilot feed water quality

Water quality parameter	Average	Range	Units
pH	6.5	6.3–6.6	pH units
Temperature	25	22.4–25.7	°C
Alkalinity	240	200–292	mg/L as $CaCO_3$
Conductivity	750	735–817	µS/cm
Total dissolved solids	455	424–492	mg/L
Dissolved organic carbon	10.8	10.6–11.0	mg/L
UV_{254}	0.410	0.401–0.417	cm^{-1}
Calcium	125	121–126	mg/L
Magnesium	4.9	4.5–5.5	mg/L
Sodium	23	19–24	mg/L

content, measured as dissolved organic carbon (DOC) and DOC's surrogate, ultraviolet absorption at 254 nm (UV_{254}), are typical for a surficial ground water source in south Florida. The average DOC concentration in the feed water is 11 mg/L, while the average UV_{254} measurement is 0.406 cm^{-1}.

2.3. Selected trace organic compounds

TrOCs evaluated in this work are presented in Table 3, along with basic chemical and physical properties. Dipole moments for TrOCs presented in Table 3 were obtained from Comerton et al. [10], while other properties including polarizability were obtained from Chemicalize.org by ChemAxon (Budapest, Hungary), which utilizes calculation methods from Miller and Savchik [23]. TrOCs were selected based on occurrence in the Town's water supply [24], the frequency of reported detection in other ground water supplies, and the high volume of research related to these TrOCs in water treatment [25–30].

TrOCs presented in Table 3 have a range of uses and chemical and physical characteristics. Of the nine TrOCs examined in this research, four are pharmaceuticals, one is a plastic derivative, one is a stimulant, one is an insect repellent, one is an estrogen, and one is an artificial sweetener. Molecular weights ranged from 191 to 398 g/mole, while the MWCO of the

Table 3
Trace organic compound uses and physical and chemical characteristics

Compound name	Abbr.	Primary use	MW (g/mol)	MV (Å^3)	Log K_{ow}	Log *D* (pH 6.5)	Polarizability (Å^3)	Dipole (Debye)	pK_a
Bisphenol A	BPA	Plasticizer	228	221	4.0	4.0	26.6	1.7	10.3
Caffeine	CAF	Stimulant	194	164	−0.55	−0.60	17.9	1.0	14.0
Carbamazepine	CBZ	Anti-epileptic	236	210	2.8	2.6	27.0	1.7	2.3, 13.9
N,N-Diethyl-meta-toluamide	DEET	Insect repellent	191	198	2.5	2.5	22.3	4.9	<2.0
Estrone	EST	Estrogen	270	263	4.3	4.4	30.8	2.0	10.3
Gemfibrozil	GEM	Lipid regulator	250	255	4.4	2.1	27.9	3.6	4.43
Naproxen	NPX	Anti-inflammatory	230	213	3.0	0.68	26.4	1.2	4.2
Sucralose	SUC	Artificial sweetener	398	305	−0.49	−0.40	32.7	4.6	3.5
Sulfamethoxazole	SMX	Antibiotic	253	205	0.79	0.36	24.2	2.1	1.8, 5.7

Notes: MW = molecular weight; MV = molecular volume; Dipole values obtained from [16]; pK_a values obtained from [9] and [12].

membranes used in this work have been reported to range from 200 to 400 Da [16,31,32]. Molecular volume and polarizability, range from 164 to 305 and 17.9 to 32.7 Å^3, respectively. TrOC hydrophobicity/hydrophilicity is represented by log K_{ow}, which ranges from −0.55 to 4.4, and log D (at a pH of 6.5), which ranges from −0.60 to 4.4. Compound hydrophobicity increases with increasing log K_{ow} and log D. The dipole of TrOCs lies within the range of 1.0–4.9. TrOC pKa values range from <2.0 for DEET to 14.0 for caffeine.

