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# Study of the removal capacity of 2-MIB and geosmin by nanofiltration membranes pretreated in water and 50% (v/v) aqueous ethanol solution

## Estudo da capacidade de remoção de 2-MIB e geosmina por membranas de nanofiltração pré-tratadas em água e solução aquosa de etanol 50% (v/v)

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## ABSTRACT

Nanofiltration membranes are highly effective in removing low-molecular weight compounds, which include the secondary metabolites 2-methylisoborneol (2-MIB) and 1,10-dimethyl trans-9-decalol (Geosmin), produced by cyanobacteria and difficult to remove by conventional treatment processes. Considering that high retention and permeate flux are important characteristics in the process, this study aimed to evaluate the efficiency of the NF90 membrane pretreated with water and 50% (v/v) ethanol solution in the retention of 2-MIB and Geosmin, considering the application of low constant working pressure values of 4, 7, and 10 bar and evaluating its permeability to water and metabolite retention capacity. Retention was evaluated from a concentration of 100 ng $L^{-1}$ of 2-MIB and Geosmin for 120 min of filtration time. The occurrence of fouling was also evaluated, noting that there was no fouling. At the three pressure values considered, membranes pretreated in 50% (v/v) ethanol solution showed a higher permeate flux (91.4 L $m^{-2}$ $h^{-1}$ at 225.4 L $m^{-2}$ $h^{-1}$) than that observed for membranes treated in water (34.08 L $m^{-2}$ $h^{-1}$ at 59.14 L $m^{-2}$ $h^{-1}$). As for retention, no significant differences were observed between the membranes, with removals of 93 and 99% being obtained for membranes pretreated in 50% (v/v) ethanol solution and water, respectively. It can be observed that the pretreatment conserved the efficiency in the retention of compounds and provided an improvement in the physical and chemical characteristics of the membrane, allowing the achievement of permeate fluxes greater than those observed with the membrane pretreated in water.

**Keywords:** secondary metabolites; nanofiltration membranes; ethanol.

## RESUMO

Membranas de nanofiltração apresentam elevada eficácia na remoção de compostos de baixa massa molar, o que inclui os metabólitos secundários 2-metilisoborneol (2-MIB) e 1,10-dimetil trans-9-decalol (Geosmina), produzidos por cianobactérias e de difícil remoção por processos convencionais de tratamento. Considerando-se que elevada retenção e fluxo permeado são características importantes no processo, este estudo teve por objetivo avaliar a eficiência da membrana NF90 pré-tratada com água e solução de etanol 50% (v/v) na retenção de 2-MIB e Geosmina, considerando-se a aplicação de baixas pressões constantes de trabalho 4, 7 e 10 bar, avaliando-se a sua permeabilidade à água e capacidade de retenção dos metabólitos. A retenção foi avaliada com a concentração de 100 ng $L^{-1}$ de 2-MIB e Geosmina por 120 minutos de tempo de filtração. A ocorrência de *fouling* foi igualmente avaliada constatando-se não haver incrustação. Nas três pressões empregadas, membranas pré-tratadas em solução de etanol 50% (v/v) apresentaram um fluxo permeado superior (91,4 L $m^{-2}$ $h^{-1}$ a 225,4 L $m^{-2}$ $h^{-1}$) ao observado para membranas tratadas em água (34,08 L $m^{-2}$ $h^{-1}$ a 59,14 L $m^{-2}$ $h^{-1}$). Quanto à retenção, não foram observadas diferenças expressivas entre as membranas, tendo-se obtido remoções de 93 e 99% para membranas pré-tratadas em solução de etanol 50% (v/v) e água, respectivamente. Pode-se observar que o pré-tratamento conservou a eficiência na retenção de compostos e propiciou a melhoria das características físicas e químicas da membrana, permitindo a obtenção de fluxos permeados maiores do que o observado com a membrana pré-tratada em água.

**Palavras-chave:** metabólitos secundários; membranas de nanofiltração; etanol.

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## Introduction

Climate changes, as well as the anthropogenic activities that result in the dumping of domestic and industrial effluents without proper treatment, cause serious health problems, which include an increase in the amount of organic matter in water bodies and uncontrolled growth of microorganisms such as microalgae and cyanobacteria, and the consequent production of secondary metabolites (Sauvé and Desrosiers, 2014; Glibert, 2017). These metabolites are produced as a defense function of these microorganisms (Herrero and Flores, 2008), some being toxic to living beings, such as cyanotoxins, while others can affect organoleptic characteristics (Bortoli and Pinto, 2015), such as 2-methylisoborneol (2-MIB) and 1,10-dimethyl trans-9-decalol (Geosmin). In a conventional water treatment system for supply, under appropriate conditions, it is possible to retain intact cells of cyanobacteria, but it is not possible to retain dissolved metabolites (Srinivasan and Sorial, 2011), which can make the distribution of water unfeasible either by the presence of toxic compounds or by the reduced acceptance of the population in terms of organoleptic quality.

The 2-MIB compounds and Geosmin, secondary metabolites commonly found in drinking water, are cyclic aliphatic tertiary alcohols that impart flavor and odor to water, being perceptible by consumers at very low concentrations, even below 4 and 20 ng $L^{-1}$ (Srinivasan and Sorial, 2011). Cortada et al. (2011) indicated that the perceptible values would be between 4 and 10 ng $L^{-1}$ for Geosmin and between 9 and 42 ng $L^{-1}$ for 2-MIB. Although there is no specific regulation (Reiss et al., 2006) and these compounds are not toxic to humans, they are associated with the taste and odor of earth and mold, causing consumer distrust of drinking water treatment and distribution companies (Zamyadi et al., 2015). These compounds can drastically affect the aquaculture and industrial and agricultural processes, as they attribute undesirable flavor to fish meat, making its commercialization unfeasible (Cortada et al., 2011; Souza et al., 2012).

As they are chemically water soluble, 2-MIB and Geosmin are not easily removed by the conventional water treatment system (Almeida et al., 2015). The process of removing these compounds is considered effective when alternative treatment techniques are used, such as adsorption on activated carbon (powdered or granular), ozonation, and membrane filtration. However, the adsorption processes have some limitations, since for their effectiveness they need a long time to reactivate the adsorbent, thus making the system expensive. In addition, the adsorption process is affected by the presence of organic compounds in water, which have a high affinity for coal, which can compromise its shelf life (Matsui et al., 2013, Faruqi et al., 2018; Mustapha et al., 2021). The promising techniques presented in studies refer to advanced oxidative processes (AOPs) that degrade emerging organic compounds (Mustapha et al., 2021); however, they have challenges in their effectiveness. In a literature review, Srinivasan and Sorial (2011) observed that these processes depend on the control of several water quality parameters such as pH, amount of organic matter, conditions such as light intensity, catalyst load, the dosage of compounds, the formation of toxic and undesirable by-products, and costly energy, material, and system control costs.

