Removal of carbamates in drinking water by nanofiltration in tangential flow

Marina Sampaio Slussarek Tateoka¹, Juliana Marques Schöntag¹*, José Carlos Cunha Petrus² and Mauricio Luiz Sens¹

¹Departamento de Engenharia Sanitária e Ambiental, Centro de Tecnologia, Universidade Federal de Santa Catarina, Campus Reitor João David Ferreira Lima, s/n., 88040-970, Florianópolis, Santa Catarina, Brazil. ²Departamento de Engenharia Química e Engenharia de Alimentos, Universidade Federal de Santa Catarina, Florianópolis, Santa Catarina, Brazil. *Author for correspondence. E-mail: juschontag@gmail.com

ABSTRACT. Membranes processes, in particular, nanofiltration and reverse osmosis, represent an important alternative for treatment of contaminated waters. In this context, the present study aims to evaluate the efficiency of the removal of the carbamates: carbaryl, carbofuran and methomyl at different concentrations from water fortified with these compounds. A pilot nanofiltration unit, operating in the tangential flow, provided with a membrane in the spiral configuration, Model NF90-4040 (Dow Filmtec Membranes) was used. Two types of fortified water with carbamates were performed: distilled water and pond water. Nanofiltration tests with distilled water were performed in a closed system, in order to maintain a constant concentration of carbamates in the feed water. In this case, the efficiency of carbamates removal was greater or equal than 89, 100 and 74% for carbaryl, carbofuran, and methomyl, respectively. When using pond water, the removal of carbamates was higher or equal: 98, 100 and 90% for carbaryl, carbofuran, and methomyl, respectively. The results indicate that by nanofiltration, it is possible to obtain drinking water from the contaminated water with carbamates, according to international guidelines.

Keywords: Nanofiltration, drinking water, pesticides, carbamates.

Remoção de carbamatos de água potável com nanofiltração por fluxo tangencial

RESUMO. Os processos de tratamento por membranas, em particular, nanofiltração e osmose inversa, representam uma alternativa importante para o tratamento de águas contaminadas. Neste contexto, o presente estudo tem como objetivo avaliar a eficiência da remoção dos carbamatos: carbaril, carbofurano e metomil em diferentes concentrações. Usou-se uma unidade de nanofiltração piloto, operando em fluxo tangencial, fornecida com uma membrana na configuração espiral, modelo NF90-4040 (Dow membranas Filmtec). Foram realizados ensaios com dois tipos de água fortificada com carbamatos: água destilada e água da lagoa. Testes com a nanofiltração com água destilada foram realizados em um sistema fechado, a fim de manter a concentração constante de carbamatos em água de alimentação. Neste caso, a eficiência de remoção de carbamatos foi maior ou igual a 89, 100 e 74% para o carbaril, carbofurano, e metomil, respectivamente. Quando se utilizou a água da lagoa, a remoção de carbamatos foi igual ou superior: 98, 100 e 90% para o carbaril, carbofurano, e methomil, respectivamente. Os resultados indicam que por nanofiltração, é possível obter água potável a partir da água contaminada com carbamatos, de acordo com as diretrizes internacionais.

Palavras-chave: Nanofiltração, água potável, pesticidas, carbamatos.

Introduction

Pesticides may affect humans, either by direct contact or through food and contaminated water. According to Sanches, Silva, Campos, and Vieira (2003), contamination by pesticides occurs in both surface water and ground water. In the latter case, they may be leached by irrigation or rain water reaching the groundwater and aquifers. Therefore, the improper and indiscriminate use of pesticides in agriculture represents a risk to the quality of water near the crops.

Contamination of water by individual pollutants has required the search for alternative technologies capable of removing them, especially when traditional technologies are unable or insufficient to reduce their concentrations at safe levels. Moreover, technologies traditionally used such as chlorination and ozonation may produce toxic by-products (Tepus, Simonic, & Petrinic, 2009).