2.4. Experimental set up

At the commencement of each experiment, a predetermined weight or volume of TrOCs (purchased from Sigma–Aldrich) was measured and delivered to a five-gallon bucket containing pretreated feed water. The five-gallon bucket was thoroughly rinsed with pilot feed water before and after each experiment was conducted. TrOC weights and volumes needed in the feed solution were determined according to calculations made based on pilot feed and TrOC feed solution pump flow rates. Upon addition to the feed solution bucket, TrOCs were completely dissolved and mixed using a stir plate and stir bar. After mixing, a 27 gallon per hour positive displacement pump was used to continuously inject the feed solution containing TrOCs to the feed stream of the pilot unit. Based on previous transient response work conducted on this pilot unit, TrOCs were continuously added to the feed stream for at least 15 min prior to sample collection [33]. Mass balance calculations were performed to ascertain if TrOC adsorbed to the membrane, process piping, or other appurtenances. It was determined that no measurable losses were observed in the data collected in this study. Table 4 presents the target TrOC feed concentrations for the 11 experiments conducted in this work. Of the 11 experiments, 4 (experiments 8 through 11) were designed to cover a wide range of caffeine concentrations in order to evaluate variable membrane loading rates; alternative TrOCs were not investigated in these instances.

Table 4
Target feed concentrations

Experiment no.	Target feed concentration (μg/L)
1	0.15
2	0.25
3	0.25
4	0.50
5	2.0
6	7.7
7	74
8	1,020
9	1,418
10	2,920
11	4,500

2.5. Analytical methods

2.5.1. Nanogram-level experiments

A portion of the water samples that were collected from the pilot were evaluated at method detection levels ranging between 5 and 100 nanograms per liter (ng/L). In this instance, two 40-mL glass amber vials were used to collect each sample. Vials contained 80 μL of 32 g/L sodium omadine (NaOmadine) and 5 mg ascorbic acid. Samples were analyzed using a fully automated online solid phase extraction, high-performance liquid chromatography (HPLC), mass spectrometry–mass spectrometry system. A detailed description of laboratory methods can be found elsewhere [34]. Method detection limits for TrOCs evaluated in experiments 1 through 7 are presented in Table 5.

2.5.2. Microgram-level experiments

For the microgram-level caffeine analysis, stock solutions of caffeine were prepared in methanol and stored at −20˚C. Further dilutions were prepared in water:methanol mixtures (40:60 v/v) and were used as working standard solutions. Water samples were collected in silanized amber bottles, and were also prepared in water:methanol mixtures (40:60 v/v) upon returning to the laboratories and stored at −20˚C until analysis.

Table 5
TrOC detection limits

TrOC	Method detection limit (ng/L)
BPA	10
CAF	5
CBZ	5
DEET	10
EST	5
GEM	5
NPX	10
SMX	5
SUC	100

Samples were analyzed using HPLC. The HPLC experiments were performed using a Perkin-Elmer series 200 HPLC (Santa Clara, CA, USA) consisting of a series 200 binary pump, a series 200 UV–vis detector with deuterium lamp set at a maximum wavelength of 273 nm, a series 200 autosampler, and a series 200 vacuum degasser. The analytical column used was a Zorbax (Agilent) SB-C18 packed column with a 4.6 × 150 mm dimensions. The mobile phase was water: methanol 40:60 (v/v) with a flow rate of 1 cm^3/min. Sample run-time was 10.0 min with a 10.0 μL injection volume and at isocratic conditions. The detection limit for caffeine was 200 μg/L for the microgram-level experiments.

3. Results and discussion

3.1. Trace organic compound rejection results

Fig. 2 presents average TrOC rejection and standard deviations for the first stage, second stage, and total pilot system. Rejection (R) of the TrOCs by the NF pilot were calculated using Eq. (1), where C_f and C_p are concentrations measured in the feed and permeate samples, respectively. First stage rejection was calculated using stage 1 feed and stage 1 permeate, second stage rejection was calculated using stage 1 concentrate (stage 2 feed) and stage 2 permeate, and total pilot rejection was calculated using stage 1 feed and total pilot permeate.

$$R = \frac{C_f - C_p}{C_f} \times 100 \tag{1}$$

Bisphenol A and estrone were not detected in a majority of samples, including feed and concentrate, indicating adsorption to pilot pipes and appurtenances; consequently, these TrOCs are omitted from Fig. 2. Adsorption was expected due to the hydrophobic nature of these compounds. GEM and SUC were below detection in permeate samples; consequently their rejection is assumed to be >99%, and results of these two TrOCs are also omitted from Fig. 2. DEET and NPX were below their respective detection limits in a portion of permeate samples; therefore rejection data for DEET and NPX were based on values that could be measured. Error bars illustrate the standard deviation of rejection values for each TrOC reported. CBZ and NPX experienced total pilot system rejection of 91 and 92%, respectively. SMX had a rejection value of 83% from the total pilot system, while DEET was rejected 84%. CAF was rejected the least, with a total pilot rejection of 68%. Although it appears that more rejection was observed in stage 2, this is due to the significantly high TrOC concentrations in the stage 1 concentrate, which provides water to the second stage of the pilot unit. It should be noted that TrOC concentrations in samples collected from stage 1 are lower than those observed in stage 2 permeate samples.

