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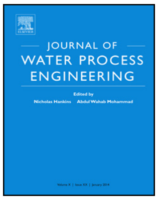

Removal of volatile organic compounds (VOCs) from groundwater by reverse osmosis and nanofiltration

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ABSTRACT

A comprehensive study was conducted to examine the removal of volatile organic compounds (VOCs) which exist in groundwater at Southlands-Botany Bay (Sydney region). The ability of nanofiltration (NF) and reverse osmosis (RO) as advanced treatments was investigated using two commercially available NF or RO membranes. Laboratory-scale tests were used with cross-flow; tests were conducted with 16 ubiquitous compounds that represented the significant volatile organic compounds found in the contaminated groundwater.

The results reported in this study indicate that the removal efficiency of reverse osmosis (RO) was better than NF in rejecting the VOCs detected in groundwater. This study revealed that the performance of NF and RO membranes in rejecting hydrophilic volatile organic compounds was higher than that for hydrophobic compounds and the highest rejection achieved by NF and RO membranes amounted 98.4% and 100%, respectively. Hydrophilic compounds can be effectively rejected by NF/RO membranes using the size exclusion mechanism (steric hindrance), whereas hydrophobic compounds can be adsorbed into NF/RO membranes and then diffuse through the dense polymeric matrix, resulting in the lower removal for these compounds compared to hydrophilic compounds.

1. Introduction

The occurrence and fate of volatile organic compounds (VOCs) in surface and groundwater has been identified as a significant environmental health concern [1,2]. It would be fair to say that there is full agreement between the scientific community and water authorities to minimise volatile organic compounds, however, the majority of these contaminants in the environment are still poorly understood, and are a topic of growing interest from both research and regulatory perspectives. Reclaimed wastewater, in particular, has some significant benefits, including high reliability of supply, a known quality and frequently, a centralized source near urban demand centers.

In the last decade, nanofiltration (NF) and reverse osmosis (RO) have been proposed as attractive technologies for removal of organic trace contaminants including volatile organic compounds from the aquatic environment instead of conventional wastewater treatment [3–7]. It can be recognised that conventional treatment processes, such as chemical precipitation, ion exchange and electrochemical removal, are insufficient to remove and minimize organic contaminants to acceptable regulatory standards. Several previous studies have demonstrated the excellent capability of NF/RO to remove a wide range of volatile organic compounds including trihalomethanes, organochloric compounds, petroleum hydrocarbons and other low molecular weight compounds such as toluene and trichloroethylene [5,8]. These studies have also revealed a substantial degree of complexity associated with the separation processes involved. As a result, various parameters such as membrane properties, solution chemistry and physicochemical properties of the volatile organic compounds can significantly affect the removal efficiency of these components by NF/RO membranes [5,8]. Also Yangali-Quintanilla et al. [9] reported that the clean NF-90 membrane (virgin) rejected almost all of the hydrophobic neutral compounds (95–98%) mainly because of size exclusion. High rejection was achieved after using the RO stage (>99% for macrolides, pharmaceuticals, cholesterol and disinfection byproducts, 95% for diclofenac, and >93% removal of sulphonamides [10]). The removal of triclosan by RO membranes was almost 100% since the molecular width of this compound was greater than the estimated mean effective membrane pore size [11]. Great rejection (90–100%) was achieved after using the RO (virgin XLE) to examine

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the removal of six pharmaceuticals and personal care products and size exclusion was the dominating mechanism [12].

A sieving mechanism, integrating molecular width and molecular length as the size parameters, and an interaction component with a logarithmic octanol–water partitioning coefficient (Log K_{ow}) gave the best expectation for the retention of volatile organic compounds by membranes. Solutes with larger widths, larger lengths and higher Log K_{ow} will have higher retentions for most of the membranes used [8]. Thus the separation of volatile organic compounds by NF/RO processes is based predominantly on size exclusion [5]. In the case of charged trace organic compounds, electrostatic interactions between the charged solute and the negatively charged membrane surface can also play a key role [13,14]. Additionally, it has been demonstrated that hydrophobic compounds can adsorb onto membrane surfaces and subsequently may diffuse through RO and especially NF membranes, resulting in lower rejections than would be expected based only on size exclusion mechanisms. In this case hydrophobicity is considered an important factor affecting rejection [15].

One of the objectives of this study was to examine the removal of volatile organic compounds by using a NF/RO filtration system. Experiments were conducted at laboratory-scale using commercially available NF/RO membranes, namely NF-90 and ESPA2. Sixteen volatile organic compounds with molecular weights between 78.11 g/mol (benzene) and 260.76 g/mol (hexachlorobutadiene) were used as model organic contaminants due to their widespread occurrence in groundwater. Removal efficiency by NF/RO filtration was linked to the physicochemical properties of these compounds to focus on the ability and effectiveness of this kind of treatment. Substantial characterisation work has been conducted to investigate the NF/RO membranes.

