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Abstract

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Keywords

polymeric, ceramic, between, comparison, membrane, chemicals, nanofiltration, organic, trace

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Nanofiltration of trace organic chemicals: a comparison between ceramic and polymeric membranes

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Abstract

The rejection of 41 trace organic chemicals (TrOCs) by a ceramic NF membrane was examined and compared with that by two polyamide-based NF membranes – namely NF90 and NF270. Rejection behaviours of TrOCs by the ceramic and polymeric NF membranes were mostly similar but there were several notable differences. The rejection of neutral TrOCs by the ceramic and polymeric NF membranes increased in the order of increasing molecular size (e.g. minimum projection area) indicating that size exclusion is the dominant mechanism governing rejection. However, in contrast to the polymeric NF membranes, where hydrophobic interaction between membrane and TrOCs influenced the rejection of neutral molecules, the impact of hydrophobic interaction was not significant for the ceramic NF membrane. The rejection of specific low molecular weight TrOCs increased in the order of NF270, NF90 and ceramic NF membranes, while molecular weight cut-off increased in the order of ceramic NF, NF270 and NF90 membranes. A notable difference of about 20% in rejection between positively and negatively charged TrOCs of similar molecular size was observed for the ceramic NF membrane but not the two polymeric ones. The results indicate that electrostatic repulsion and attraction of charged TrOCs with the inorganic membrane differ from those with polymeric membrane materials.

Keywords: Ceramic membrane; potable water treatment; nanofiltration; trace organic chemicals (TrOCs).

1. Introduction

Membrane separation using ceramic materials has been an important tool for many industries. Ceramic membranes are usually manufactured from inorganic materials such as alumina, zirconia, silica and titanium. Consequently, compared to their polymeric counterparts, ceramic membranes are physically and chemically more durable [1]. Thus, they have been widely used in highly specialised applications under extreme operating conditions (such as high temperature or with aggressive solvents), beyond the capacity of typical polymeric membranes. These filtration applications can be found in many industries such as food processing, beverage production, chemical manufacturing, and biotechnology. In recent years, ceramic membranes have been increasingly used for water purification due to a considerable decrease in manufacturing cost [2-4]. A large number of small-scale drinking water treatment processes using ceramic membranes have been deployed in Japan over the past decade [5]. PWN Technologies has recently announced the construction of a drinking water ceramic membrane filtration plant in the Netherlands with a capacity of 120,000 m³/day [6].

Given their ability to sustain intermittent operations and frequent and aggressive chemical cleaning while maintaining a stable and reliable performance, ceramic membranes offer an ideal platform for strategic drinking water supply from compromised water sources for disaster relief and military operations. In these applications, the removal of trace organic chemicals (TrOCs) of significant health risk is an important concern. However, to date, ceramic membrane applications for drinking water treatment have been primarily limited to microfiltration and ultrafiltration. Membrane separation for the removal of small contaminants such as TrOCs has traditionally been viewed as the domain of polymeric nanofiltration (NF) membranes. In fact, there have been numerous drinking water treatment plants using polymeric NF membranes to specifically target the removal of TrOCs [7]. The nominal molecular weight cut-off (MWCO) of polymeric NF membranes used for drinking water applications is typically in the range of 200-300 Da. Although polymeric NF membranes can offer high flux and TrOC rejection at the early stage of their lifetime, the gradual deterioration of membrane integrity due to repetitive chemical cleaning is still a great concern [8]. For example, a previous study performed by Simon et al. [9] reported that caustic chemical cleaning to polymeric (polyamide-based) NF membranes can result in a considerable decrease in the rejection of neutral and hydrophobic TrOCs. Simon et al. [10] explained the mechanism

of the separation deterioration by reference to a conformational change in the polymeric matrix of the membrane active skin layer. Since concentrations of TrOCs in feed and product water are not monitored online in treatment plants, the vulnerability of water treatment applying polymeric NF membranes is a potential risk for potable water quality management. Due to long-life and chemically resilient properties of ceramic membrane, it is apparent that the improved and more reliable water quality management for potable water applications can be achieved using ceramic NF membranes despite their relatively high capital cost. While ceramic NF membranes with relatively loose pore size (e.g. MWCO > 500 Da) have been commercially available for more than a decade [1], very recent developments on ceramic materials and manufacturing technologies have allowed ceramic NF membranes with smaller pore size (e.g. MWCO = 200 Da) to be commercially produced.

To date, no previous studies have attempted to evaluate the rejection of TrOCs by ceramic NF membranes. In contrast, numerous previous studies have reported the rejection of TrOCs by polymeric NF membranes [11-20]. In general, the separation performance of TrOCs by polyamide-based NF membranes is dependent on the membrane characteristics. This is because MWCOs for polymeric NF membranes typically used for brackish water treatment (200-300 Da) are close to the molecular weight of most regulated TrOCs. For example, the rejection of neutral TrOCs can increase considerably with increasing molecular weight [17, 18]. Hydrophobic interaction between membranes and compounds also influences rejections [17, 20]. Electrostatic repulsion and attraction between charged compounds and membranes is a further important factor determining the rejection of charged compounds [18, 19]. Thus, careful attention should be paid for selecting polymeric NF membranes. Likewise, understanding fundamental separation behaviour of TrOCs by ceramic NF membranes is important when considering their use as an option for drinking water applications.

