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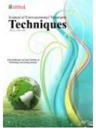

Influence of the Solution pH on Adsorption and Rejection of Race Organic Contaminants from Wastewater by a Nanofiltration Membrane

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Abstract

This study investigated the influence of the feed solution pH on the adsorption and rejection of the trace organic contaminants by a loose nanofiltration membrane NF270. The compounds examined were tested using a cross flow NF/RO cell membrane filtration system for 24 hours under three different pH conditions (4.7, 7 and 11). The feed solution pH effected considerably on the hydrophobicity, charge and the adsorption of dissociable organic compounds and therefore it affected the rejection efficiency of these compounds. Experimental results showed that most of the hydrophobic trace organic contaminants significantly adsorbed onto the membrane, whereas hydrophilic trace organic contaminants less adsorbed compared with hydrophobic compounds at the experimental conditions. Results reported in this study also indicated that the hydrophilic compounds exhibited better rejection values compared to hydrophobic compounds. The rejection efficiency of all these compounds was different depending on the feed solution pH as well as the physicochemical properties of each compound.

Keywords: Nanofiltration (NF), Trace organic contaminants (TrOCs), Adsorption, Rejection efficiency

1 Introduction

Over the last few decades, there has been much research on the rejection of trace organic contaminants (TrOCs) such as endocrine disrupting chemicals (EDCs), pharmaceuticals and pesticides by nanofiltration (NF) membranes [1-4]. The rejection of TrOCs by NF membranes can be governed by several mechanisms. These include size exclusion, adsorption onto the membrane surface, diffusion across the membrane, and electrostatic interaction [5,6]. In addition, there are a number of factors which may influence their rejection including the physicochemical properties of the compounds, characteristics of the membrane, operating conditions and feed water composition [7]. In particular, the feed solution pH can be considered one of the most important parameters influencing the hydrophobicity, the adsorption and the chemical speciation of dissociable organic compounds as well as the membrane surface charge during the experiment. Therefore, pH is expected to affect the effective rejection of organic compounds [8,9].

Braeken et al. [10] and Arsuaga et al. [11] observed a decrease in rejection with increasing compound hydrophobicity due to adsorption onto the membranes during filtration. Additionally, Nghiem et al. [12,13] found that the solution pH affected the hydrophobicity and net charge of selected pharmaceutically active compounds (PhACs) and that this influenced their adsorption and rejection throughout the experiment by NF membranes. Furthermore, Boussu et al. [14] argued that charged TrOCs were better rejected at pH 10 than at pH 3. More recently, Schäfer et al. [15] reported that rejection of estradiol at pH 11 stabilised at 85 %, while at pH 7 rejection was only 60 %. This was attributed to the occurrence of charge repulsion between the negatively charged NF membranes and the negatively charged estradiol, leading to greater rejection at pH 11 compared to pH 7. Although these recent studies have explored the removal of TrOCs by NF membranes and underlying mechanisms under different pH conditions, the current understanding of the rejection of these compounds remains rather limited. Moreover, amongst the various rejection mechanisms, the influence of adsorption of organic compounds onto the NF membranes is still difficult to quantify. Therefore, a complete understanding of the adsorption mechanism of TrOCs onto NF membranes as well as the effective rejection of these compounds in treatment processing is still a challenging issue and requires further study.

The objectives of the current work are to study the adsorption of the selected TrOCs onto the NF270 membrane at different pH values (4.7, 7, and 11) and evaluate their effective rejection. Experiments were conducted using a laboratory scale cross flow NF/RO cell membrane filtration system with 8 selected hydrophilic and hydrophobic TrOCs. These compounds have a wide range of physicochemical properties and represent major classes of contaminant. The results enable the evaluation of the role of adsorption on rejection performance of trace organic compounds during NF separation.