Membrane technology has become increasingly important in the tertiary treatment (polishing) of wastewater, aiming for its reuse and boiler water treatment. More recently, it has been employed in
the softening of brackish water and removing hazardous contaminants to human health, present in the water supply, as the pesticides used in agriculture. Generally, the membranes of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are most commonly used to produce drinking water or in industrial use (Duranceau, Taylor, & Alexander, 2001). The NF and RO membranes have been widely used for the removal of hardness and desalination of water, respectively. Research of Van Der Bruggen and Vandecasteele (2003) and other recent studies as Ormad, Miguel, Claver, Matesanz, and Ovelleiro (2008) and Sanches et al. (2013) approach the use of nanofiltration for the removal of various pollutants in water, including pesticides, such as diuron, simazine, atrazine, and isoproturon.

Kosutic and Kunst (2002) evaluated the removal of atrazine, MCPA (2-methyl-4-chlorophenoxyacetic acid), triadimefon and propram by nanofiltration membranes and reverse osmosis. For all pesticides (except for triadimefon) the removals were greater than 80% for nanofiltration and reverse osmosis membranes. Tepus et al. (2009) studied the removal of atrazine and deethylatrazine in groundwater through the nanofiltration membrane using different pressures. The removal of atrazine varied from 50 to 61% and the concentration of this compound in the permeate varied from 0.07 to 0.09 μg L⁻¹, depending on the pressure used. For deethylatrazine removal varied from 0 to 10% and final concentrations were established from 0.2 to 0.18 μg L⁻¹.

The present study aims to evaluate the efficiency of nanofiltration, using a commercial membrane, removing three pesticides from the carbamates group: carbaryl, carbofuran and methomyl, added at different concentrations in distilled water, and single concentration in pond water.

**Material and methods**

### Carbamates used in the experiments

The physicochemical properties of the carbamates: carbaryl, carbofuran and methomyl used in this study are presented in Table 1. Small differences were verified in their molar masses but their chemical structures are very different, which certainly influence in their solubility in water. These unique characteristics also confer different loads and load densities.

These properties are important when studying the selectivity of a substance of low molecular weight, such as carbamates, through a nanofiltration membrane whose selectivity is not restricted to the molar mass of the compound, that is, the size of the molecule. Berg, Hagneyer, and Gimbel (1997) discussed the influence of physicochemical properties on nanofiltration process in a study, where the chemical structure was related to the removal efficiency by the membrane. Van Der Bruggen, Everaert, Wilms, and Vandecasteele (2001) concluded that the main mechanisms involved in pesticides removal by nanofiltration are the molecule size and the dipole moment. Kosutic and Kunst (2002) showed the importance of the size of the molecule and of the membrane pore, as well as the physicochemical effects (regarding both physical and chemical properties) in the process on pesticides removal by nanofiltration.

**Water used in the experiments**

Two types of water used were distilled water and pond water from Lagoon of Peri - Florianópolis, state Santa Catarina, Brazil, which were fortified with carbaryl, carbofuran and methomyl. Before fortification with the carbamates, the pond water was previously subjected to coagulation with polyaluminum chloride and through a filter consisting of polystyrene beads instead of sand, through direct downward filtration. The diameter of the polystyrene beads ranged from 0.5 to 1.2 mm, a specific diameter of 0.68 mm and a sphericity coefficient of 0.96 (Schöntag & Sens, 2014). After filtration with polystyrene beads the water was submitted to a microfiltration process. The microfiltration was performed on a polypropylene filter of 5 Micron in a maximum operational pressure of 35 psi to 38°C. Maximum operational temperature was 71°C to 15 psi. The cartridge for microfiltration was made by GE Power and Water - Hytrex (Cartridge – GX05-20/05 micron).