The aim of this study was to provide an understanding of TrOC rejection by a ceramic NF membrane. The rejection of a range of TrOCs by a ceramic NF membrane (MWCO = 200 Da) was investigated using a laboratory-scale NF filtration system. Relationships between physicochemical properties of TrOCs and their rejections were evaluated. These results were compared with those obtained for two polymeric NF membranes.

2. Materials and methods

2.1. NF membranes and laboratory-scale NF filtration system

A tubular ceramic NF membrane (Fraunhofer Institute for Ceramic Technologies and Systems, Germany) and two polymeric NF membranes – namely NF90 and NF270 (Dow Chemical, USA) – were used (Table 1). According to the manufacturer, the ceramic membrane has a TiO₂ separation layer with a thickness of approximately 50 nm on the top of an aluminium oxide (α -Al₂O₃) supporting layer. The ceramic membrane was supplied as a tubular module with length, outer and inner diameters of 250, 10, and 7 mm, respectively. The effective membrane surface area of this element is 55 cm². The element was installed in stainless steel housing and was operated in the inside-out configuration. The NF90 and NF270 are both polyamide-based thin-film composite NF membranes. They were obtained as flat sheet samples and could be mounted onto a stainless steel cross flow cell holding an effective membrane surface area of 40 cm² (4 cm × 10 cm) with a channel height of 2 mm.

A laboratory-scale NF filtration system, which can be integrated with either the tubular ceramic membrane module or the flat sheet membrane cell, was used (Figure 1). The feed solution in a stainless steel reservoir was transferred to the tubular membrane module (or membrane cell) by a high pressure pump (Hydra-Cell, Wanner Engineering Inc., Minneapolis, MN, USA). Permeate flow was monitored by a digital flow meter (FlowCal, GJC Instruments Ltd., UK), which was connected to a computer for data acquisition. The permeate and concentrate were recirculated back to the feed reservoir. The feed solution temperature was controlled via a stainless steel heat exchanging coil connected to a temperature control unit (Neslab RTE 7, Thermo Scientific Inc., USA).

[Table 1]

[Figure 1]

2.2. Chemicals

A set of 41 organic chemicals to cover important classes of TrOCs including disinfection by-products (e.g. N-nitrosamines), pesticides, personal care products, pharmaceuticals, and industrial chemicals were selected (Table 2). Their physicochemical properties such as

molecular weight (MW), charge, and hydrophobicity vary over a wide range, thus, allowing for a comprehensive assessment of their rejection behaviour by NF membranes. These chemicals were obtained from Sigma-Aldrich (St Louis, MO, USA) and were each of analytical grade. These TrOCs were classified into four groups: neutral hydrophilic ($\log D < 2$), neutral hydrophobic ($\log D \geq 2$), and negatively and positively charged compounds [18, 21]. $\log D$ is the logarithm of the apparent water-octanol distribution coefficients (D) which represents the hydrophobicity of the compound at a given pH. Compounds that are ionised by more than 50% at pH 8 are categorised as “charged”. Based on this criterion, in this study, hydroxyzine, about 40% of which is ionised at pH 8, is classified as a neutral compound (Table 2). Minimum projection area (MPA) summarised in Table 2 is defined as the area of the conformer projected with the minimum plane of its circular disk (Figure 2) which is calculated based on the Van der Waals radius.

Two separate stock solutions were prepared in methanol to cover all selected TrOCs. One stock solution contained 10 mg/L of each N-nitrosamine. The other stock solution contained the remaining 33 TrOCs at 10 mg/L of each compound. Deuterated isotope compounds obtained from CDN isotopes (Pointe-Claire, Quebec, Canada) were used as surrogate standards. An N-nitrosamine surrogate stock solution prepared in pure methanol contained 50 $\mu\text{g/L}$ of each deuterated N-nitrosamine. Another surrogate stock solution prepared in pure methanol contained 50 $\mu\text{g/L}$ of each deuterated compound of all other TrOCs. These stock solutions were kept in the dark at $-18\text{ }^\circ\text{C}$. Analytical grade NaCl, CaCl_2 and NaHCO_3 obtained from Ajax Finechem (Australia) were used to prepare background electrolytes for the test solutions.

[Table 2]

[Figure 2]

2.3. Experimental protocols

Prior to each filtration experiment, the polymeric NF membranes were operated at 1,000 kPa using Milli-Q water for at least 3 hours to ensure a stabilised permeate flux. Pure water permeability of each membrane was determined. Although compaction is not necessary for the ceramic membrane, for consistency, the same experimental protocol was also used for the ceramic membrane. The cross flow velocity and solution temperature were 0.43 m/s and

20.0±0.1 °C, respectively. However, because of the difference in membrane module configuration, there can be a difference in the hydraulic condition (e.g. Reynolds Number). Rejection experiments were carried out using a clean water matrix. Following the stabilisation step, electrolytes were added to obtain a feed water solution containing 20 mM NaCl, 1 mM CaCl₂ and 1 mM NaHCO₃ at approximately pH 8. The stock solutions of TrOCs were also added into the feed to obtain approximately 250 ng/L of each N-nitrosamine and 300 ng/L of each other compound. Thereafter, the permeate flux was adjusted to 20 L/m²h. The system was continuously operated for at least 8 hours before the first permeate and concentrate samples were taken for analysis.