Nanofiltration is considered an appropriate complementary technology for the removal of low-molecular weight compounds, including cyanotoxins, 2-MIB, and Geosmin (Mody, 2004; Dixon et al., 2011). However, there are few studies related to the retention of 2-MIB and Geosmin metabolites by nanofiltration membranes without previous treatment. Some of them evaluated the retention efficiency of the compounds in a tangential filtration system in different types of nanofiltration membranes. Mody (2004) found that only two of the tested nanofiltration membranes (NF90 and LFC1) were efficient in removing 2-MIB and Geosmin, with retention values greater than 92% at a 7 bar pressure, obtaining permeate concentrations lower than those perceptible to humans. Other studies evaluated the efficiency of rejection of these compounds in water supplies by NF90 (polyamide) nanofiltration membranes, obtaining results of retentions above 80% of these compounds in water (Dixon et al., 2011; Zat and Benetti, 2011; Yu et al., 2014). To obtain these results, Dixon et al. (2011) considered a concentration of metabolites equal to 100 ng $L^{-1}$, 4.8 bar working pressure, and a contact time of 220 h. Zat and Benetti (2011) used an analyte concentration of 1.184 ng $L^{-1}$, with pressure values of 8.1 and 9 bar for a contact time of 125 min. Yu et al. (2014), in turn, evaluated the removal at a concentration of 2000 ng $L^{-1}$, at 4.1 bar and a contact time of 3 h. Chung et al. (2018) used nanofiltration ceramic membranes to remove Geosmin and obtained 65% removal. Li et al. (2019) employed the solvent-free NF90 membrane in a pilot water treatment unit in China and obtained removal rates of 75.69 and 58.20% for 2-MIB and Geosmin (168.28 and 182.31 Da), respectively. This demonstrates that nanofiltration allows the removal of compounds with a molar mass lower than 200 Da. Li et al. (2020) obtained 75.09 and 58.20% removals for 2-MIB and Geosmin, respectively, from a nanofiltration system with an NF90 membrane, having feeding flux from a conventional water treatment system. The previously mentioned studies obtained high-retention values without any kind of previous treatment to improve the permeate flux in the membranes, having only evaluated the retention efficiency of these compounds.

To improve long-term, permeate flux performance, increase membrane stability and permeability, and maintain removal efficiency, surface treatment of membranes with organic solvents has been studied and used in water treatment for the removal of organic and inorganic compounds (Geens et al., 2004; Vankelecom et al., 2005; Zhao; Yuan, 2006a, 2006b). Zhao and Yuan (2006b) used organic solvents as a supply to assess the permeability of nanofiltration membranes and observed that the interaction between membrane and supply resulted in significant changes in the permeate flux. In the analysis of contact angle measurements and surface tension calculations in nanofiltration membranes (N30F, NF-PES-010, MPF-44, MPF-50, MPF-44, N30F, and NF-PES-010) treated with organic solvents (ethanol, n-hexane, ethyl acetone, acetone, and methylene chloride), Geens et al. (2004) confirmed a change in hydrophilicity on the polymeric surface of the membranes, leading to a difference in water permeability before and after treatment, characterized by a reorganization of the membrane material, which results in differences in porosity and changes in rejection capacity. Geens et al. (2005), in the use of pretreatment in binary solvent mixtures (water + organic solvent — methanol or ethanol) in nanofiltration membranes (MPF-44, MPF-50, N30F, NF-PES-010 Desal-5-DL, and Desal-5-DK SolSep-030505), highlighted that the hydrophilicity and polarity mechanisms originated by organic solvents are essential for good retention. During tests with binary water-ethanol mixtures (50%), the authors obtained retentions of 8–99% of raffinose (100 mg $L^{-1}$) and 8–41% when the proportion of the organic solvent in the mixture was less than 50%.

Although some studies have shown that the permeate flux of membranes pretreated with organic solvents is lower than those without treatment, no records were found regarding the evaluation of the pretreatment of NF90 nanofiltration membranes immersed in 50% (v/v) ethanol solution in the removal of taste and odor metabolites. NF90 immersed in ethanol solvent was used in the removal of other compounds and different concentrations of organic solvent. Martínez et al. (2012) in an evaluation of the NF90 membrane preserved for 24 h in absolute ethanol (99% purity), applying a 14 bar pressure to obtain the permeate flux and retention during 270 min, achieved rejection results of 92% of pharmaceutical grade 1-(5-bromo-fur-2-yl)-2-bromo-2-nitroethane 296 Da. Zhang et al. (2021) studied NF90 membranes treated with a ternary mixture of ethanol (70%), water (30%), and sodium hydroxide (1 mol $L^{-1}$) for 20 min and obtained removals of sodium chloride and sodium sulfate above 95% for an initial concentration of 2,000 mg $L^{-1}$ and permeate flux from 13 (without treatment) to 15.5 L $m^{-2}$ $h^{-1}$ bar (with treatment) in the use of the mixture with the ethanol solvent, with a 19% increase in permeate flux using a 5 bar working pressure.

Flavor and odor compound directly interfere with water treatment. The aforementioned studies evaluated the retention of 2-MIB compounds and Geosmin in nanofiltration membranes but did not consider the evaluation of retention and permeate flux in NF90 membranes pretreated in the organic solvent. The choice of 2-MIB compounds and Geosmin in the retention evaluation is because they are contaminating organic compounds that commonly interfere in water treatments and industrial processes and have a molar mass of 168.28 and 182.31 Da, respectively, less than 200 Da (NF90 molecular weight cutoff). Another interesting point when considering the use of nanofiltration is the evaluation of its permeability capacity even at low working pressure values for a perpendicular flux passage process. These aspects were considered in the present study to evaluate the influence of the organic solvent ethanol (50%, v/v solution) on the membrane characteristics and how much this would affect its performance in terms of retention and permeate flux, while still maintaining a low working pressure.

## Materials and Methods

### Membranes

This study used the NF90 polyamide nanofiltration membrane, provided by Dow Chemical Company®. Table 1 lists the physicochemical characteristics of the membranes.

#### *Morphological determination of the NF90 membrane*

To verify the influence of the treatments on the surface characteristics of the NF90 membrane, atomic force microscopy analyses were performed on membranes pretreated with ultrapure water and 50% (v/v) ethanol solution, and without pretreatment. The surface images were obtained at a resolution of 512 pixels × 512 pixels, an acquisition speed from 1 Hz, and treated in the WSxM 5.0 program, resulting in images in three dimensions. The analyses were carried out using a Nanosurf equipment model, FlexAFM, operated in an intermittent contact mode.

### 2-MIB and Geosmin Solutions

For the secondary metabolite retention assays, working solutions were prepared from a commercial standard (Supelco Analytical) with a concentration equal to 100 µg $mL^{-1}$ and purity equal to 98.3 and 99.8% for 2-MIB and Geosmin, respectively. From the standard, which contained the two metabolites, a new 500 mL solution was prepared at a concentration of 100 ng $L^{-1}$ in ultrapure water. The working concentration was defined from studies already carried out by other authors, which evaluated concentrations between 30 and 230 ng $L^{-1}$ of these two compounds (Mody, 2004; Dixon et al., 2011; Zat and Benetti, 2011) (Table 2).

### Experimental development

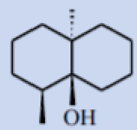
The filtration experiments were carried out in an AISI 316 stainless steel device, with a capacity of 375 mL, with perpendicular flux operation, under constant pressure, performed from a pressurized liquid nitrogen cylinder linked to the equipment, controlled by a manometer (Figure 1).

**Table 1 – Physical and chemical characteristics of the NF90 membrane.**

| | |
|---|---|
| **Material** | Polyamide |
| **Molecular weight cutoff (Da)** | 200[b,c] |
| **Structure** | Thin film compound |
| **pH range** | 2–10[a] |
| **Porosity (nm)** | 0.55 ± 0.13[c] |
| **Zeta potential (mV)** | -24.9[b,c] |
| **NaCl retention (%)** | 85–95[d] |
| **$MgSO_4$ retention (%)** | > 97[d] |
| **Specific flux (L $m^{-2}$ $h^{-1}$ bar)** | 5.8 ± 0.3[c] |
| **Hydrophobicity** | Hydrophobic |

Source: [a]Mody (2004); [b]Xu et al. (2006); [c]Plakas and Karabelas (2008); [d]Manufacturer.