**Experiments**

All experiments were performed in a pilot unit of nanofiltration in two different configurations as shown in Figure 1 and 2. The pilot unit had a feed tank of 200L capacity, a centrifugal pump, a pressure valve, a cartridge prefilter of polypropylene (GE Power and Water - Hytrex) with an opening of about 5 microns, and membrane nanofiltration NF90-4040 (Filmtec Membranes - Dow), with a spiral configuration and filtration area of 7.6 m². Experiments on membrane permeability showed that the permeate flow varied depending on the pressure applied according to $y = 0.3518x - 6.4451$ equation ($r^2 = 0.9905$). All experiments were conducted at room temperature (25°C) and at a pressure around 5 bars. The average permeate flow was of 18.8 L m⁻² hour⁻¹ and 76.8% recovery. The pressure applied was selected based on maximum pressure allowed on the cartridge prefilter.
Table 1. Physical and chemical properties of the carbamates: carbaryl, carbofuran and methomyl.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Carbaryl</th>
<th>Carbofuran</th>
<th>Methomyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar Mass (g mol⁻¹)</td>
<td>201.22</td>
<td>221.26</td>
<td>162.21</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td>C₁₂H₁₁NO₂</td>
<td>C₁₂H₁₅NO₃</td>
<td>C₅H₁₀N₂O₂S</td>
</tr>
<tr>
<td>Chemical Structure</td>
<td><img src="image1" alt="Chemical Structure Carbaryl" /></td>
<td><img src="image2" alt="Chemical Structure Carbofuran" /></td>
<td><img src="image3" alt="Chemical Structure Methomyl" /></td>
</tr>
<tr>
<td>Solubility in Water (20°C) (mg L⁻¹)</td>
<td>9.1</td>
<td>322.0</td>
<td>55000.0</td>
</tr>
<tr>
<td>pH Stability</td>
<td>5</td>
<td>4</td>
<td>5-7</td>
</tr>
<tr>
<td>Octanol-water partition coefficient (log Kow) pH 7, 20 ºC</td>
<td>2.36</td>
<td>1.80</td>
<td>1.24</td>
</tr>
</tbody>
</table>


Distilled water fortified with carbamates

First of all, the efficiency of removal of pesticides by nanofiltration was evaluated, using distilled water fortified with carbamates: carbaryl, carbofuran, and methomyl in different concentrations between 8 and 70 μg L⁻¹. Carbamates concentration on membrane feed water varies due to the influence of the entire system in this process, such as the prefilter, which was not evaluated in this study. This experiment was conducted with total recirculation of the permeate and concentrate to maintain the concentration of the carbamates constant in the feed, as shown schematically in Figure 1.

Four different experiments were performed, with varied concentrations of carbamates in the fortified feed water: Carbaryl (8.0; 9.5; 18; 40 μg L⁻¹); Carbofuran (9.0; 17; 35; 70 μg L⁻¹); Methomyl (7.5; 15; 35; 70 μg L⁻¹) as shown in Tables 3 to 5. Each concentration is one experiment. Each experiment lasted 3 hours. At the beginning of nanofiltration and at intervals of 1 hour, the permeate fluxes were measured and samples were collected for the analysis of the carbamates.

Pond water fortified with carbamates

The pond water used in the experiment, before fortification with carbamates, was previously submitted to coagulation with Polyaluminum Chloride and filtered with a filter consisting of polystyrene beads, through direct downward filtration. After fortification, the water was clarified by microfiltration using a 5 microns polyethylene filter.
This experiment was performed in a double open system. In that case, no recirculation of permeate and concentrate was used, once it could affect the feed water characteristics during the experiment, as shown schematically in Figure 2.

The duration of the experiment was 50 min. At the beginning of nanofiltration and at 10 min intervals the permeate flows were measured and samples were collected for analysis of carbamates. It was also evaluated conductivity, turbidity, apparent color, true color and total dissolved solids (TDS).