2.4. Analytical techniques

The analysis of N-nitrosamine concentration in this study was undertaken by gas chromatography (GC) coupled with tandem mass spectrometry (MS/MS) following solid phase extraction (SPE). This analytical technique was previously reported by McDonald et al. [22] and only a brief summary is described here. Prior to the SPE process, N-nitrosamine surrogate stock solution was dosed to each sample (200 mL) at 50 ng/L of each surrogate N-nitrosamine to account for SPE recovery efficiency. N-nitrosamines in each sample were extracted to a 2 g SupelcleanTM Coconut Charcoal cartridge (Supelco, St Louis, MO, USA). N-nitrosamines in these samples were separated using an Agilent 7890A GC with electron ionisation and their concentrations were determined using an Agilent 7000B triple quadrupole MS/MS. The detection limits of N-nitrosamines in this study were determined at 10 ng/L or lower.

The concentrations of all other TrOCs were determined based on an analytical method previously described by Tadkaew et al. [23]. This method comprises isotope dilution, SPE, and subsequent quantification using high performance liquid chromatography (HPLC) – mass spectrometry (MS). Deuterated surrogate stock solution was first added to each sample (500 mL) to make up at 50 ng/L of each surrogate concentration. Compounds in each sample were then extracted on a 6cc Oasis HLB SPE cartridge (Waters, Milford, MA, USA). TrOC concentrations were quantified using a HPLC system consisting of an Agilent 1200 series HPLC system (Palo Alto, CA, USA) coupled with an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA). The detection limits of these compounds here were determined at 20 ng/L or lower.

An Orion 4-Star Plus pH/conductivity meter (Thermo Fisher Scientific, Waltham, MA, USA) was used to analyse pH, electrical conductivity and temperature of solutions.

Solute rejection (R) was calculated using $R [\%] = \left(1 - \frac{C_p}{C_f}\right) \times 100$, where C_p and C_f are measured permeate and feed concentrations, respectively. If the permeate concentration is not detected, the reporting detection limit is used for rejection calculation.

3. Results and discussion

3.1. Rejection of neutral TrOCs

The rejection of neutral TrOCs by the ceramic and two polymeric (i.e. NF90 and NF270) NF membranes increased in the order of their molecular weight increase (Figure 3). The actual MWCO can be obtained from the data in Figure 3 and the values differ somewhat from the nominal MWCO reported by the manufacturers. The NF90 membrane showed the lowest MWCO (191 Da) followed by the NF270 membrane (326 Da) and the ceramic NF membrane (345 Da). Nevertheless, it is noteworthy that the rejection of the smallest compound – NDMA – by the ceramic NF membrane (20%) was higher than that by the NF90 membrane (8%) and NF270 membrane (4%). Likewise, the ceramic NF membrane exhibited higher rejections of the three next smallest compounds (NEMA, NPYR, and NDEA) than the two polymeric NF membranes. These results indicate that while size exclusion is the dominating rejection mechanism for both the ceramic and polymeric NF membranes, they respond differently to other factors that can also influence TrOC rejection.

In a good agreement with previous studies, considerable adsorption of hydrophobic TrOCs to the ceramic and polymeric NF membranes was observed [24, 25]. Triclocarban, which has the highest hydrophobicity ($\text{Log } D = 4.93$) among the neutral TrOCs used here, is a notable example. Triclocarban concentration in the feed solution decreased from 300 ng/L to 10-20 ng/L after eight hours of filtration. Since the detection limit of triclocarban (i.e. 10 ng/L) was very close to concentrations in the feed, it was excluded from results reported here.

[Figure 3]

In addition to molecular weight, molecular volume and minimum projection area of neutral TrOCs exhibited a good correlation with their rejections by the ceramic NF membrane (Figure 4a). In contrast, compound rejections by the polymeric membranes (i.e. NF270 and NF90) were most correlated with their minimum projection area (Figure 4b and c). Overall, minimum projection area of neutral TrOCs commonly governs their rejections by the ceramic and polymeric NF membranes. Hydrophobic interaction also influenced the rejection of neutral TrOCs by the polymeric NF membranes. This effect was apparent for small and hydrophobic TrOCs that have the minimum projection area of about 30 \AA^2 (Figure 4b and c). These hydrophobic compounds that were influenced by hydrophobic interaction exhibited 10-40% lower rejections than their counterpart hydrophilic TrOCs.

Among the hydrophobic compounds, bisphenol A (minimum projection area = 44 \AA^2) exhibited remarkably low rejections (28 and 50%) by the NF270 and NF90 membranes, respectively (Figure 4b and c). Bisphenol A is the second most hydrophobic compound (Log $D = 4.04$) among the neutral TrOCs just after triclocarbon (Table 1). A previous laboratory-scale study conducted by Drewes et al. [26] revealed low rejections (33-53%) of bisphenol A (minimum projection area = 44 \AA^2) by a NF membrane (ESNA1-LF/Hydranautics), while the rejection of the other neutral compound, primidone (minimum projection area = 44 \AA^2), was >99%. The very low rejections observed here can be attributed to its chemical structure containing two phenol groups. Matsuura and Sourirajan [27, 28] investigated the rejection of alcohol, phenols and monocarboxylic acids using a cellulose acetate RO membrane, and reported that their rejections decreased considerably with increasing their relative hydrogen-bonding ability (or referred as molecular relative acidity). They suggested that neutral chemicals whose acidity is stronger than the water solution are preferably absorbed on the membrane surface. This is because membrane surface has net proton acceptor characteristics and these adsorbed and accumulated chemicals diffuse through membranes, resulting in a lower rejection [29]. However, this interaction with bisphenol A was not observed for the ceramic NF membrane (Figure 4a). Ceramic material including TiO_2 is hydrophilic by nature and is very likely to have lower hydrogen bonding potentials (e.g. acceptors and donors) such as carbonyl and amine groups than polyamide membranes [30].