**Table 2 – Chemical characteristics of 2-MIB compounds and Geosmin.**

| Characteristic | Compounds | |
|---|---|---|
| Compound name | 2-Methylisoborneol | 1,10-Dimethyl trans-9-decalol |
| Synonym | AT | 1,8,8-Dimethyl decahydro-1naphthalenol |
| Chemical formula | $C_{11}H_{20}O$ | $C_{12}H_{22}O$ |
| Usual name | 2-MIB | Geosmin |
| Molar mass (Da) | 168.28 | 182.31 |
| Taste and odor | Mold | Dirt |
| Structural formula |  |  |

Source: adapted from You (2012, p. 2) and Mustapha et al. (2021, p. 4).

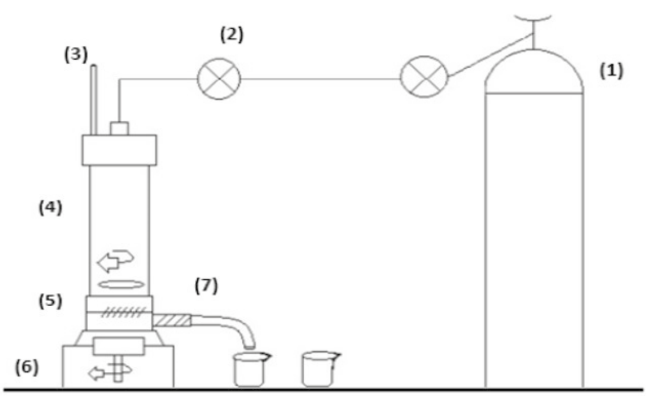



**Figure 1 – Schematic representation of the filtration system: (1) liquid nitrogen cylinder; (2) manometer; (3) thermometer; (4) filtration cell; (5) arrangement of the filtering membrane on a metallic screen inside the cell; (6) magnetic stirrer and metal heating plate; (7) permeate outlet.**

Two membrane pretreatment conditions were evaluated: (1) immersion in ultrapure water and (2) immersion in 50% (v/v) ethanol solution for 60 min. The behavior of membranes previously treated under conditions (1) and (2) in terms of permeate flux and retention of compounds was evaluated at pressure values of 4, 7, and 10 bar. All filtration experiments with pretreated membranes were performed in triplicate. For the tests with the membrane without treatment in time (60 min) and evaluated pressure values (4, 7, and 10 bar), no permeate flux was obtained.

The experimental procedure developed was evaluated in the following steps and order.

### *Permeate flux analysis*

After pretreatment, the membrane was subjected to compaction in ultrapure water for 35 min at each of the pressure values of 4, 7, and 10 bar, consecutively. During this period, water samples were collected every 5 min for 35 min and evaluated the permeate flux of the membrane. The collected volumes were quantified from the water mass and presented as permeate flux (L $m^{-2}$ $h^{-1}$). In terms of calculation, the permeate flux was represented concerning the volume of liquid that passed through the membrane, considering its useful area ($5.8\times10^{-4}$ $m^2$) per unit of time, according to Equation 1 (Nunes and Peinemann, 2006; Diel, 2010).

$$J_0 = \frac{V}{A.t} \tag{1}$$

Where:

$J_0$: the permeate flux (L $m^{-2}$ $h^{-1}$);

V: the sample volume (L);

A: the effective surface area of the membrane ($m^2$);

t: the collection time.

### *Retention analysis*

Filtration of the solution with the metabolites was carried out for 120 min (2 h). The quantification of metabolites in the permeate was performed from sample collections at times 0–10, 30–40, 60–70, 90–100, and 110–120 min. The rejection or retention factor was also evaluated in this study to verify the retention efficiency of metabolites in membranes pretreated in water and 50% (v/v) ethanol solution, which was determined from Equation 2.

$$R\% = 100\left(1 - \frac{Cp}{Ci}\right) \tag{2}$$

Where:

R%: the retention coefficient;

Cp: the analyte concentration in the permeate (μg $L^{-1}$);

Ci: the concentration of the analyte in the working solution (μg $L^{-1}$).

### *Fouling and cleaning analysis*

The last step consisted of determining the occurrence of metabolite deposition on the surface or pores (fouling) of membranes pretreated in water and 50% (v/v) ethanol solution, and the evaluation was performed from the passage of ultrapure water through the membrane for 35 min at pressure values of 4, 7, and 10 bar. Next, the membranes were physically cleaned with the aid of a common sponge, followed by the passage of ultrapure water through the membrane for a period equal to 35 min, also at the three working pressure values.

## Analytical procedure for quantification of 2-MIB and Geosmin

Considering that 2-MIB and Geosmin are volatile organic compounds, to avoid losses during the collection period, the permeate and retentate samples were collected in 30 mL *vials* and refrigerated before identification and quantification. The quantification of metabolites was performed by solid phase microextraction (SPME) in an Agilent 7890B gas chromatograph, equipped with an Agilent GC Sampler 120 autosampler, configured to operate in (SPME) mode with the mixed fiber of carboxy/divinylbenzene/dimethylpolysiloxane (Car/DVB/PDMS) of 30-µm film thickness and 1 cm long (Supelco). A 900-µL ultra inert, glass wool-free liner for split-flux injections (splitless) and a Merlin seal were used in the multimode inlet. An Agilent 7000C triple quadrupole sequential mass spectrometer (GC-MS/MS) coupled to a gas chromatograph was used as the detector. For the direct determination in the equipment, the 2-MIB compounds and Geosmin were separated in an Agilent J&W HP-5MS Ultra Inert capillary chromatographic column, with a phenyl/methylpolysiloxane stationary phase (5/95%) measuring 30 m × 0.25 mm × 0.25 µm (length × inner diameter × film thickness).

## Results and Discussion

Before the permeability and retention study, the morphology of NF90 membranes pretreated in water and 50% (v/v) ethanol solution was observed by atomic force microscopy. When analyzing Figure 2, it was found that the untreated membrane presents a greater number of ridges and valleys, which defines the high roughness of the membrane pretreated in water and 50% (v/v) ethanol solution. According to Diaz (2008), NF90 membranes have rougher surfaces and are, therefore, more rugged, denoting hydrophobicity with less rough membranes. Boussu et al. (2006) considered that high roughness directly interferes with permeate flux, as there is a lower chemical affinity between the liquid and the membrane surface, which leads to a decrease in permeate flux.

In the atomic force microscopy images, it was possible to verify that there were changes in the roughness of the membrane when it was submitted to treatments in water (Figure 2B) and 50% (v/v) ethanol solution (Figure 2C), where a considerable decrease in roughness was observed due to the lower presence of ridges on its surface.

In membranes treated in water and 50% (v/v) ethanol solution (Figure 2C), the contact with the solvents suppresses the appearance of high roughness, as they act on the microscopic wetting of the active layer (superficial layer of polyamide). In the treatment with the ethanol solvent, the wetting of the active layer is more accentuated and can also cause swelling of the polymer and an increase in the polymeric surface (Louie et al., 2011); these events result in reduced resistance to mass transport and an increase in water permeability (Li et al., 2019). This phenomenon is even more highlighted when using a binary mixture of water+alcohol (50%); the increase in the polarity of the organic solvent has a greater affinity with the polymeric material of the membrane, which facilitates and better enables the passage of water and increases the hydrophilicity characteristic (Geens et al., 2005).