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2 Materials and Methods

2.1 Nanofiltration membrane

The NF270 membrane (Dow-Filmtec, Minneapolis, MN) was selected for this study. According to the manufacturer, it is a thin-film composite polyamide membrane that is widely used for water and wastewater treatment application. This is a loose NF membrane with a relatively high permeability (of approximately 11 L/bar m^2 h). At pH 4 and above, this membrane is negatively charged [12]. The flat sheet membrane samples were stored dry before use.

2.2 Trace organic contaminants and analytical chemicals

The target TrOCs for this research have been chosen from the major classes of EDCs and PhACs. They have diverse physicochemical properties such as hydrophobicity, charge, solubility, and molecular size. A stock solution was prepared at a concentration of 1 mg/mL in pure methanol. A working solution of these TrOCs was also prepared in pure methanol. Both these solutions were stored in a freezer at -18 ºC prior to use.

The major physicochemical properties of the target organic contaminants are shown in Table 1. The compounds selected for this investigation exhibited considerably difference in their physicochemical properties. These compounds have low molecular weight. However, they are markedly different in their dissociation constants (pK_a) and hydrophobicity properties. Most TrOCs are weak acids and will dissociate into an ionic form at pH above the pK_a. Based on the selected organic compounds pK_a values listed in Table 1, it can be seen that carbamazepine is uncharged and exists in a neutral form at all pH conditions of the experiment, whereas diclofenac and ibuprofen are mostly deprotonated, resulting in negative charge. At pH 4.7, the other all organic contaminants are uncharged and exist in mostly as a neutral species. When the experiments are performed at pH 7, gemfibrozil has a net negative charge whereas the other TrOCs are uncharged. At pH 11, carbamazepine is uncharged while all the other TrOCs are negatively charged.

On the other hand, it is striking to note that the intrinsic hydrophobicity of TrOCs was further found to be key to their adsorption onto the membrane surface and was an important factor in determining their rejection by a NF/RO process [11]. The logarithm of the effective octanol-water distribution coefficient, log D, is a good parameter which can be used to evaluate the hydrophobicity of TrOCs at any pH value [16,17]. Organic compounds with log D equal to 3 or higher are generally referred to as hydrophobic. By contrast, organic compounds with log D below 3 are referred to as hydrophilic [17,18]. Apart from that, data in Table 1 indicate that the log D of ibuprofen, gemfibrozil, and diclofenac decrease while the log D of other compounds do not change as the pH increases from 4.7 to 7. However, when the pH increases to 11, except for carbamazepine, the log D of almost all the other organic compounds decrease, leading to a variation in their hydrophobicity behaviour. The changes in hydrophobicity and other physicochemical properties of the compound at different pH values may have significant implications for the rejection mechanisms of these organic contaminants.

Table 1: Physicochemical properties of the selected trace organic contaminants

Organic compounds	Molecular formula	Molecular weight (MW) (g/mol)	Log K_{ow} ^{a}	pK_a ^{a}	Log D ^{b}		
					pH 4.7	pH 7	pH 11
Carbamazepine	$C_{15}H_{12}N_2O$	236.27	1.895	13.94	1.89	1.89	1.89
Estriol	$C_{18}H_{24}O_3$	288.38	2.527	10.25	2.53	2.53	1.71
Ibuprofen	$C_{13}H_{18}O_2$	206.28	3.502	4.41	3.03	0.94	-3.09
Gemfibrozil	$C_{15}H_{22}O_3$	250.33	4.302	4.75	4.03	2.07	-1.95
Diclofenac	$C_{14}H_{11}Cl_2NO_2$	296.15	4.548	4.18	3.91	1.77	-2.27
4-tert-butylphenol	$C_{10}H_{14}O$	150.22	3.397	10.13	3.40	3.40	2.47
4-tert-octylphenol	$C_{14}H_{22}O$	206.32	5.180	10.15	5.18	5.18	4.27
4-n-nonylphenol	$C_{15}H_{24}O$	220.35	6.142	10.15	6.14	6.14	5.23

^{a} Scifinder Scholar, ^{b} calculated by the equation: $\log D_{(pH)} = \log K_{ow} - \log(1+10^{(pH-pK_a)})$.