[Figure 4]

3.2. Rejection of charged TrOCs

Over half of the charged TrOCs selected here exhibited high rejections (over 90%) by the ceramic NF membrane (Figure 5a). Substantial adsorption of triclosan to membrane was observed for the three membranes. Concentration of this compound in the feed decreased dramatically from 300 ng/L to 30-50 ng/L after eight hours of filtration period. Triclosan is a hydrophobic ionisable compound [31], thus, despite being a negative charged species at pH 8, it is also highly hydrophobic ($\text{Log } D = 4.57$). As a result, triclosan concentration in the feed solution decreased from about 300 ng/L to 30-50 ng/L. Since the detection limit of triclosan in the permeate was 10 ng/L, its rejection could not be accurately calculated and should be treated with caution.

[Figure 5]

In contrast to polymeric NF membranes, in which no clear impact of the type of compound charge was observed (Figure 6b and c), the ceramic NF membrane exhibited a notable difference in rejection between positively and negatively charged TrOCs (Figure 6a). The rejection of positively charged TrOCs by the ceramic NF membrane was relatively low (about 70%) with the exception of verapamil (minimum projection area = 81 \AA^2), while the rejection of most negatively charged TrOCs was high (90%). As a result, the rejection of charged TrOCs by the ceramic NF membrane was not strongly correlated with their minimum projection area (Figure 6a). Electrostatic repulsion that occurs between negatively charged chemicals and membrane surface enhances chemical rejection, while electrostatic attraction force occurs between positively charged chemicals and negatively membrane surface [32]. Thus, the “charge concentration polarisation” effect due to the electrostatic attraction force can be expected for the positively charged compounds.

[Figure 6]

4. Conclusions

The rejection of TrOCs by the ceramic NF membrane was generally similar to that by the two polymeric NF membranes but there were several notable differences. The NF90 membrane showed the lowest MWCO (191 Da) followed by the NF270 membrane (326 Da) and the ceramic NF membrane (345 Da). Nevertheless, the ceramic NF membrane exhibited the highest rejection for low molecular weight neutral TrOCs (e.g. NDMA and NMEA). In

general, the rejection of neutral TrOCs by the ceramic and polymeric NF membranes increased in the order of increasing molecular size (e.g. minimum projection area). Hydrophobic interaction influenced TrOC rejection by the NF90 and NF270 membranes, while its impact was not apparent for the ceramic NF membrane. A remarkable difference in rejection between positively and negatively charged compounds was observed for the ceramic membrane. The rejection of most negatively charged TrOCs by the ceramic membrane was high (over 90%), while most positively charged compounds exhibited lower rejections (i.e. approximately 70%). The polymeric NF membranes showed no apparent differences in the rejection of these negatively and positively charged species. Overall, the ceramic NF membrane used in this investigation has the capability of removing TrOCs equivalent to the polymeric NF membranes. This suggests that the ceramic NF membrane can be used for the removal of TrOCs under a range of aggressive conditions that are not suitable for polymeric membranes. Nevertheless, further development of ceramic NF membranes to increase their permeability is necessary to make them economically viable for water treatment applications.

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Table 1: NF membranes used in this study.

Membrane material	Name	Manufacturer	MWCO [Da]	Permeability ^a [L/m ² hbar]	Conductivity rejection ^b [%]
Ceramic	-	IKTS	200	3.9 ± 0.2	23
	NF90	Dow/Filmtec	200	14.6 ± 0.2	81
Polymer	NF270	Dow/Filmtec	400	21.1 ± 1.8	16

^a Determined with Milli-Q water at 1000 kPa and 20 °C feed temperature. Values reported here are average and ranges of duplicate experiments.

^b Determined with feed solution containing 20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, at permeate flux 20 L/m²h, feed pH 8.0 ± 0.1 and feed temperature 20.0 ± 0.1 °C.

Table 2: Physicochemical characteristics of the selected TrOCs.

Compound	MW [Da]	Log <i>D</i> at pH 8 ^a	pK _a (pK _b) ^a	Ionisation at pH 8 ^a [%]	MPA ^a [Å ²]
N-nitrosodimethylamine (NDMA)	74.1	0.04	(3.5)	0	19.5
N-nitrosomethylethylamine (NMEA)	88.1	0.40	(3.4)	0	22.1
N-nitrosopyrrolidine (NPYR)	100.1	0.44	(3.3)	0	25.0
N-nitrosodiethylamine (NDEA)	102.1	0.75	(3.3)	0	25.4
N-nitrosopiperidine (NPIR)	114.1	0.89	(3.3)	0	27.2
N-nitrosomorpholine (NMOR)	116.1	-0.18	(3.1)	0	25.2
N-nitrosodipropylamine (NDPA)	130.1	1.80	(3.3)	0	28.3
Paracetamol	151.2	0.91	9.5	3	21.8
Caffeine	194.2	-0.55	(0.9)	0	30.0
Simazine	201.7	1.78	(3.2)	0	35.8
Atrazine	215.7	1.32	(3.2)	0	39.0
Primidone	218.3	1.12	11.5	0	42.7
Meprobamate	218.3	0.93	15.2	0	45.8
Triamterene	253.3	1.11	(1.9)	0	35.2
Tris(2-chloroethyl)phosphate (TCEP)	285.5	1.96	n.a.	0	49.9