It is possible to note that the difference in roughness can directly interfere with the interaction with water molecules or a polar solvent. In tests with the membrane without any treatment and for 3–5 h at pressure values below 10 bar, no flux was observed. Prior contact with polar solvents before starting the filtration process is essential for there to be an activation of the active layer and hydration. These interactions increase the affinity with the feeding solution. The increase in hydrophilicity and the ease of permeability to water due to the interaction of the organic solvent with the membrane material is represented in Figure 3. When observing the results obtained at the three working pressure values (4, 7, and 10 bar), the permeate fluxes of the average values of the membrane pretreated in 50% (v/v) ethanol solution were higher than the membrane pretreated in water, with results in the range of 26.55 L $m^{-2}$ $h^{-1}$ at a 4 bar pressure, 34.08 L $m^{-2}$ $h^{-1}$ at a 7 bar pressure, and 59.13 L $m^{-2}$ $h^{-1}$ at a 10 bar pressure.

The pretreatment in ethanolic solution (v/v) provided an increase in water permeability, with a scale of 3–4 times greater than that obtained in the pretreatment in water, with average flux values of 85.34 L $m^{-2}$ $h^{-1}$ at a 4 bar pressure, 167.01 L $m^{-2}$ $h^{-1}$ at a 7 bar pressure, and 224.60 L $m^{-2}$ $h^{-1}$ at a 10 bar pressure. The increase in flux values is evident when observing the data at the three study pressure values, which is in agreement with Heffernan et al. (2013), who stated that ethanol does not adversely affect membrane performance in terms of flux and retention.

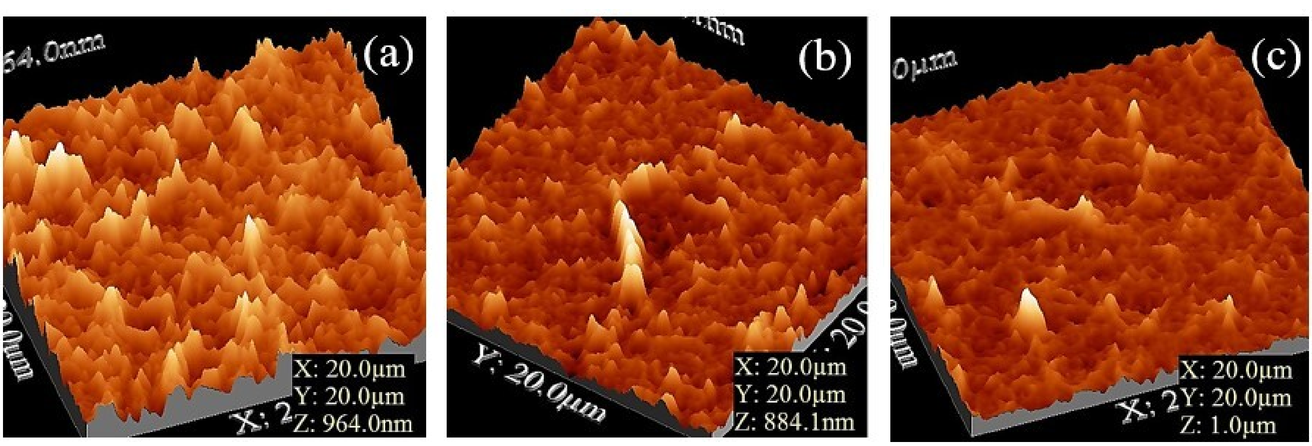



**Figure 2 – Atomic force microscopy images of the NF90 membrane surface: (A) membrane without previous treatment; (B) membrane immersed in water; (C) membrane immersed in 50% (v/v) ethanol solution.**

It is noticed that there is a strong interaction between the treatment solvent and the membrane material, which causes the fluxes to change. Kirsh et al. (1995) and Khorshidi et al. (2016), in evaluating the permeate flux efficiency in a polyamide membrane with the interaction of organic solvents, concluded that the solvent provides structural and morphological changes in the membrane, such as alteration of the polymeric material, pore size, and electrostatic interactions. Van der Bruggen et al. (2002) emphasized that the increase in flux and the ease with which water passes through the membrane in the ethanol treatment is due to the originally hydrophobic structure of the membrane becoming hydrophilic when immersed in the organic solvent. This characteristic can be attributed to the breakage of the polymeric chain of the membrane when it is immersed in a 50% (v/v) ethanol solution, which gives rise to the exposure of hydrophilic groups on the membrane surface (Li et al., 2019). This deformation was also observed by Zhao and Yuan (2006a), who reported that it is a common phenomenon in membranes that remain in contact with the organic solvent.

The reduction of mass transport resistance due to the interaction of the membrane with the organic reagent, as observed by Li et al. (2019), was also observed during this study. This same behavior was observed in the tests to evaluate the permeate flux with the contaminants 2-MIB and Geosmin. As these compounds are tertiary alcohols and are in low concentrations, the average permeate flux values (Figure 4) were similar to those obtained in the initial analysis of water permeability in membranes pretreated in water and 50% (v/v) ethanol solution. From a statistical analysis using the Microsoft Excel application, considering the least significant difference (LSD) obtained from the ANOVA test, it was observed that there was no significant difference ($p > 0.05$) between the permeate flux values in the water permeability step and when filtering the sample with the analytes for the three pressure values when pretreating the membrane with water (Table 3). For the pretreatment with 50% (v/v) ethanol solution, only for the 10 bar pressure, there was a significant difference ($p < 0.05$) between the permeate fluxes. It is suggested that the retention of compounds by the membranes did not affect the reduction of permeate flux in most treatments.

This same finding is verified during the stages of evaluation of the occurrence of fouling in the three study pressure values (4, 7, and 10 bar), suggesting that the fouling or any other encrustation phenomenon occurred in a small proportion, not influencing the performance of the membrane in terms of permeate flux, with or without pretreatment with 50% (v/v) ethanol solution (Figure 5).

Furthermore, it was observed that after the surface cleaning of the membrane, the permeate flux remained very similar to that found for the membrane before and after the passage of the sample, which evidences the fact that no encrustation occurred in the membrane due to the filtration of contaminants (Figure 5).

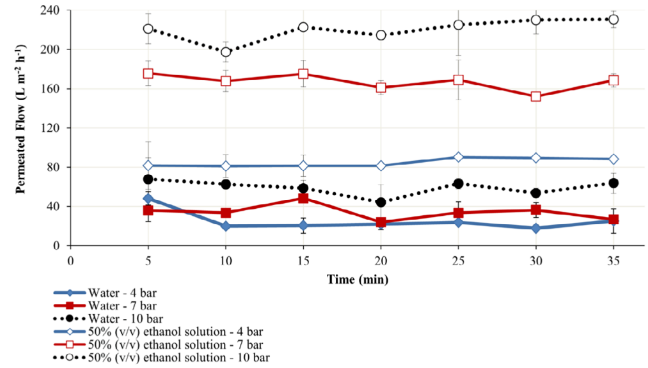



**Figure 3 – Behavior of the permeate flux in water obtained for the NF90 membrane when pretreated with water and 50% (v/v) ethanol solution.**