**Analysis of the carbamates**

For quantification of the carbamates, high performance liquid chromatography (HPLC) was used, using the EPA Method 531.2 (2001) with some adjustments. The method consisted of injecting 1000 μL in a chromatograph equipped with a reverse phase C18 column. Following, the analyses were hydrolyzed in a post- column reaction with 0.075 N sodium hydroxide (NaOH) at 80°C to form methylamine which reacted with o-phthalaldehyde (OPA) and 2- mercaptoethanol forming a compound identifiable in a fluorescence detector. A flow of 0.3 mL min⁻¹ for each post-column reagent was maintained, and unlike the proposed method, the sample injection volume was 300 μL. The column temperature was maintained at 30°C and the flow used was 1.0 mL min⁻¹. Ultra-pure water and a Mallinckrodt-Baker acetonitrile were used as the mobile phase. The gradient used was 30 to 100% acetonitrile in 20 min. The post-run was 3 min, maintaining 30% of acetonitrile.

The limits of detection and quantification of the pesticides obtained are shown in Table 2. These limits extend far in terms of concentration when considering the concentration of carbamates found, from 7.5 to 70 μg L⁻¹. That certifies the reliability of the method.

**Results and discussion**

The following presents the results of the performance of the nanofiltration membrane and the removal of the carbaryl, carbofuran and methomyl, added at different concentrations in the fortification of distilled water and pond water.

**Removal of the carbamates in distilled water**

Each of the carbamates - carbaryl, carbofuran, and methomyl were used in different concentrations, making up 12 nanofiltration experiments. The average concentrations of the carbamates obtained in the feed water, the permeate and the average removal efficiency of the nanofiltration membrane, are presented in Table 3, 4 and 5 for carbaryl, carbofuran and methomyl, respectively.

Table 3. Concentration of carbaryl in feed and permeate, and percentage of removal in different concentrations in distilled water.

<table>
<thead>
<tr>
<th>Fortification Levels</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed (μg L⁻¹)</td>
<td>8.0</td>
<td>9.5</td>
<td>18.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Permeate (μg L⁻¹)</td>
<td>0.7</td>
<td>1.0</td>
<td>1.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Removal (%)</td>
<td>90.6</td>
<td>89.0</td>
<td>91.0</td>
<td>91.0</td>
</tr>
</tbody>
</table>

Table 4. Concentration of carbofuran in feed and permeate, and percentage of removal at different concentrations in distilled water.

<table>
<thead>
<tr>
<th>Fortification Levels</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed (μg L⁻¹)</td>
<td>9.0</td>
<td>17.0</td>
<td>35.0</td>
<td>70.0</td>
</tr>
<tr>
<td>Permeate (μg L⁻¹)</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
</tr>
<tr>
<td>Removal (%)</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

LOD – Limit of Detection.

Table 5. Concentration of methomyl in feed and permeate, and percentage of removal in different concentrations in distilled water.

<table>
<thead>
<tr>
<th>Fortification Levels</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed (μg L⁻¹)</td>
<td>7.5</td>
<td>15.0</td>
<td>35.0</td>
<td>70.0</td>
</tr>
<tr>
<td>Permeate (μg L⁻¹)</td>
<td>1.8</td>
<td>3.0</td>
<td>5.9</td>
<td>13.0</td>
</tr>
<tr>
<td>Removal (%)</td>
<td>74.0</td>
<td>81.0</td>
<td>83.0</td>
<td>81.0</td>
</tr>
</tbody>
</table>

For carbaryl and carbofuran, removal efficiency was higher at all concentrations used (Table 3 and 4), ranging between 89 and 100%. Carbaryl removal efficiency was similar in all cases, even with different fortification levels dosed in the feed water, and it was the same for carbofuran. Similar results were found by Bueno, Coral, Sens, and Lapoli, 2016) and Van Der Bruggen, Schaep, Maes, Wilms, and Vandecasteele (1998), nevertheless, in this case, higher concentrations were evaluated. It was concluded that the concentration from 100 to 500 μg L⁻¹ of atrazine, simazine, diuron and isoproturon pesticides in the feed water did not influence the removal efficiency. A removal of about 95% was obtained from the nanofiltration membrane (NF-70) for all pesticides in that study.

For methomyl, Table 5, it appears that there was a significant difference only in fortification level C1,
which is when the lowest concentration was used. This removal efficiency was lower than 75% and in other fortification levels were higher than 80%.