Chemical solutions and feed waters were prepared with Milli-Q water. Both the solvents used for solid phase extraction and analysis of samples including methanol and dichloromethane, purchased from Sigma-Aldrich (Sydney, Australia). Internal standard of bisphenol A-d_{16} and N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) containing 1 % of trimethylchlorosilane (TMCS). Pyridine used in the derivatization process. All reagents and chemicals were purchased from Sigma-Aldrich (Sydney, Australia).

2.3. Cross flow NF/RO membrane filtration system

A cross flow membrane filtration system used in this study (Figure 1). The system consisted of a stainless steel NF/RO membrane cell with an effective surface area of 40 cm^2 (4 cm × 10 cm) with a channel height of 2 mm, and a stainless steel feed reservoir of 10 litres. A Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN) capable of providing a maximum pressure of 6,800 kPa and a flow rate of 4.2 litres per minute was employed. The temperature of the experimental solution was controlled by a chiller/heater (Neslab RTE 7) equipped with a stainless steel heat exchanger coil submersed in a stainless steel feed reservoir. A digital flow meter (Optiflow 1000, Agilent Technologies, Palo Alto, CA) connected to a PC was utilized to measure permeate flow, and the cross flow was monitored with a manual flow meter.

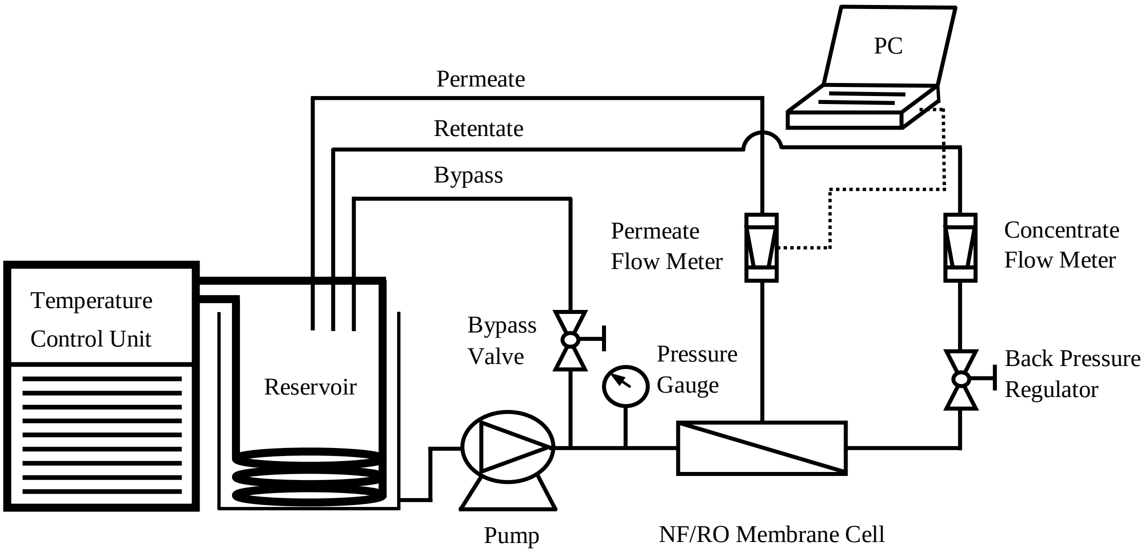

Figure 1: Schematic diagram of the cross flow NF/RO filtration system

2.4 Experimental protocol

All experiments were performed in background buffer solutions under three different pH conditions (pH 4.7, 7 and 11) and conducted over 24 hours. Before use, all the membrane samples were rinsed with tap water and Milli-Q water to remove any preservative layer. Subsequently, they were compacted using Milli-Q water at 1,000 kPa for at least one hour until a stable permeate flux has been obtained. The background buffer solution was then added to the feed reservoir, and made up to the total feed volume of 10 litres. For the experiment at pH 4.7, an acetate buffer solution containing 1 mM of $CaCl_2$, 5.5 mM of CH_3COOH, and 5.5 mM of CH_3COONa was utilized. A phosphate buffer solution contained 10 mM of NaCl, 1 mM of $CaCl_2$, and 1 mM of NaH_2PO_4 was used for the experiment at pH 7. The pH 11 experiment was conducted in a carbonate buffer solution, which contained 0.2 mM of NaCl, 0.3 mM of $NaHCO_3$, and 4.5 mM of Na_2CO_3. During the experiment, the feed reservoir temperature and cross flow velocity were kept constant at 20 ± 0.1 °C and 42 cm/s, respectively. The permeate flux was set to the manufacturer's quoted nominal membrane flux of 42 L/m^2h throughout the experiment. Both permeate and retentate were recirculated to the feed reservoir. A mixture of 8 selected trace organics was then added to the feed reservoir to obtain a