Hydrophilic

	Trimethoprim	290.3	1.28	(7.2)	12	51.1	
	N-nitrosodi-n-butylamine (NDBA)	158.1	2.69	(3.3)	0	28.8	
	N,N-Diethyl-meta-toluamide (DEET)	191.3	2.50	(0.1)	0	40.1	
	Bisphenol A	228.3	4.04	9.8; 10.4	2	44.0	
	Diuron	233.1	2.53	13.2	0	28.6	
	Carbamazepine	236.3	2.77	16.0	0	38.8	
Hydrophobic	Linuron	249.1	2.68	12.0	0	30.8	
	Dilantin	252.3	2.18	9.5	3	47.3	
	Diazepam	284.7	3.08	(2.9)	0	47.8	
	Triclocarban	315.6	4.93	11.4	0	50.1	
	Clozapine	326.3	3.40	(3.9; 7.8)	36	55.5	
	Omeprazole	345.4	2.43	(4.8); 9.3	2	43.5	
	Hydroxyzine	374.9	3.24	(2.1; 7.8)	40	64.7	
		Ibuprofen	206.3	0.97	4.9	100	35.4
		Naproxen	230.3	-0.16	4.2	100	34.8
	⊖	Gemfibrozil	250.3	1.33	4.4	100	43.4
	Sulfamethoxazole	253.3	0.39	6.2	99	45.2	
	Ketoprofen	254.3	0.48	3.9	100	41.7	

Triclosan	289.5	4.57	7.7	68	38.5
Diclofenac	296.1	1.16	4.0	100	43.3
Enalapril	376.5	-0.91	3.7; (5.2)	100	60.0
Simvastatin hydroxy acid	436.6	0.63	4.2	100	65.1
Atenolol	266.3	-1.18	(9.7)	98	36.9
Amitriptyline	277.4	3.02	(9.8)	98	58.2
⊕ Fluoxetine	309.3	2.46	(9.8)	98	44.3
Verapamil	454.6	3.44	(9.7)	98	81.2

^a Chemaxon (<http://www.chemicalize.org/>).

LIST OF FIGURES

Figure 1: Schematic diagram of the cross flow NF filtration system.

Figure 2: Schematic figure of minimum projection area. The line perpendicular to the circular disk represents the centre axis of the minimum projection area.

Figure 3: Rejection of neutral TrOCs by the (a) ceramic, (b) NF90 and (c) NF270 membranes (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, permeate flux 20 L/m²h, feed pH 8.0 ± 0.1, feed temperature 20.0 ± 0.1°C). The molecular weight (Da) is shown in the parentheses. Values reported here are the average and ranges of duplicate samples. Open symbol indicates that the permeate concentration was below the detection limit.

Figure 4: Rejection of neutral TrOCs by the (a) ceramic, (b) NF90 and (c) NF270 membranes as a function of their molecular weight, molecular volume and minimum projection area. Experimental conditions are described in Figure 3.

Figure 5: Rejection of charged TrOCs by the (a) ceramic, (b) NF90 and (c) NF270 membranes. Experimental conditions are described in Figure 3. The molecular weight (Da) is shown in the parentheses. Values reported here are the average and ranges of duplicate samples. Open symbol indicates that the permeate concentration was below the detection limit.

Figure 6: Rejection of charged TrOCs by the (a) ceramic, (b) NF90 and (c) NF270 membranes as a function of their minimum projection area. Experimental conditions are described in Figure 3.