Figure 3a and d shows the concentration of pesticide in permeate during nanofiltration for different concentrations in distilled water. In general, it was found that the concentration of carbamates in permeate presented very low values at the beginning of the process and remained without major changes.

![Figure 3](image)

**Figure 3.** Concentrations of the pesticides during the nanofiltration permeate - (a) C1 (8.0; 9.0; 7.5 μg L$^{-1}$ for carbaryl, carbofuran and methomyl, respectively on feed water) (b) C2 (9.5; 17.0; 15 μg L$^{-1}$ for carbaryl, carbofuran and methomyl, respectively on feed water), (c) C3 (18.0; 35.0; 35.0 μg L$^{-1}$ for carbaryl, carbofuran and methomyl, respectively on feed water), (d) C4 (40.0; 70.0; 70.0 μg L$^{-1}$ for carbaryl, carbofuran and methomyl, respectively on feed water).

Among the studied pesticides, carbofuran showed the lowest concentration in permeate at levels below the detection limit and was considered as zero for the calculation of removal efficiency.

Considering the value established by the World Health Organization (WHO, 2011), which establishes the limit of 7 μg L$^{-1}$ of Carbofuran in drinking water, the quality of the permeate meeting the legislation, even when the feed water showed concentrations than 10 times higher the maximum value allowed showing that, WHO does not have limits for carbaryl and methomyl. However, there is an Australian law that sets limits for the three pesticides to evaluated in this study: carbaryl, carbofuran and methomyl, being these limits, 30 and 10 g L$^{-1}$ and 20 mg L$^{-1}$ (Natural Resource Management Ministerial Council [NRMMC], 2011) respectively.

The removal efficiency in all experiments was higher for carbofuran, followed by carbaryl, which in turn, was greater than methomyl. This increased retention complies with the molar mass of the carbamates - carbofuran (221.26 g mol$^{-1}$), carbaryl (201.22 g mol$^{-1}$) and methomyl (162.21 g mol$^{-1}$).

The same behavior was observed by Kosutic and Kunst (2002), Berg et al. (1997), Van Der Bruggen et al. (2001), Chen, Taylo, Mulford, and Norris (2004), Plakas and Karabelas (2011) and Sanches et al. (2012), who concluded that one of the factors that influence in removal efficiency of pesticides by nanofiltration membranes is the molar mass and other factors such as the pore size of the membrane, the space between the polymer chains or polymer constituents of membranes.

There are other important factors on pesticides removal by membranes. Chen et al. (2004) described the influence of the diffusion in this process, where Van der Walls and other interactions can affect the mass transfer. Therefore, considering the hydrophobicity through octanol-water partition coefficient, methomyl is the one with the lowest value for this coefficient and the highest solubility in water. These physicochemical properties also explain the lowest efficiency removal for methomyl, comparing with the others carbamates evaluated in this study. High retentions of carbaryl and carbofuran can also be related to these parameters whereas they have highest octanol-water partition coefficient value and lowest solubility in water.

### Tests conducted with pond water

Table 6 shows, as expected, the nanofiltration parameters of reduced conductivity, turbidity, apparent color, true color and total dissolved solids (TDS) in pond water.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Feed SD</th>
<th>Permeate SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (μS cm$^{-1}$)</td>
<td>63.47 0.56</td>
<td>7.03 4.59</td>
</tr>
<tr>
<td>Turbidity (μT)</td>
<td>0.63 0.05</td>
<td>0.28 0.09</td>
</tr>
<tr>
<td>Apparent Color (uH)</td>
<td>10.83 0.75</td>
<td>0.00 0.00</td>
</tr>
<tr>
<td>True Color (uH)</td>
<td>2.53 0.41</td>
<td>0.00 0.00</td>
</tr>
<tr>
<td>TDS (mg L$^{-1}$)</td>
<td>40.63 0.36</td>
<td>4.50 2.94</td>
</tr>
</tbody>
</table>

TDS – Total Dissolved Solids; SD – Standard Deviation.