concentration of 25 μg/L of each. To maintain the feed solution pH during the experiment, a certain amount of 0.2 M of CH_3COOH, 1 M of NaOH and 1 M of Na_2CO_3 was added to adjust the solution pH for the experiment at pH 4.7, pH 7 and pH 11, respectively. Approximately 100 mL of feed and permeate samples were taken at specific times. Samples were stored in clean glass bottles, wrapped in aluminium foil, stored in the fridge for subsequent extraction and GC/MS analysis.

The effective rejection was defined as R (%): $R = 100 \times (1 - \frac{C_p}{C_f})$, where C_f and C_p were the feed and the permeate concentrations, respectively. Adsorption of TrOCs (A, %) onto the membranes at the end of filtration stage was determined by mass balance: $A = 100 \times (1 - \frac{C_{f2}}{C_{f1}})$, where C_{f1} and C_{f2} were the initial and final organic compound concentration in the feed solution, respectively.

2.5 Analytical methods

The Oasis HLB SPE cartridges (6 mL, 200 mg, Waters, Milford, MA, USA) for extraction of the trace organic contaminants in feed and permeate samples were used in this investigation. The feed and permeate samples of 100 mL were allowed to reach room temperature and adjusted by 4 M sulphuric acid to pH range between 2 and 3. Before the samples were extracted, the SPE cartridges were conditioned sequentially by 7 mL dichloromethane and methanol (1:1, v/v), 7 mL methanol, and about 2 x 7 mL reagent water on a vacuum manifold at a flow rate of 2 mL/min. Subsequently, the samples were passed through the cartridges with a flow rate of 2 mL/min. The loaded cartridges were washed with 6 x 7 mL of Milli-Q water and dried under vacuum for 30 minutes along with a stream of nitrogen. The SPE columns containing the TrOCs were eluted with 7 mL methanol followed by 7 mL dichloromethane and methanol (1:1, v/v) at a flow rate of 1 - 5 mL/min. The elution volume was then evaporated to dryness under a gentle stream of nitrogen in a water bath at 40 °C. An amount of 200 µL methanol solution containing 5 µg bisphenol $A\text{-}d_{16}$ was utilized to dissolve the extracted residues, and was transferred into 1.5 mL vials before further evaporation to dryness under a gentle nitrogen stream. Finally, the derivatization of the dried residues in the vials was performed by adding 100 µL of BSTFA (N,O-bis (trimethylsilyl) trifluoroacetamide) (1 % TMCS (trimethylchlorosilane)) and 100 µL of pyridine (dried with KOH solid). The conditions of the derivatization reaction were 30 min at 60 - 70 °C. The derivatives were allowed to cool to room temperature before analysis by GC-MS [19].

A Shimadzu GCMS-QP5000 system consisting of a Shimadzu AOC 20i autosampler and a Phenomenex Zebron ZB-5 (5 % diphenyl - 95 % dimethylpolysiloxane) capillary column (30 m × 0.25 mm ID, df = 0.25 µm) was used to determine the concentrations of the organic compounds.