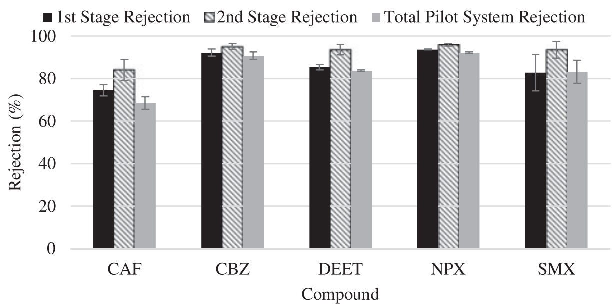

Fig. 2. TrOC rejection from the first stage, second stage, and total pilot system.

Table 6 presents the number of times that a specific TrOC was detected in permeate samples, as well as the number of experiments conducted for each TrOC. Due to the high cost associated with purchasing large amounts of certain TrOCs, not every TrOC could be incorporated into the experimentation, as indicated in Table 6.

Table 6
Number of rejection values obtained

	Number of permeate detections/number of experiments conducted*		
TrOC	First stage	Second stage	Total pilot
CAF	10/11	10/11	11/11
CBZ	5/5	5/5	5/5
DEET	2/2	2/2	2/2
NPX	2/5	4/5	2/5
SMX	5/5	5/5	5/5

*BPA and EST were not detected in the feed or permeate streams. GEM and SUC were not detected in the permeate.

3.2. Solute rejection mechanisms

In this research, the relationships between TrOC rejection and compound properties including polarizability, molecular volume, molecular weight, and hydrophobicity/hydrophilicity (represented by the octanol–water partition coefficients log K_{ow} and log D), were evaluated for their influence on TrOC rejection. The acid dissociation constant was negatively correlated with TrOC rejection. Table 7 presents a summary of the statistical analysis conducted to determine if linear correlations between properties and rejection exist. The R^2 values describing the relationship between rejection and polarizability and molecular volume are both 0.94. Alternatively, the R^2 values describing the relationship between rejection and log K_{ow}, log D, and molecular weight are weak (0.87, 0.43, and 0.30 R^2, respectively).

Critical F and t values were obtained using a 95% confidence interval. Based on their respective F-statistics, polarizability, molecular volume, and log K_{ow} are well-correlated with TrOC rejection since the F-statistic for each of these properties is significantly greater than the critical F-value. Additionally, since the t-observed values for polarizability, molecular volume, and log K_{ow} are greater than the critical t-value, the slope generated by plotting rejection vs. these parameters is useful in predicting TrOC removal. Alternatively, log D and molecular weight do not have F-statistic or t-observed values significantly greater than the critical F or t values; consequently this suggests that these parameters are not well-correlated with rejection [35].

Polarizability describes the ability of electrons to move throughout the molecule, and typically increases with molecular volume [32]. It is well known that more negatively charged TrOCs experience greater rejection rates in a polyamide membrane process due to the electrostatic interactions between the compound and the inherent negative charge of the membrane [1,36,37]. It is reasonable to expect that TrOCs that exhibit higher polarizability should experience higher rejection rates due to the ability of the molecule's electrons to move more freely than compounds having lower polarizability values. This is because molecules possessing higher polarizability, due to free electron movement, could create a condition where greater repulsive forces between the membrane and chemical would result in higher rejection rates.

Figs. 3–7 illustrate the relationship between TrOC rejection (across both pilot stages) and polarizability, molecular volume, log K_{ow}, log D, and molecular weight, respectively. TrOCs in Fig. 3 through 7 include CAF, CBZ, DEET, NPX, and SMX as previously shown in Fig. 2.

3.3. Examining polarizability with independent sources

The results obtained in pilot experiments were combined with results from other similar studies to investigate the relationship between rejection and TrOC properties. Literature was reviewed for studies that evaluated solute rejection data utilizing polyamide NF membranes with a relatively large MWCO (>250 Da), and 14 prior studies were identified for use in evaluating TrOC properties for further analysis. These prior studies were selected to correspond to the use of "loose" NF membranes possessing the higher MWCOs that included the NF270 (DOW), NF200 (DOW), and HL Desal (GE Osmonics).