As shown in Table 7, the average removal of the carbamates was greater than 90% in all tests. It was found that the removal was higher in carbofuran.
compared to carbaryl, which in turn was greater than methomyl. Similar to the previous experiment, it also appears to be a relationship between the molar mass of the carbamates and their retention by the nanofiltration membrane.

Table 7. Average concentration of the carbamate in feed water, and permeate removal efficiency.

<table>
<thead>
<tr>
<th></th>
<th>Carbaryl</th>
<th>Carbofuran</th>
<th>Methomyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed (μg L⁻¹)</td>
<td>20.5</td>
<td>17.4</td>
<td>23.0</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>2.8</td>
<td>1.03</td>
<td>2.4</td>
</tr>
<tr>
<td>Permeate (μg L⁻¹)</td>
<td>0.4</td>
<td>&lt; LOD</td>
<td>2.3</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.5</td>
<td></td>
<td>2.3</td>
</tr>
<tr>
<td>Removal (%)</td>
<td>98.0</td>
<td>99.5</td>
<td>90.0</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>2.8</td>
<td>1.3</td>
<td>9.0</td>
</tr>
</tbody>
</table>

LOD – Limit of Detection.

Comparison between removal efficiency of carbamates in distilled water and pond water

Figure 4 shows the nanofiltration efficiency in the removal of carbamates in two types of water used in the experiments. A pressure of 70 psi and a carbamate concentration in the feed water of about 20 μg L⁻¹ was used.

![Figure 4](image_url)

Figure 4. Comparison of removal efficiency of pesticides by nanofiltration at 70 psi and at a concentration in the water supply of 20 μg L⁻¹ of distilled water and pond water.

It was observed that there was a greater retention of the carbamates in the pond water when compared with distilled water. The removal efficiency of carbaryl increased from 91% in distilled water to 98% in pond water. For the carbofuran average, removal efficiency was 100% for both types of water used. And an increase of 81% in distilled water to 90% in pond water, as in the removal of methomyl.

The influence of water composition on the removal efficiency of pesticides by nanofiltration membranes has already been observed by other researchers. Plakas and Karabelas (2011) concluded that pH, ionic strength and the presence of organic matter are the factors in feed water that influence to remove these compounds. The presence of organic matter and its influence on the removal of pesticides when using a nanofiltration membrane, was also cited by Berg et al. (1997), Zhang, Van Der Bruggen, Chen, Braeken, and Vandecasteele (2004) and Devitt, Ducellier, Cote, and Wiesner (1998).

**Conclusion**

Nanofiltration is a process that can contribute to the partial removal of carbamates in water, showing in some circumstances, a complete removal of these compounds.

Parameters of water may influence carbamates retention. These deductions are also influenced by molecular weight, octanol-water partition coefficient, and solubility. There is removal greater or equal than 89% for carbaryl, 100% for carbofuran and 74% for methomyl.

Considering experiments with distilled water, different concentrations levels of carbamates in the feed water did not interfere on carbofuran and carbaryl. There was only removal variation on methomyl.

Nanofiltration membrane was performed well in the removal of pesticides in pond water, allowing it to achieve values of concentration in permeate lower than the limit of quantification (0.53 μg L⁻¹) for carbaryl, limit of detection (0.33 μg L⁻¹) for carbofuran, and less than 3.0 μg L⁻¹ for methomyl. These concentrations of carbamates permeated meet the limits established by Brazilian (Brasil, 2011), Australian (NRMMC, 2011) and Canadian (Canada, 2014) legislations. In pond water, the removal efficiency of the nanofiltration membrane was greater than 90% for all pesticides studied.

This study showed the technical feasibility of the removal of carbamates in distilled and pond waters in compliance with current legislation.

Suggestions for further studies: Analyze the dissolved organic carbon or performing other analysis to evaluate the influences of organic compounds on removal of carbamates. Only then more objective answers might be obtained for the present study.

**References**


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