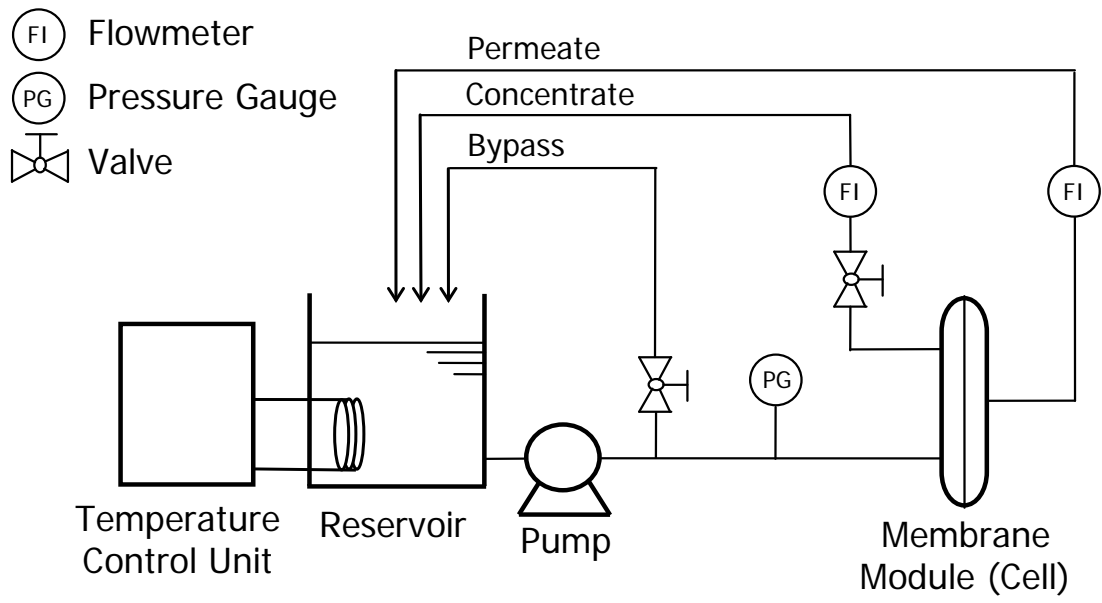


Figure 1

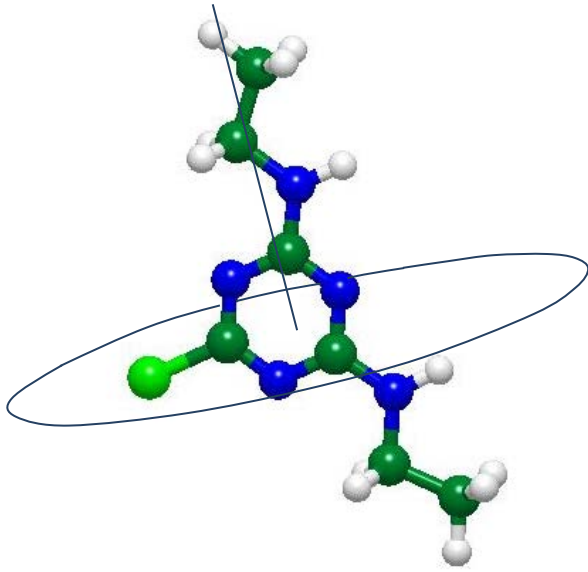


Figure 2