Initially, the entire data-set was analyzed by plotting TrOC rejection as a function of polarizability. However, a weak correlation existed (0.44 R^2) using the entire data-set. Consequently, the data was further sorted by flux, membrane type, MWCO, and inclusive of an absolute rejection boundary. Of these 14 independent sources, 6 sources were removed from the data-set due to the operation of experimental units with water flux rates not representative of actual practice, or those values outside the range of 17 and 34 $\mathrm{L\,m^{-2}\,h^{-1}}$ (15 ± 5 gsfd). An additional three sources were removed because the flux rate or membrane type was unknown. Furthermore, TrOCs with polarizability values greater than 30 $\mathring{A}^3$ were excluded from the data-set, since rejection approached >99%. As a result, five independent studies were selected for more detailed analysis.

The external evaluation, once sorted, resulted in the identification of 61 TrOC that provided 95 discrete data values [38–41]. This information was combined with the 5 TrOCs examined in the pilot plant experiments as described herein; the 5 TrOCs investigated in the pilot study were a match for 5 of the chemicals tested in several of the outside studies. This combined

Table 7
Statistical analysis for correlations between TrOC properties and rejection

Property	R^2	F-statistic	Critical F-value	F-statistic > critical F-value?	t-observed value	Critical t-value	t-observed > critical t-value?
Polarizability	0.94	47.6	10.1	Yes	6.9	3.2	Yes
MV	0.94	51.4	10.1	Yes	7.2	3.2	Yes
Log K_{ow}	0.87	20.0	10.1	Yes	4.5	3.2	Yes
Log D	0.43	2.23	10.1	No	1.5	3.2	No
MW	0.30	1.31	10.1	No	1.2	3.2	No

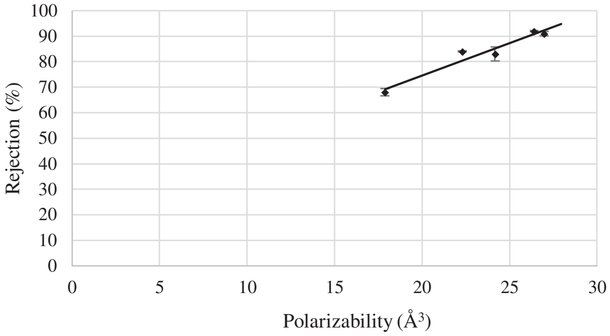

Fig. 3. Rejection vs. TrOC polarizability (R^2 = 0.94).

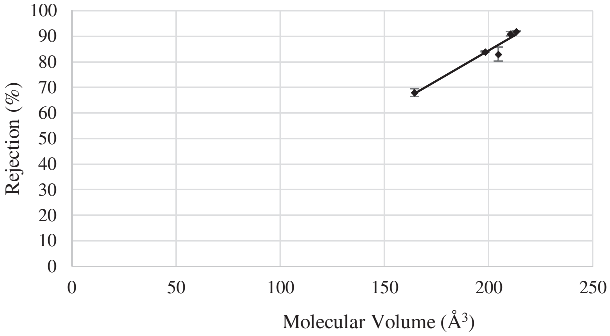

Fig. 4. Rejection vs. TrOC molecular volume (R^2 = 0.94).

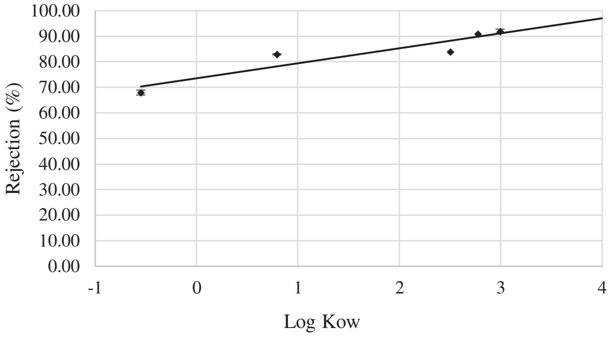

Fig. 5. Rejection vs. TrOC Log K_{ow} (R^2 = 0.87).

data-set of 61 different TrOCs possessed polarizabilities ranging from 3.21 to 29.8 Å^3. Additionally, TrOCs in the combined data-set included compounds that exhibited a variety of chemistries, including chemicals that were ionic or neutrally charged, as well as chemicals exhibiting hydrophobic or hydrophilic properties (log K_{ow} values range from −4.53 to 5.28). Of these 61 different compounds, 25 were duplicates, while 10 represented triplicate data points. Findings suggested that as the water flux increased, the coefficient of determination describing the relationship between