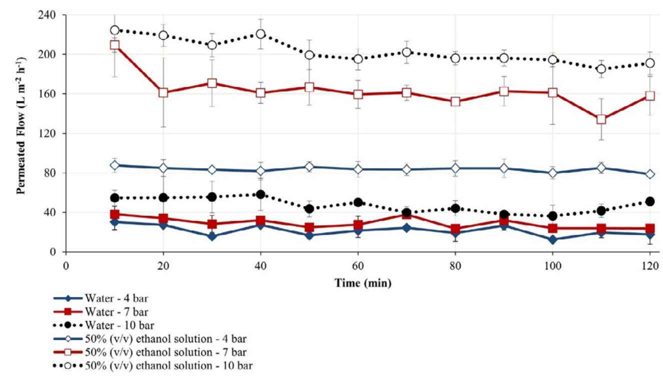



**Figure 4 – Behavior of the permeate flux obtained for the NF90 membrane, with pretreatment in water and 50% (v/v) ethanol solution during the filtration of the sample containing 2-MIB and Geosmin at pressure values of 4, 7, and 10 bar.**

Although the permeate flux values have increased after exposing the NF90 membrane to the 50% (v/v) ethanol solution, the permeability of the membrane with or without the presence of contaminants in the feeding solution has remained close when quantifying the retention of flavor and odor compounds; the retention values of 2-MIB and Geosmin were between 91 and 99%. Even with high retention values, a small reduction (between 1 and 5%) during the filtration process was observed for both pretreatments, this difference being more visible for the membrane pretreated with 50% (v/v) ethanol solution. Although in the study by Li et al. (2020) there was a significant difference in removal between MIB and Geosmin, in the present study, this difference was not high. The behavior of 2-MIB and Geosmin retention by membranes can be seen in Figure 6.

NF90 membranes have amphoteric characteristics, a dense surface superimposed on a porous layer, and a cutoff value from 150 to 300 Da. Due to these characteristics, in contact with the organic solvent, there may be swelling mechanisms (hydration/solvation) of the porous layer, which reduces the pore diameter and, consequently, increases the solute rejection, in addition to increasing the hydrophilicity of the dense layer (Geens et al., 2004; Silva et al., 2005; Ebert et al., 2006;).

**Table 3 – Statistical comparison of the permeate fluxes in the permeability and filtration steps of the samples containing the analytes.**

| Pressure (bar) | Pretreatment with water | | | Pretreatment with 50% (v/v) ethanol solution | | |
|---|---|---|---|---|---|---|
| | Average P | Average A | \|Average\| | Average P | Average A | \|Average\| |
| 4 | 26.55 ± 6.66 | 21.51 ± 0.40 | 5.04 | 85.34 ± 4.86 | 83.59 ± 6.48 | 1.75 |
| 7 | 34.08 ± 2.61 | 29.16 ± 0.73 | 4.92 | 167.01 ± 6.82 | 160.89 ± 7.74 | 6.12 |
| 10 | 59.13 ± 16.00 | 47.33 ± 4.19 | 11.80 | 224.60 ± 17.73 | 200.67 ± 8.50 | 23.93 |

Average P: average of the permeate flux in the water permeability step; Average A: average of the permeate flux of the solution with the analytes; |Average|: average modulus between treatments; Least significant difference = 21.65 (value used for comparison with average values in module).

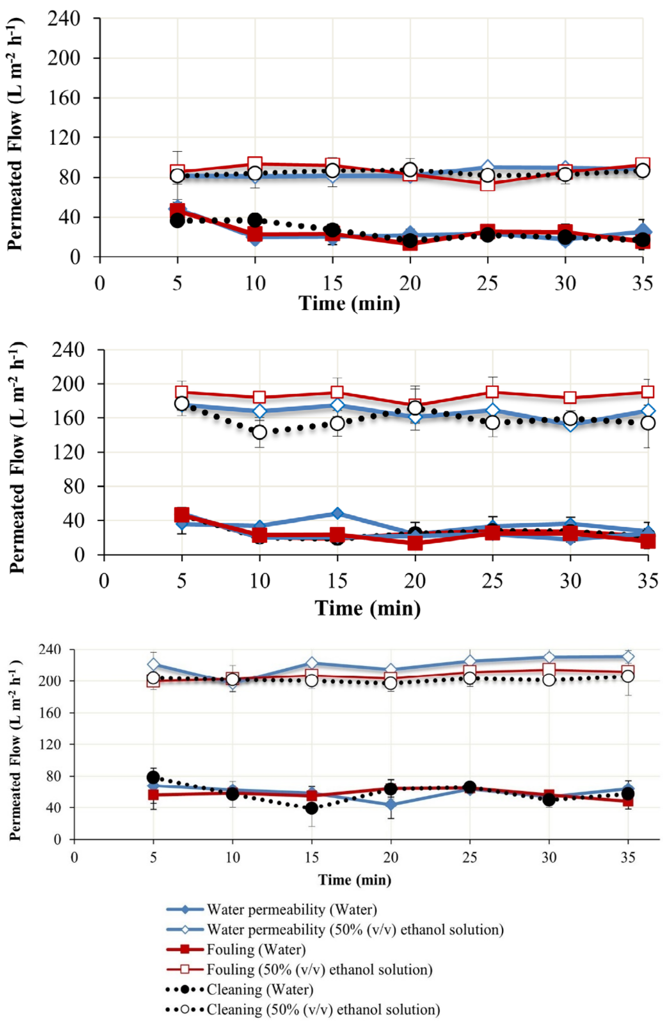



**Figure 5 – Behavior of the permeate flux for the NF90 membrane in the steps of water permeability, fouling characterization, and after cleaning at pressure values of (A) 4 bar, (B) 7 bar, and (C) 10 bar.**

Thus, it can be suggested that the 2-MIB compounds and Geosmin, being tertiary, hydrophilic, and polar alcohols and negatively charged (Hsieh et al., 2012), are retained in the swollen porous layer. However, the retention of these compounds is related not only to the phenomenon of size exclusion but also to electrostatic interaction with the hydrophilic layer of the membrane.