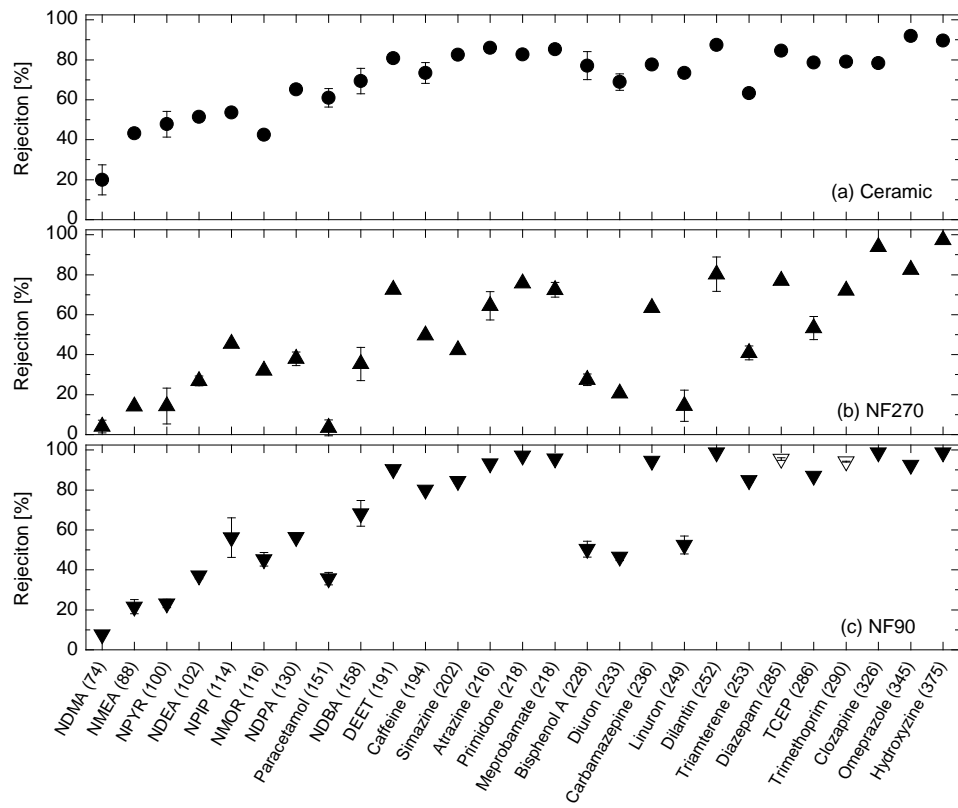


Figure 3

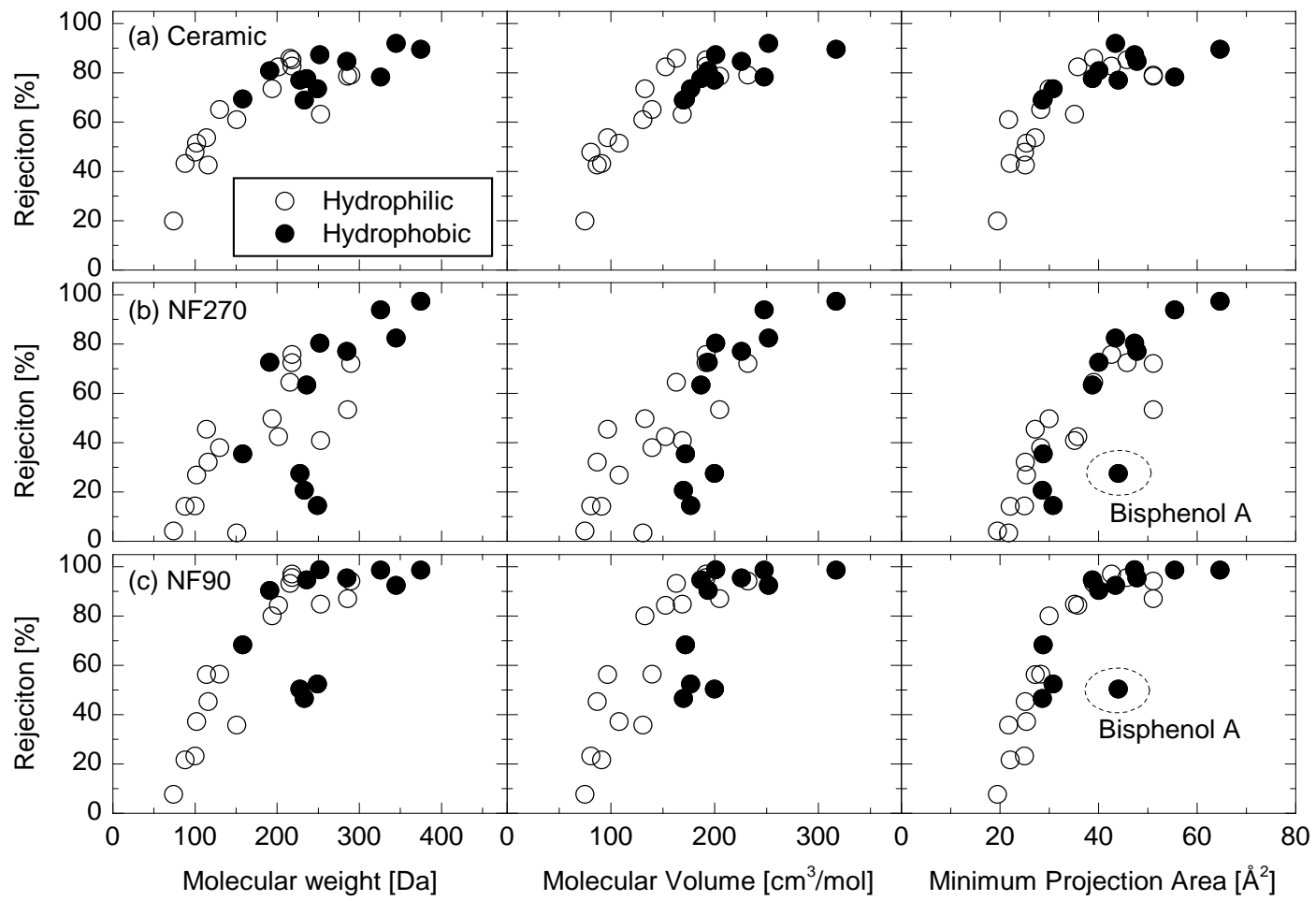


Figure 4