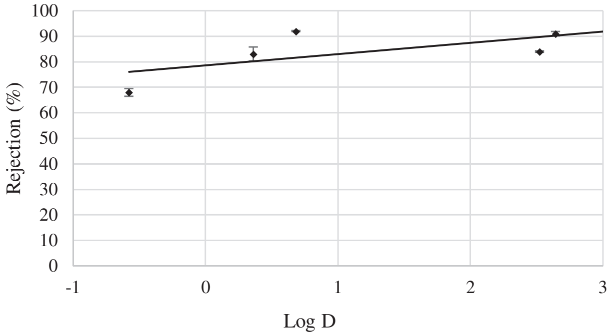

Fig. 6. Rejection vs. TrOC Log D (R^2 = 0.43).

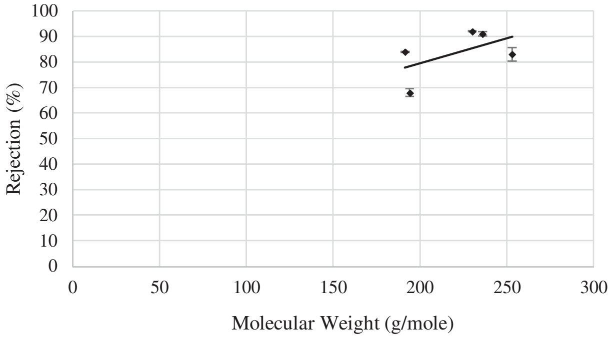

Fig. 7. Rejection vs. TrOC molecular weight (R^2 = 0.30).

polarizability and rejection decreased. Consequently, by including only that data obtained from experiments using flux rates typically observed in full-scale nanofiltration treatment processes, it was found that polarizability exhibited a predictive means for determining rejection.

A statistical analysis was performed on the sorted data-set, and results are presented in Table 8. Figs. 8–11 depict rejection as a function of polarizability, molecular volume, log K_{ow}, and molecular weight, respectively. When rejection was plotted as a function of polarizability and molecular volume, the R^2 value was 0.71 and 0.72, respectively. It is suspected that this decrease in R^2 could be explained by the variability of experimental operations from the additional sources. Research has indicated that experiments utilizing bench-scale units may achieve different rejection under identical operating conditions compared to experiments conducted using a pilot unit or full-scale plant [7,8,11,12]. Furthermore, source water from the additional data had different chemical properties, including variable dissolved organic content as well as varying cation concentrations, which have also been shown to impact TrOC rejection [10,16]. The decreased R^2 could also be due to the possibility that hydrophobicity/

Table 8
Statistical analysis for correlations between TrOC properties and rejection

Property	R^2	*F*-statistic	Critical *F*-value	*F*-statistic > critical *F*-value?	*t*-observed value	Critical *t*-value	*t*-observed > critical *t*-value?
Polarizability	0.71	235	3.94	Yes	1.98	15.3	Yes
MV	0.72	252	3.94	Yes	1.98	15.9	Yes
Log K_{ow}	0.14	15.4	3.94	Yes	1.98	3.92	Yes
MW	0.67	197	3.94	Yes	1.98	14.0	Yes

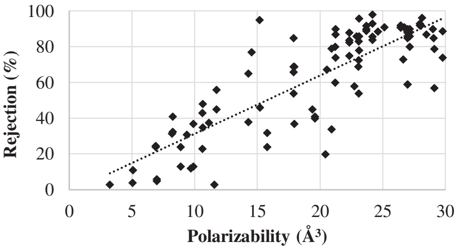

Fig. 8. Rejection vs. TrOC polarizability (R^2 = 0.71).

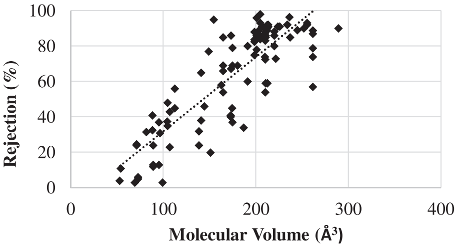

Fig. 9. Rejection vs. TrOC molecular volume (R^2 = 0.72).