1.1. Study area

In this study contaminated groundwater samples have been collected from Botany Bay. In the Botany area samples have been collected from two contaminated sites, namely EWB10D and EWB13D. Fig. 1 illustrates samples sites in the Sydney (Botany Bay) region.

2. Materials and methods

2.1. Laboratory-scale NF/RO filtration system

A laboratory-scale, cross-flow membrane filtration system with a stainless steel cross-flow cell was constructed for this study (Fig. 2). The cell had an effective membrane area of 40 cm^2 (4 cm × 10 cm) and a channel height of 2 mm. The system was equipped with a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN). The temperature of the test solution was kept stable using a Neslab RTE 7 chiller/heater equipped with a stainless steel heat exchanger coil that was submerged directly into a stainless steel reservoir. The permeate flow was measured by a digital flow meter (Optiflow 1000, Agilent Technologies, Palo Alto, CA) connected to a personal computer, and the cross-flow rate was monitored using a rotameter.

2.2. NF/RO membranes

A NF membrane (namely NF-90) and a RO membrane (namely ESPA2) were used in this project. NF-90 was obtained from Dow Film Tec (Minneapolis, MN, USA) whereas the ESPA2 was obtained from Nitto Denko (Oceanside, CA, USA). These membranes were received as flat sheet samples and stored dry. All membranes used in this study are made of a thin aromatic (or semiaromatic) polyamide active layer and thicker more porous supporting layer. Physicochemical characteristics of these membranes are illustrated in Table 1. Based on their estimated pore size, the NF-90 membrane could be classified as a tight nano-filtration membrane whereas ESPA2 can be assumed to have no obviously defined pore structure.

2.3. NF/RO membrane characterisation

The surface streaming potential of the membrane was measured using a SurPASS Electrokinetic Analyzer (Anton Paar GmbH, Graz, Austria) in a 1 mM KCl background solution. To calculate the zeta potential from the measured streaming potential the Fairbrother–Mastin method was used, which was performed at 500 mbar and at room temperature (25 ± 1 °C). The zeta potential of each membrane sample was measured four times, by repeatedly reversing the direction of electrolyte flow at each pH value. Apparatus error counted for less than 0.5 mV of the measurement at any given pH value. Analytical grade potassium hydroxide and hydrochloric acid were used to regulate the pH via automatic titration.

According to Alturki et al. [16] the contact angle can be measured with a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ) by means of the standard sessile drop method. Milli-Q water is used as the reference solvent. The membranes are air dried before the measurement. No less than 5 droplets are applied onto duplicate membrane samples and contact angle is measured on both sides of the droplet.

The surface topography for NF/RO membranes was investigated by means of atomic force microscopy (AFM). On the other hand, the surface morphology and distribution of organic compounds deposited on the membrane surface were examined using field-emission scanning electron microscopy (SEM) on a JEOL JSM-7500FA—(BRUKER-QUANTAX 400), with additional semi-quantitative energy dispersive spectrometer (EDS) analysis.

2.4. Model organic contaminants

Sixteen compounds were used in this study to represent the major organic groups considered contaminants in groundwater samples—namely volatile organic compounds (e.g., dichloromethane, trichloroethylene, tetrachloroethylene, toluene and benzene). The analysis of these compounds was also based on their widespread occurrence in groundwater and their diverse physicochemical properties (e.g., hydrophobicity and molecular size). Key physicochemical properties of these organic contaminants are shown in (Table 2). The volatile organic compounds had molecular weights between 78.11 g/mol (benzene) and 167.85 g/mol (1,1,2,2-tetrachloroethane). The intrinsic hydrophobicity of these compounds varied significantly, as was reflected by the values of their octanol–water partitioning coefficient (Log K_{ow}) or Log K_{ow} at specific pH (Log D). As can be seen in Table 2, the properties of the selected volatile organic compounds demonstrated that some compounds are hydrophilic (Log $D > 2.5$) while others are hydrophobic (Log $D < 2.5$) and ranged between 1.40 and 3.07 (log D at pH 7 and 8). However, most volatile organic compounds which were examined in this study are hydrophobic (Log $D < 2.5$).

2.5. Volatile organic compounds analysis

All samples collected before and after using the NF/RO filtration system were analyzed at ORICA Botany Environmental Laboratories. VOCs were analyzed using a Shimadzu purge and trap/Gas Chromatography/Mass Spectrometer Detector based on USEPA Methods 5030 and 8260. Method 5030 can be utilized for most volatile organic compounds that have boiling points below 200 °C and are insoluble or somewhat soluble in water. This method can include volatile water-soluble compounds; nevertheless,