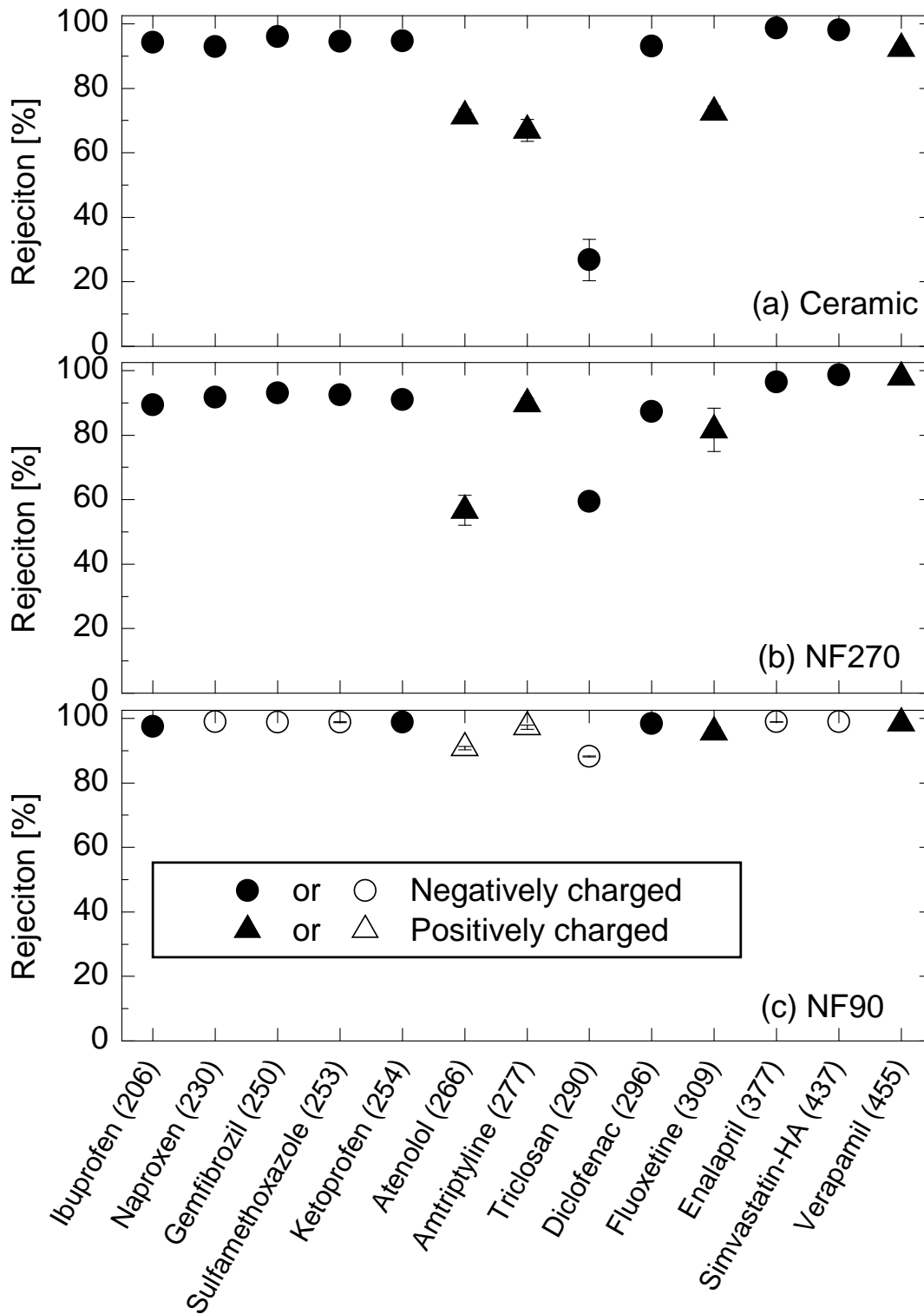


Figure 5

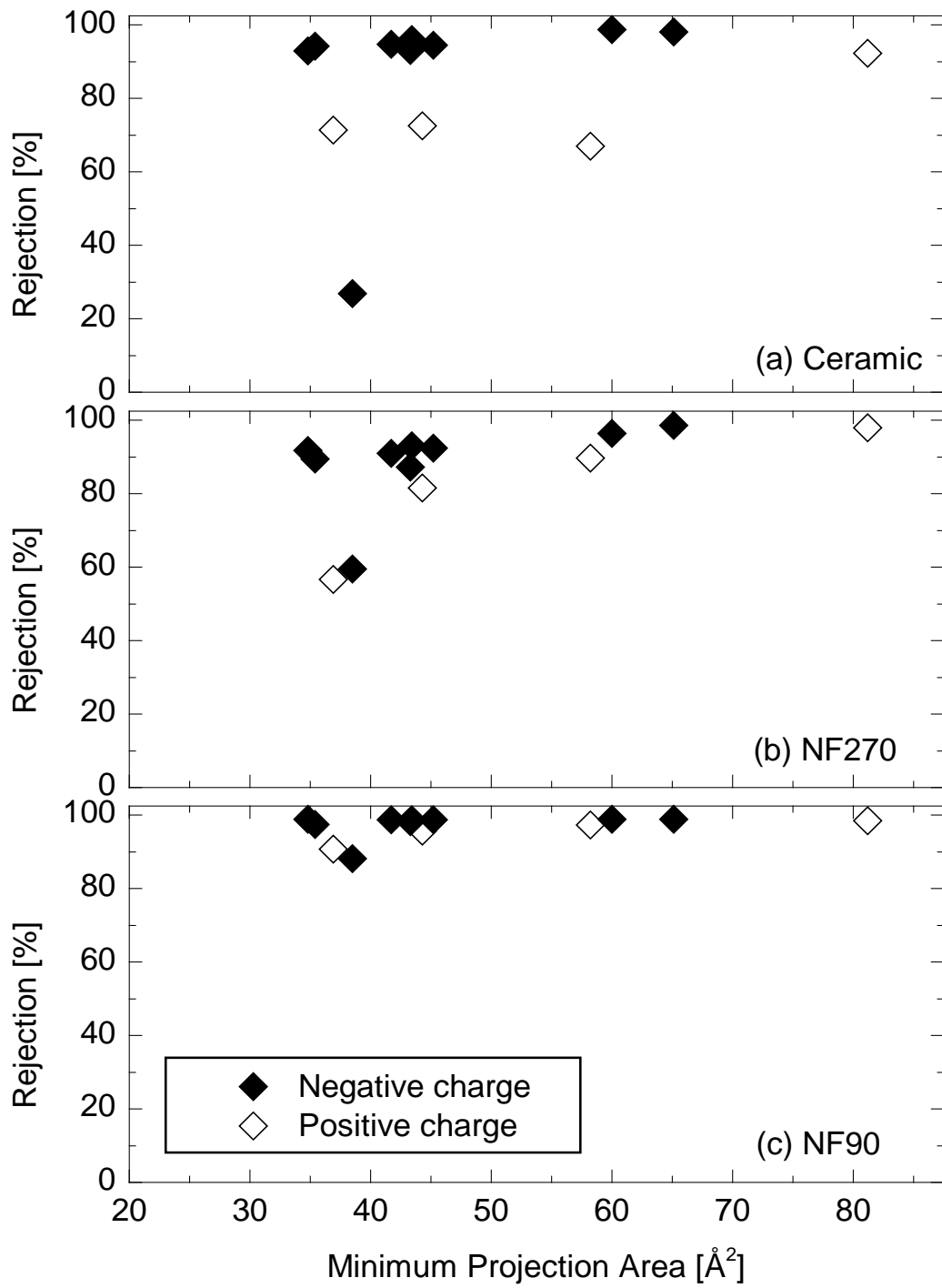


Figure 6