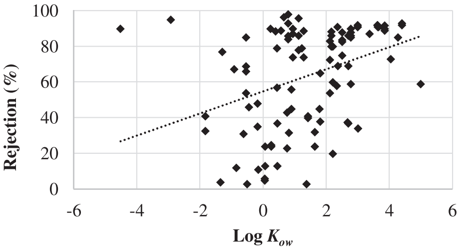

Fig. 10. Rejection vs. TrOC Log K_{ow} (R^2 = 0.14).

hydrophilicty and molecular weight also influence rejection. Additionally, this correlation appears to apply when a water flux similar to that of a full-scale NF membrane plant is used, and might not hold true for laboratory-scale experiments operating under unrealistic operating conditions.

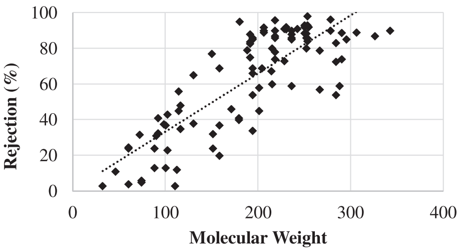

Fig. 11. Rejection vs. TrOC molecular weight (R^2 = 0.67).

Because the *F*-statistic values describing the relationships between polarizability, molecular volume, log K_{ow}, and molecular weight with rejection were larger than the critical *F*-value, the hypothesis that there is no relationship between rejection and these properties can be rejected. However, the *F*-statistic for log K_{ow} is relatively small compared to the *F*-statistic values for polarizability, molecular volume, and molecular weight, indicating this parameter does not impact rejection to the same extent as does polarizability, molecular volume, and molecular weight. Furthermore, the *t*-observed values for these properties were greater than the critical *t*-value, indicating the slope generated by plotting rejection as a function of these properties is useful when estimating rejection. Again, the critical *t*-value calculated for log K_{ow} is relatively small compared to those obtained for polarizability, molecular volume, and molecular weight, further demonstrating the lack of relationship between log K_{ow} and TrOC rejection.

4. Conclusions

The main objective of this work was to investigate solute-NF membrane interactions as determined by TrOC polarizability. The impact of several physical and chemical properties on TrOC rejection were evaluated using a pilot unit housing NF270 membranes operating at full-scale plant conditions, operating at a feed flow rate of 60,636 L/h (267 gpm), a flux of

25.6 L m^{-2} h^{-1} (15.1 gsfd), and 85% water recovery. Results indicate that TrOC polarizability and molecular volume were well-correlated with rejection (0.94 R^2).

Independent, analogousliterature sources reporting on TrOC removal in "loose" NF processes were also used to investigate polarizability and molecular volume as rejection mechanisms, whereupon the R^2 value describing the relationship between these properties and rejection was shown to be 0.71 and 0.72, respectively. Additionally, after incorporating independent literature results, the molecular weight R^2 value was 0.67, indicating a correlation between this parameter and TrOC rejection. Alternatively, the R^2 value (0.14) describing the relationship between rejection and TrOC log K_{ow} values indicated there was no correlation between this property and rejection. TrOCs with polarizability values and molecular volumes greater than 30 and 290 $Å^3$, respectively, are expected to be rejected by loose NF membranes. Findings indicate that water flux plays an important role in whether or not polarizability can be used as an indicator for TrOC rejection by polyamide NF membranes. As the water flux increased, the R^2 representing the correlation between polarizability and rejection decreased. Hence, it may be possible to use polarizability to qualitatively predict full-scale "loose" polyamide NF performance without the need to conduct expensive confirmation experiments.

Results of multiple experiments evaluating the rejection of TrOC's dosed in fresh ground water by a NF pilot unit were presented and discussed. Nine TrOCs were evaluated at varying feed concentrations ranging from 150 ng/L to 4.5 mg/L, and rejection of seven TrOCs ranged from 68% for caffeine to below detection in the permeate for gemfibrozil and sucralose, while it was reasoned there was a high probability that estrone and bisphenol A were not detected in a majority of samples due to adsorption based on the work others [14].

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References

[1] S.J. Duranceau, J.S. Taylor, L.A. Mulford, SOC removal in a membrane softening process, J. AWWA 84 (1992) 68–78.

[2] B. Van der Bruggen, J. Schaep, W. Maes, D. Wilms, C. Vandecasteele, Nanofiltration as a treatment method for the removal of pesticides from ground waters, Desalination 117 (1998) 139–147.

[3] B. Van der Bruggen, J. Schaep, D. Wilms, C. Vandecasteele, Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration, J. Membr. Sci. 156 (1999) 29–41.