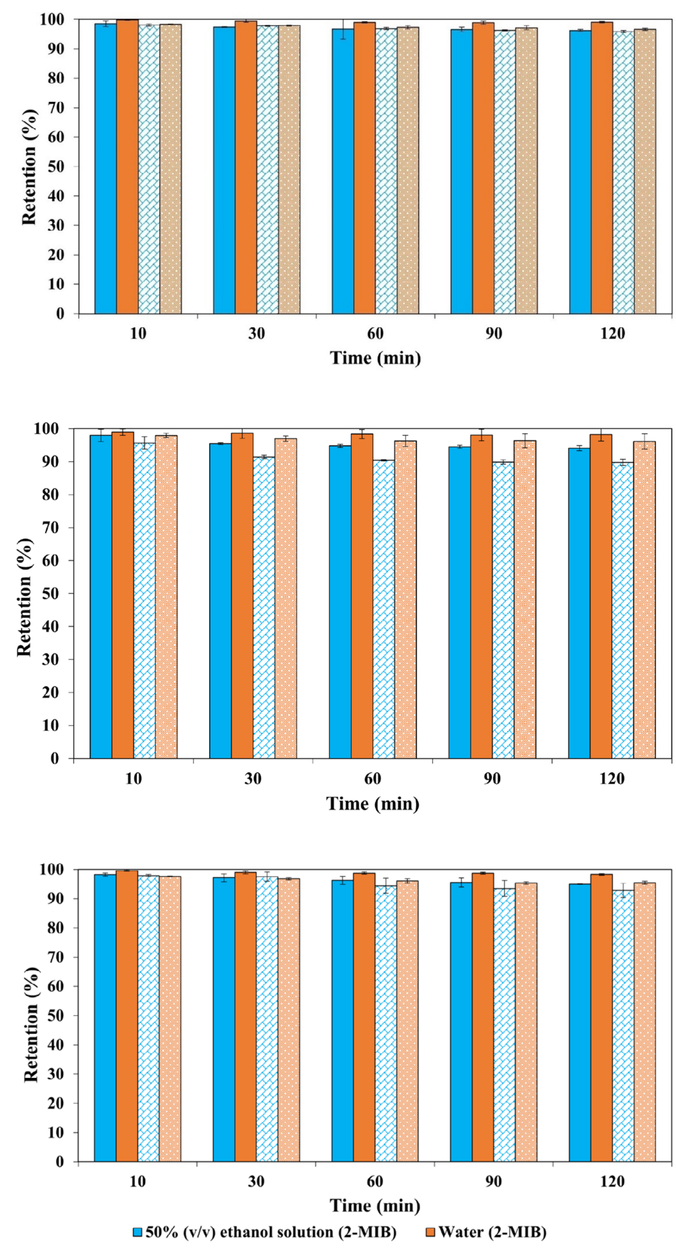



**Figure 6 – Removal of 2-MIB and Geosmin at pressure values of (A) 4, (B) 7, and (C) 10 bar from membranes with pretreatment in water and 50% (v/v) ethanol solution.**

Artuğ et al. (2007) highlighted that there is a strong dependence on the charge of the solution and on the solutes to be retained on the membrane surface. The 2-MIB compounds and Geosmin, being tertiary alcohols, have hydrophilic characteristics, which cause them to be repelled from the surface of the membrane, which is polarized and hydrophilized due to interaction with the organic solvent (Yu et al., 2014). According to Geens et al. (2006), the contact of hydrophobic membranes with organic solvents increases their repulsion properties as they become hydrophilic. The electronegativity that occurs on the outer surface of the membrane and the pore surface is due to the distribution of ions in the permeation solution (Teixeira et al., 2005). The more negatively charged the membrane, the greater the repulsion of substances that have the same charge, due to ionic strength (Kwon et al., 2012). Thus, retention occurs through the Donnan exclusion mechanism, which determines that compounds with the same charge as the membrane material are repelled by its surface to satisfy electroneutrality in the system (Teixeira et al., 2005).

Similar 2-MIB retention results obtained during this study (91–99%) were achieved in studies with nanofiltration membranes without prior treatment (Table 4). Dixon et al. (2011), in a study of the efficiency of removing microcystin, 2-MIB, Geosmin, and Cylindrospermopsin in water from a treatment plant using nanofiltration membranes (NF90, NF270, and DK) at pressure values from 4.1 to 8.2 bar in the reservoirs of water from South Australia, reached removal levels above 75%, mainly for the flavor and odor compounds, and the NF90 membrane showed the best removal and flux efficiency among those tested. Yu et al. (2014) obtained 96% rejection rates of 2-MIB and Geosmin at a 4.1-bar pressure nanofiltration process with an NF membrane composed of polyamide (NE 4040-90) used in a drinking water treatment plant in Siheung, Korea. Zat and Benetti (2011), when evaluating the removal of 2-MIB and Geosmin at pressure values from 8.1 to 9.0 bar, achieved removals of 97 and 96%, respectively, in spiral polyamide membranes (DK4040F). Mody (2004), when observing the retention of secondary metabolites in fluxes at a 7 bar pressure with different nanofiltration membranes, found that NF90, NF270, and LFC show a capacity of rejection of flavor and odor compounds above 90%.

When observing the previously mentioned studies, it can be seen that the retention values of 2-MIB compounds and Geosmin were close to those obtained in this study. However, all of them used membranes without previous treatment, tangential filtration at pressure values between 4 and 11 bar, resulting in flux values between 11 and 32.3 L $m^{-2}$ $h^{-1}$, values much lower than those observed in the present study, even when performed with perpendicular filtration (Table 4). It is worth noting that tangential filtration is usually more efficient than perpendicular filtration, considering that phenomena such as polarization by concentration, formation of the gel layer, and clogging can be reduced or delayed depending on the flux rate of the feeding solution and turbulence over the membrane (Tsibranska and Tylkowski, 2013), thus providing a higher permeate flux during a longer filtration period.

This study, under the conditions evaluated, demonstrates that membranes previously immersed in ethanol solution are efficient for improving the permeate flux behavior at low-pressure values without changing the performance of the membrane in terms of retention of compounds with a molar mass. Pretreatment in ethanol solution causes chemical and physical changes that can benefit the treatment system for low-molecular mass contaminants and enable energy use with the increased flux at low-pressure values.

## Conclusion

It can be verified through the results obtained of flux and retention versus time that the changes that occurred in the membrane from the pretreatment in 50% (v/v) ethanol solution were beneficial, since they allowed an increase in the permeate flux, maintaining high retention efficiency of 2-MIB compounds and Geosmin (between 95 and 99% on average).

**Table 4 – Comparison of studies already carried out using NF90 membranes to remove 2-MIB and Geosmin.**

| Author (year) | Membrane | Pretreatment | Experimental condition (filtration type and pressure) | Obtained flux (L $m^{-2}$ $h^{-1}$) | Retention (%) |
|---|---|---|---|---|---|
| Mody (2004) | NF90 | without treatment | Tangential filtration<br>7 bar pressure | 32.31 | > 90 |
| Dixon et al. (2011) | NF90 | without treatment | Tangential filtration<br>Pressure up to 8.2 bar | 11.2 | > 75 |
| Zat and Benetti (2011) | DK4040F | without treatment | Tangential filtration<br>Pressure values between 8.1 and 9 bar | 28.71 | ≥ 96 |
| Yu et al. (2014) | NE 4040-90 | without treatment | Tangential filtration<br>4.1 bar pressure | 20.83 | 96 |
| This study | NF90 | Water | Perpendicular filtration<br>4, 7, and 10 bar pressure values | 4 bar = 21.51<br>7 bar = 29.16<br>10 bar = 47.33 | ≥ 98 |
| | | 50% (v/v) ethanol solution | | 4 bar = 83.59<br>7 bar = 160.89<br>10 bar = 200.67 | ≥ 95 |

The retention values of 2-MIB compounds and Geosmin remained below the detection limits identified by end consumers (4 and 10 ng $L^{-1}$ for Geosmin and between 9 and 42 ng $L^{-1}$ for 2-MIB) (Cortada et al., 2011). It is suggested that the flux increase is due to the physicochemical interactions of the organic solvent with the membrane material, which changes hydrophobicity and facilitates water flux due to affinity and polarity. Regarding the high retention during the passage of the organic compounds in a membrane pretreated in 50% (v/v) ethanol solution, the beneficial involvement of the alcoholic compounds with the membrane material was evidenced without the retention change. It can be suggested that the pretreatment of membranes in 50% (v/v) ethanol solution facilitates the treatment process without loss of rejection efficiency but with a significant increase in permeate flux. Based on the results obtained, it is suggested that, among the three pressure values evaluated, the 7 bar pressure would be the best option for the proposed treatment since at this pressure greater hydraulic permeability was obtained compared to the others, in addition to high retention of compounds. Additionally, and mainly due to its simplicity, the proposed framework can be useful for further work regarding the retention of compounds with low molar mass and different loads in membranes pretreated in 50% (v/v) ethanol solution.

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## Contribution of authors:

SATO, C. S.: Methodology; Formal Analysis; Investigation; Writing — Original Draft Preparation; Writing — Review and Editing; SCHMOELLER, M.P.: Formal Analysis; CORAL, L. A. A.: Conceptualization; Writing — Review and Editing; Supervision; BASSETTI, F. J.: Conceptualization; Resources; Writing — Review and Editing; Supervision; Project Administration; Funding Acquisition.