Helium was used as the carrier gas at a constant flow rate of 1.3 mL/min. The GC oven temperature program was conducted as follows: 100 °C for 1 min, first ramp 10 °C/min to 175 °C, 3 min at 175 °C, second ramp 30 °C to 210 °C, third ramp 2 °C/min to 228 °C, fourth ramp 30 °C to 260 °C, fifth ramp 3 °C/min to 290 °C, 3 min at 290 °C. The injector port and the temperature of the GCMS interface were set at 280 °C. A sample volume of 1 µL was injected in splitless mode.

The MS was obtained by electron impact ionisation in full scan mode from 50 to 600 of m/z, and later on in selected ion monitoring (SIM) mode for qualitative determinations. The most abundant ions of each organic compound were selected from its spectrum for quantitation, in accordance with previous studies [20,21]. A series of standard TrOCs at 1, 10, 50, 100, 500, and 1000 ng/mL and a bisphenol A-d_{16} internal standard were prepared for the instrument calibration. The calibration curves obtained for each compound had correlation coefficients greater than 0.99. The detection limits and quantification limits for analytes were estimated with the signal to noise (s/n) ratio higher than 3 and higher than 10, respectively.

A Metrohm model 744 pH Meter was calibrated before beginning of an experiment and utilized to measure the feed solution pH for the duration of the experiment.

3 Results and Discussions

3.1 Adsorption of trace organic contaminants to NF270 membrane

Adsorption levels of both hydrophilic and hydrophobic organic compounds to NF270 membrane under the three different pH conditions (pH 4.7, 7 and 11) is shown in Figure 2, Figure 3 and Figure 4.

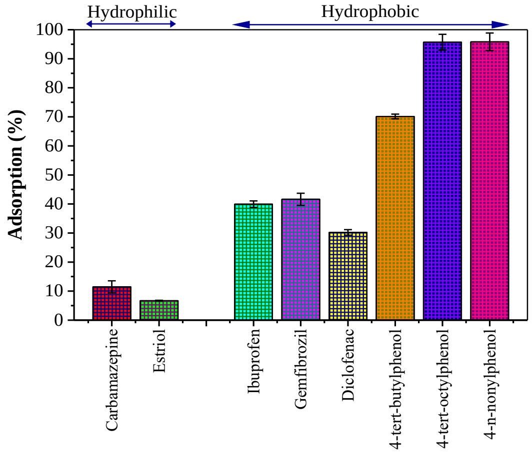

Figure 2: Adsorption of hydrophilic and hydrophobic TrOCs to the NF270 membrane at pH 4.7. The error bars present standard deviation of data obtained from two independent experiments

It can be observed that at all pH conditions, the hydrophobic TrOCs significantly adsorbed onto the NF270 membranes after 24 hours of filtration, while the hydrophilic TrOCs exhibited much lower and more variable adsorption levels. They adsorbed much less compared to hydrophobic species at all pH conditions employed. Adsorption levels of hydrophobic TrOCs approximately ranged from 30 to 96%, 80 to 94% and 69 to 93% at pH 4.7, pH 7 and pH 11, respectively. The corresponding values for hydrophilic TrOCs were approximately in the range of 7 - 11%, 6 - 29% and 3 - 43% at pH 4.7, pH 7 and pH 11, respectively.

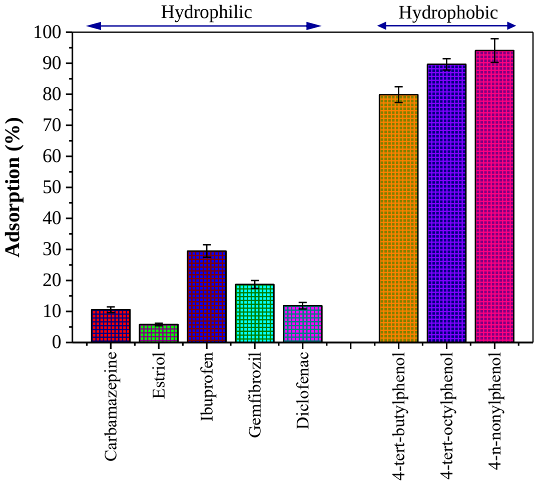

Figure 3: Adsorption of hydrophilic and hydrophobic TrOCs to the NF270 membrane at pH 7. The error bars present standard deviation of data obtained from two independent experiments