[4] J.A.M.H. Hofman, E.F. Beerendonk, H.C. Folmer, J.C. Kruithof, Removal of pesticides and other micropollutants with cellulose acetate, polyamide and ultra-low pressure reverse osmosis membranes, Desalination 113 (1997) 209–214.

[5] S.S. Chen, J.S. Taylor, L.A. Mulford, C.D. Norris, Influences of molecular weight, molecular size, flux, and recovery for aromatic pesticide removal by nanofiltration membranes, Desalination 160 (2004) 103–111.

[6] J.A.M.H. Hofman, A.J. Gijsbertsen, E. Cornelissen, Nanofiltration Retention Models for Organic Contaminants, American Water Works Association Research Foundation and Kiwa Water Research, Denver, CO, 2007.

[7] C. Bellona, J.E. Drewes, Viability of a low-pressure nanofilter in treating recycled water for water reuse applications: A pilot-scale study, Water Res. 41 (2007) 3948–3958.

[8] J. Radjenović, M. Petrović, F. Ventura, D. Barceló, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, Water Res. 42 (2008) 3601–3610.

[9] A.H.M. Sadmani, R.C. Andrews, D.M. Bagley, Nanofiltration of pharmaceutically active and endocrine disrupting compounds as a function of compound interactions with DOM fractions and cations in natural water, Sep. Purif. Technol. 122 (2014) 462–471.

[10] A.R.D. Verliefde, E.R. Cornelissen, S.G.J. Heijman, J.Q.J.C. Verberk, G.L. Amy, B. Van der Bruggen, J.C. van Dijk, Construction and validation of a full-scale model for rejection of organic micropollutants by NF membranes, J. Membr. Sci. 339 (2009) 10–20.

[11] S. Gur-Reznik, I. Koren-Menashe, L. Heller-Grossman, O. Rufel, C.G. Dosoretz, Influence of seasonal and operating conditions on the rejection of pharmaceutical active compounds by RO and NF membranes, Desalination 277 (2011) 250–256.

[12] V. Yangali-Quintanilla, S.K. Maeng, T. Fujioka, M. Kennedy, Z. Li, G. Amy, Nanofiltration vs. reverse osmosis for the removal of emerging organic contaminants in water reuse. Desalin. Water Treat. 34 (2011) 50–56.

[13] A.R.D. Verliefde, E.R. Cornelissen, S.G.J. Heijman, J.Q.J.C. Verberk, G.L. Amy, B. Van der Bruggen, J.C. van Dijk, The role of electrostatic interactions on the rejection of organic solutes in aqueous solutions with nanofiltration, J. Membr. Sci. 322 (2008) 52–66.

[14] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment—A literature review, Water Res. 38 (2004) 2795–2809.

[15] S. Hajibabania, A. Verliefde, J.A. McDonald, S.J. Khan, P. Le-Clech, Fate of trace organic compounds during treatment by nanofiltration, J. Membr. Sci. 373 (2011) 130–139.

[16] A.M. Comerton, R.C. Andrews, D.M. Bagley, C. Hao, The rejection of endocrine disrupting and pharmaceutically active compounds by NF and RO membranes as a function of compound and water matrix properties, J. Membr. Sci. 313 (2008) 323–335.

[17] V. Yangali-Quintanilla, A. Sadmani, M. McConville, M. Kennedy, G. Amy, Rejection of pharmaceutically active compounds and endocrine disrupting compounds by clean and fouled nanofiltration membranes, Water Res. 43 (2009) 2349–2362.

[18] H.Q. Dang, L.D. Nghiem, W.E. Price, Factors governing the rejection of trace organic contaminants by nanofiltration and reverse osmosis membranes, Desalin. Water Treat. 52 (2014) 589–599.

[19] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Removal of natural hormones by nanofiltration membranes: Measurement, modeling, and mechanisms, Environ. Sci. Technol. 38 (2004) 1888–1896.

[20] B. Van der Bruggen, L. Braeken, C. Vandecasteele, Evaluation of parameters describing flux decline in nanofiltration of aqueous solutions containing organic compounds, Desalination 147 (2002) 281–288.

[21] I. Vorobyov, T.W. Allen, The electrostatics of solvent and membrane interfaces and the role of electronic polarizability, J. Chem. Phys. 132 (2010) 1–13.

[22] C. Bellona, D. Heil, C. Yu, P. Fu, J.E. Drewes, The pros and cons of using nanofiltration in lieu of reverse osmosis for indirect potable reuse applications, Sep. Purif. Technol. 85 (2012) 69–76.