## References

Almeida, L.C.; Fernandes Jorge, T.B.; Pinto, R.; Canevari G.C., 2015. Cyanobacteria and cyanotoxins risk factors for water supply (Cianobactérias e cianotoxinas fatores de risco para o abastecimento de água). Revista Científica Univiçosa (Online), v. 7, (1), 508-513.

Artuğ, G.; Roosmasari, I.; Richau, K.; Hapke, J., 2007. A comprehensive characterization of commercial nanofiltration membranes. Separation Science and Technology (Online), v. 42, (13), 2947-2986. https://doi.org/10.1080/01496390701560082.

Bortoli, S.; Pinto, E., 2015. Cyanotoxins: general characteristics, history, legislation and analysis methods. In: Pompêo et al. (Eds.). Ecology of reservoirs and interfaces (Cianotoxinas: características gerais, histórico, legislação e métodos de análises. São Paulo: Instituto de Biociências da Universidade de São Paulo, p. 319-339.

Boussu, K.; Zhang, Y.; Cocquyt, J.; Van Der Meeren, P.; Volodin, A.; Van Haesendonck, C.; Martens, J.A.; Van Der Bruggen, B., 2006. Characterization of polymeric nanofiltration membranes for systematic analysis of membrane performance. Journal of Membrane Science (Online), v. 278, (1-2), 418-427. https://doi.org/10.1016/j.memsci.2005.11.027.

Chung, Y.; Lee, M.-Y.; Park, H.; Park, Y.-I.; Nam, S.-E.; Lee, P.B.; Hwang, Y.-S.; Kang, S., 2018. Novel preparation of ceramic nanofiltration membrane for the removal of trace organic compounds. Desalination and Water Treatment (Online), v. 101, 31-36. https://doi.org/10.5004/dwt.2018.21642.

Cortada, C.; Vidal, L.; Canals, A., 2011. Determination of geosmin and 2-methylisoborneol in water and wine samples by ultrasound-assisted dispersive liquid–liquid microextraction coupled to gas chromatography–mass spectrometry. Journal of Chromatography A, v. 1218, (1), 17-22. https://doi.org/10.1016/j.chroma.2010.11.007.

Diaz, A.S., 2008. Application of nanofiltration and reverse osmosis membrane technology for the treatment of aqueous solutions of phenolic compounds and carboxylic acids. (Aplicación de la tecnología de membranas de nanofiltración y ósmosis inversa para el tratamiento de disoluciones acuosas de compuestos fenólicos y ácidos carboxílicos). 2008. 258f. Thesis (Doctorate in Chemical and Environmental Technology) – Departamento de Tecnologia Química e Ambiental, Universidad Rey Juan Carlos, Madrid.

Diel, J.L., 2010. Functional characterization of ceramic micro- and ultrafiltration membranes. (Caracterização Funcional de Membranas Cerâmicas de Micro e Ultrafiltração). 2010. 131f. Dissertation (Masters in Engineering) – Graduate Program in Chemical Engineering, Universidade Federal do Rio Grande do Sul, Porto Alegre.

Dixon, M.B.; Falconet, C.; Ho, L.; Chow, C.W.K.; O'neill, B.K.; Newcombe, G., 2011. Removal of cyanobacterial metabolites by nanofiltration from two treated waters. Journal of Hazardous Materials (Online), v. 188, (1-3), 288-295. https://doi.org/10.1016/j.jhazmat.2011.01.111.

Ebert, K.; Koll, J.; Dijkstra, M.F.J, Eggers, M., 2006. Fundamental studies on the performance of a hydrophobic solvent stable membrane in non-aqueous solutions. Journal of Membrane Science (Online), v. 285, (1-2), 75-80. https://doi.org/10.1016/j.memsci.2006.07.037.

Faruqi, A.; Henderson, M.; Henderson, R.K.; Stuetz, R.M.; Gladman, B.; McDowall, B.; Zamyadi, A., 2018. Removal of algal taste and odour compounds by granular and biological activated carbon in full-scale water treatment plants. Water Science & Technology Supply (Online), v. 18, (5), 1531-1544. https://doi.org/10.2166/ws.2018.001.

Geens, J.; Peeters, K.; Van Der Bruggen, B.; Vandecasteele C., 2005. Polymeric nanofiltration of binary water–alcohol mixtures: Influence of feed composition and membrane properties on permeability and rejection. Journal of Membrane Science (Online), v. 255, (1-2), 255-264. https://doi.org/10.1016/j.memsci.2005.01.039.

Geens, J.; Van Der Bruggen, B.; Vandecasteele, C., 2004. Characterisation of the solvent stability of polymeric nanofiltration membranes by measurement of contact angles and swelling. Chemical Engineering Science (Online), v. 59, (5), 1161-1164. https://doi.org/10.1016/j.ces.2004.01.003.

Geens, J.; Van der Bruggen, B.; Vandecasteele, C., 2006. Transport model for solvent permeation through nanofiltration membrane. Separation and Purification Technology (Online), v. 48, (3), 255-263. https://doi.org/10.1016/j.seppur.2005.07.032.

Glibert, P.M., 2017. Eutrophication, harmful algae and biodiversity — challenging paradigms in a world of complex nutrient changes. Marine Pollution Bulletin, v. 124, (2), 591-606. https://doi.org/10.1016/j.marpolbul.2017.04.027.

Heffernan, R.; Semião, A.J.C.; Desmond, P.; Cao, H.; Safari, A.; Habimana, O., Casey, E., 2013. Disinfection of a polyamide nanofiltration membrane using ethanol. Journal of Membrane Science (Online), v. 448, 170-179. https://doi.org/10.1016/j.memsci.2013.07.069.

Herrero, A.; Flores, E., 2008. The cyanobacteria Molecular Biology, Genetics and Evolution. Norfold: The cyanobacteria Molecular Biology, Genetics and Evolution, (1).

Hsieh, W.-H.; Hung, W.-N.; Wang, G.-S., Hsieh, S.-T.; Lin, T.-F., 2012. Effect of pH on the analysis of 2-MIB and geosmin in water. Water Air and Soil Pollution (Online), v. 223, 715-721. https://doi.org/10.1007/s11270-011-0896-4.

Khorshidi, B.; Thundat, T.; Fleck, B.A.; Sadrzadeh, M. 2016. A novel approach toward fabrication of high performance thin film composite polyamide membranes behnam. Scientific Reports (Online), v. 6, (1), 22069. https://doi.org/10.1038/srep22069.

Kirsh, Y.E.; Fedotov, Y.A.; Semenova, S.I.; Vdovin, P.A.; Valuev, V.V.; Zemlianova, O.Y.; Timashev, S.F., 1995. Sulfonate containing aromatic polyamides as materials of pervaporation membranes for dehydration of organic solvents: hydration, sorption, diffusion and functioning. Journal of Membrane Science (Online), v. 103, (1-2), 95-103. https://doi.org/10.1016/0376-7388(94)00312-M.

Kwon, Y.; Shih, K.; Tang, C.; Leckie, J.O., 2012. Adsorption of perfluorinated compounds on thin-film composite polyamide membranes. Journal of Applied Polymer Science (Online), v. 124, (2), 1042-1049. https://doi.org/10.1002/app.35182.

Li, H.; Chen, Y.; Zhang, J.; Dong, B., 2020. Pilot study on nanofiltration membrane in advanced treatment of drinking water. Water Supply, v. 20, (6), 2043-2053. https://doi.org/10.2166/ws.2020.089.