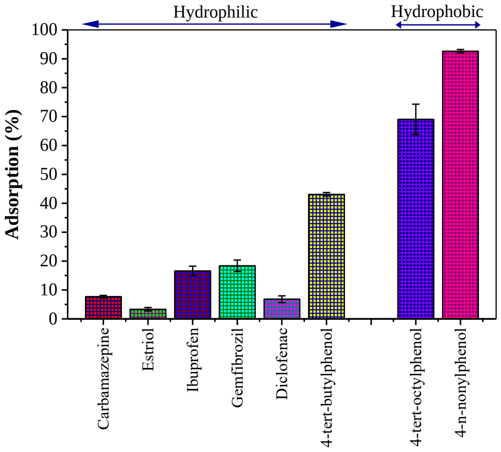

Figure 4: Adsorption of hydrophilic and hydrophobic TrOCs to the NF270 membrane at pH 11. The error bars present standard deviation of data obtained from two independent experiments

These study results could be explained by the specific interactions between the TrOCs and membranes surface. The hydrophobic TrOCs showed significant affinity with the NF270 membrane, leading to an increased partitioning and a facilitated transport of them onto the membrane, resulting in their strong adsorption onto this membrane. In contrast, hydrophilic TrOCs have a lower affinity for the membrane, displayed by their relatively low log D values (< 3). As a result, they were adsorbed less compared to hydrophobic species at all pH conditions. These results were in general agreement with numerous previous studies [8,13,14]. Kimura et al. [22] and Yoon et al. [23] reported that hydrophobic TrOCs were adsorbed onto the membrane surface depending on membrane properties and feed solution pH. In addition, previous studies have found that hydrophobic TrOCs adsorbed quite strongly onto membrane over a relatively long period of time, whereas hydrophilic TrOCs less adsorbed and among them, there are many compounds did not adsorb to the membrane during the filtration [14,24,25].

3.2 Rejection of trace organic contaminants by NF270 membrane

The difference in rejection efficiency of hydrophilic and hydrophobic TrOCs after 24 hours of filtration using the NF270 membrane at three pH values of pH 4.7, 7 and 11 is illustrated in Figure 5, Figure 6 and Figure 7.

In most cases, the rejection efficiency for most hydrophilic TrOCs were higher than for hydrophobic TrOCs at all experimental pH conditions. Rejection efficiency of the hydrophilic TrOCs were up to 79%, 98% and 99% at pH 4.7, pH 7 and pH 11, respectively, while the corresponding maximum rejection values of hydrophobic TrOCs were 76%, 77% and 83% at pH 4.7, pH 7 and pH 11, respectively. These phenomena can be attributed to the dominance of adsorption as a rejection mechanism. Hydrophobic TrOCs significantly adsorbed onto the membrane, resulting in an increase partitioning of these compounds into the membrane and therefore a rise in transport through the membrane, resulting in a reduced rejection. These observations can be supported by the investigations of Boussahel et al. [26] and Bellona and Drewes [3], who also hypothesized that the adsorbed solute can partition and diffuse across a membrane and reduce rejection considerably through partitioning into the permeate during long-term operation. Findings in this study also agree with the surveys made by Kunst and Košutić [27], who suggested that hydrophobicity of TrOCs also bring about the evolution of the permeate concentration, showing a decrease of their rejection efficiency due to these compounds adsorption on the membrane surface or inside the membrane pores. Kimura et al. [22] and Hu et al. [28] concluded the same from their study.