[23] K.J. Miller, J.A. Savchik, A new empirical method to calculate average molecular polarizabilities, J. Am. Chem. Soc. 101 (1979) 7206–7213.

[24] R. Wilder, S.J. Duranceau, S. Jeffery, D. Brown, and A. Arrington, Contaminants of emerging concern: Occurrence in shallow groundwater and removal by nanofiltration, Proceedings from the American Membrane Technology Association Conference, San Antonio, TX, 2016.

[25] K.K. Barnes, D.W. Kolpin, E.T. Furlong, S.D. Zaugg, M.T. Meyer, L.B. Barber, A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States—I) Groundwater, Sci. Total Environ. 402 (2008) 192–200.

[26] E. Estévez, M. del Carmen Cabrera, A. Molina-Díaz, J. Robles-Molina, M. del Pino Palacioz-Díaz, Screening of emerging contaminants and priority substances (2008/105/EC) in reclaimed water for irrigation and groundwater in a volcanic aquifer (Gran Canaria, Canary Islands, Spain), Sci. Total Environ. 433 (2008) 538–546.

[27] J. Fawell, C.N. Ong, Emerging contaminants and the implications for drinking water, Int. J. Water Resour. Dev. 28 (2012) 247–263.

[28] D.B. Mawhinney, R.B. Young, B.J. Vanderford, T. Borch, S.A. Snyder, Artificial sweetener sucralose in U.S. Drinking water systems, Environ. Sci. Technol. 45 (2011) 8716–8722.

[29] Z. Li, X. Xiang, M. Li, Y. Ma, J. Wang, X. Liu, Occurrence and risk assessment of pharmaceuticals and personal care products and endocrine disrupting chemicals in reclaimed water and receiving groundwater in China, Ecotoxicol. Environ. Saf. 119 (2015) 74–80.

[30] S. Wang, W. Wu, F. Liu, S. Yin, Z. Bao, H. Liu, Spatial distribution and migration of nonylphenol in groundwater following long-term wastewater irrigation, J. Contam. Hydrol. 177–178 (2015) 85–92.

[31] N. Garcia, J. Moreno, E. Cartmell, I. Rodriguez-Roda, S. Judd, The application of microfiltration-reverse osmosis/nanofiltration to trace organics removal for municipal wastewater reuse, Environ. Technol. 34 (2013) 3183–3189.

[32] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review: Recent advances and future prospects, Desalination 356 (2015) 226–254.

[33] S. Jeffery-Black, S.J. Duranceau, Mass transfer and transient response time of a split-feed nanofiltration pilot unit, Desalin. Water Treat. doi: 10.1080/19443994.2016.1155498 (in press).

[34] J. Oppenheimer, A. Eaton, M. Badruzzaman, A.W. Haghani, J.G. Jacangelo, Occurrence and suitability of sucralose as an indicator compound of wastewater loading to surface waters in urbanized regions, Water Res. 45 (2011) 4019–4027.

[35] W. Mendenhall, T. Sincich, Statistics for Engineering and The Sciences, Pearson Prentice-Hall, Upper Saddle River, NJ, 2007.

[36] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Role of electrostatic interactions in the retention of pharmaceutically active contaminants by a loose nanofiltration membrane, J. Membr. Sci. 286 (2006) 52–59.

[37] K. Kosutic, D. Dolar, D. Asperger, B. Kunst, Removal of antibiotics from a model wastewater by RO/NF membranes, Sep. Purif. Technol. 53 (2007) 244–249.

[38] V. Yangali-Quintanilla, S.K. Maeng, T. Fujioka, M. Kennedy, G. Amy, Proposing nanofiltration as acceptable barrier for organic contaminants in water reuse, J. Membr. Sci. 362 (2010) 334–345.

[39] C. Bellona, D. Heil, C. Yu, P. Fu, J.E. Drewes, The pros and cons of using nanofiltration in lieu of reverse osmosis for indirect potable reuse applications, Sep. Purif. Technol. 85 (2012) 69–76.

[40] A. Shahmansouri, C. Bellona, Application of quantitative structure-property relationships (QSPRs) to predict the rejection of organic solutes by nanofiltration, Sep. Purif. Technol. 118 (2013) 627–638.

[41] T. Fujioka, S.J. Khan, J.A. McDonald, L.D. Nghiem, Nanofiltration of trace organic chemicals: A comparison between ceramic and polymeric membranes, Sep. Purif. Technol. 136 (2014) 258–264.