Li, Y.; Wong, E.; Mai, Z.; Van der Bruggen, B., 2019. Fabrication of composite polyamide/Kevlar aramid nanofiber nanofiltration membranes with high permselectivity in water desalination. Journal of Membrane Science (Online), v. 592, 117396. https://doi.org/10.1016/j.memsci.2019.117396.

Louie, J.S.; Pinnau, I.; Reinhard, M., 2011. Effects of surface coating process conditions on the water permeation and salt rejection properties of composite polyamide reverse osmosis membranes. Journal of Membrane Science (Online), v. 367, (1-2), 249-255. https://doi.org/10.1016/j.memsci.2010.10.067.

Martínez, M.B.; Van Der Bruggen, B.; Negrin, Z.R.; Alconero, P.L. 2012. Separation of a high-value pharmaceutical compound from waste ethanol by nanofiltration. Journal of Industrial and Engineering Chemistry (Online), v. 18, (5), 1635-1641. https://doi.org/10.1016/j.jiec.2012.02.024.

Matsui, Y.; Nakao, S.; Taniguchi, T.; Matsushita, T., 2013. Geosmin and 2-methylisoborneol removal using superfine powdered activated carbon: Shell adsorption and branched-pore kinetic model analysis and optimal particle size. Water Research (Online), v. 47, (8), 2873-2880. https://doi.org/10.1016/j.watres.2013.02.046.

Mody, A.J. 2004. Feasibility of using nanofiltration as a polishing process for removal of cyanobacterial exudates from treated surface water. Thesis (PhD in Science in Environmental Engineering) – College of Engineering, University of South Florida, Florida.

Mustapha, S.; Tijani, J.O.; Ndamitso, M.; Abdulkareem, A. S; Shuaib, D.T; Mohammed, A. K., 2021. A critical review on geosmin and 2-methylisoborneol in water: sources, effects, detection, and removal techniques. Environmental Monitoring and Assessment (Online), v. 193, (4), 204. https://doi.org/10.1007/s10661-021-08980-9.

Nunes, S.P.; Peinemann, K.V. 2006. Membrane technology in the chemical industry. 2. ed. Wiley, Weinheim, 592 pp. https://doi.org/10.1002/3527600388.ch4.

Plakas, K.V.; Karabelas, A.J., 2008. Membrane retention of herbicides from single and multi-solute media: The effect of ionic environment. Journal of Membrane Science (Online), v. 320, (1-2), 325-334. https://doi.org/10.1016/j.memsci.2008.04.016.

Reiss, C.R.; Robert, C.; Owen, C.; Taylor, J.S., 2006. Control of MIB, geosmin and TON by membrane systems. Journal of Water Supply: Research and Technology - AQUA (Online), v. 55, (2), 95-108. https://doi.org/10.2166/aqua.2006.071.

Sauvé, S.; Desrosiers, M., 2014. A review of what is an emerging contaminant. Chemistry Central Journal (Online), v. 8, (1), 1-15. https://doi.org/10.1186/1752-153X-8-15.

Silva, P.; Han, S.; Livingston, A.G., 2005. Solvent transport in organic solvent nanofiltration membranes. Journal of Membrane Science (Online), v. 262, (1-2), 49-59. https://doi.org/10.1016/j.memsci.2005.03.052.

Souza, S.M.G.; Mathies, V.D.; Fioravanzo, R.F. 2012. Off-flavor by geosmin and 2-Methylisoborneol in aquaculture (Off-flavor por geosmina e 2-Metilisoborneol na aquicultura). Semina: Agricultural Sciences, v. 33, (2), 835-846. https://doi.org/10.5433/1679-0359.2012v33n2p835.

Srinivasan, R.; Sorial, G.A., 2011. Treatment of taste and odor causing compounds 2-methyl Isoborneol and geosmin in drinking water: A critical review. Journal of Environmental Sciences (Online), 23, (1), 1-13. https://doi.org/10.1016/S1001-0742(10)60367-1.

Teixeira, M.R.; Rosa, M.J.; Nyström, M., 2005. The role of membrane charge on nanofiltration performance. J. Membrane Science (Online), v. 265, (1-2), 160-166. https://doi.org/10.1016/j.memsci.2005.04.046.

Tsibranska, I.H.; Tylkowski, B., 2013. Concentration of ethanolic extracts from Sideritis ssp. L. by nanofiltration: Comparison of dead-end and cross-flow modes. Food and Bioproducts Processing (Online), v. 91, (2), 169-174. https://doi.org/10.1016/j.fbp.2012.09.004.

Van Der Bruggen, B.; Geens; J.; Vandecasteele, C., 2002. Fluxes and rejections for nanofiltration with solvent stable polymeric membranes in water, ethanol and n-hexane. Chemical Engineering Science (Online), v. 57, (13), 2511-2518. https://doi.org/10.1016/S0009-2509(02)00125-2.

Vankelecom, I.F.J; Smet, K.D.; Gevers, L.E.M; Jacobs, P.A., 2005. Nanofiltration membrane materials and preparation. In: Schäfer, A.I.; Fane, A.G.; Waite, T.D. (eds.). Nanofiltration: Principles and Applications. Oxford: Elsevier, p. 33.

Xu, P.; Drewes, J.E.; Kim, T-U.; Bellona, C.; Amy G., 2006. Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications. Journal of Membrane Science (Online), v. 279, (1-2), 165-175. https://doi.org/10.1016/j.memsci.2005.12.001.

You, Y.-W. 2012. Sensitive Detection of 2-MIB and Geosmin in Drinking Water. California: Agilent Technologies.

Yu, Y.-B.; Choi, Y.-H.; Kim, D.J.; Kwon, S.-B.; Kim, C.-H., 2014. Rejection property of geosmin and 2-Methylisoborneol (MIB) with high concentration level at multi stage nanofiltration (NF) membrane system. Journal of Korean Society of Water and Wastewater (Online), v. 28, (4), 397-409. https://doi.org/10.11001/jksww.2014.28.4.397.

Zamyadi, A.; Henderson, R.; Stuetz, R.M.; Hofmann, R.; Ho, L; Newcombe, G. 2015. Fate of geosmin and 2- methylisoborneol in full-scale water treatment plants. Water Research, v. 83, 171-183. https://doi.org/10.1016/j.watres.2015.06.038.

Zat, M.; Benetti, A.D., 2011. Removal of the odoriferous compounds geosmin and 2-methylisoborneol from drinking water by the processes of cascade aeration, air stripping and nanofiltration. Engenharia Sanitária e Ambiental (Online), v. 16, (4), 353-360. https://doi.org/10.1590/S1413-41522011000400006.

Zhang, R.; Su, S.; Gao, S.; Tian J., 2021. Reconstruction of the polyamide film in nanofiltration membranes via the post-treatment with a ternary mixture of ethanol-water-NaOH: Mechanism and effect. Desalination (Online), v. 519, 115317. https://doi.org/10.1016/j.desal.2021.115317.

Zhao, Y.; Yuan, Q., 2006a. A comparison of nanofiltration with aqueous and organic solvents. Journal of Membrane Science (Online), v. 279, (1-2), 453-458. https://doi.org/10.1016/j.memsci.2005.12.040.

Zhao, Y.; Yuan, Q., 2006b. Effect of membrane pretreatment on performance of solvent resistant nanofiltration membranes in methanol solutions. Journal of Membrane Science (Online), v. 280, (1-2), 195-201. https://doi.org/10.1016/j.memsci.2006.01.026.