Findings in the current study also showed rejection values of most of the hydrophilic and hydrophobic TrOCs at pH 11 were remarkably higher than their corresponding data at pH 4.7 and pH 7. The contribution of the increased negative charge of both the membrane and the compounds are directly responsible for the improved rejection through electrostatic repulsion at basic pH. It was already reported in most investigations on electrostatic interactions that an increase in rejection of negatively charged compounds by NF membranes due to electrostatic repulsion between the negatively charged solute and the negatively charged membrane [6,13].

4. Conclusions

The results demonstrated that significant adsorption of hydrophobic TrOCs to the NF270 membrane at pH 4.7, 7 and 11 occurred over 24 hours of filtration. At all experimental pH conditions, the adsorption of hydrophobic TrOCs was considerably higher than for the hydrophilic TrOCs. This was influenced by the affinity interactions between the TrOCs and membranes surface.

Results reported here also show that hydrophilic TrOCs showed better rejection efficiencies compared to hydrophobic TrOCs all experimental pH conditions. This can be due to the adsorption and diffusion of these compounds across membrane. Higher rejection efficiency of TrOCs at pH 11 compared to pH 4.7 and pH 7 could be attributed to the importance of electrostatic repulsion at high pH in addition to the effect of adsorption.

Acknowledgements

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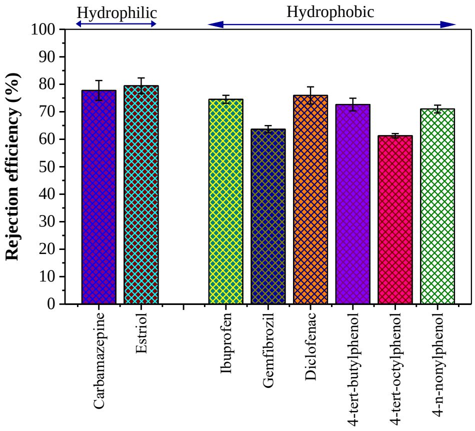

Figure 5: Rejection of the hydrophilic and hydrophobic TrOCs by the NF270 membrane at pH 4.7. The error bars present standard deviation of data obtained from two independent experiments

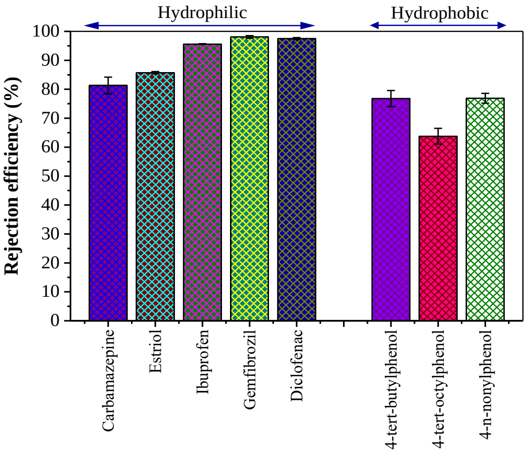

Figure 6: Rejection of the hydrophilic and hydrophobic TrOCs by the NF270 membrane at pH 7. The error bars present standard deviation of data obtained from two independent experiments

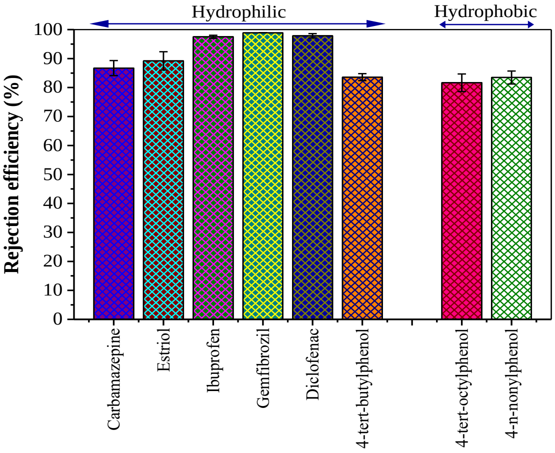

Figure 7: Rejection of the hydrophilic and hydrophobic TrOCs by the NF270 membrane at pH 11. The error bars present standard deviation of data obtained from two independent experiments

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