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1. Introduction

Due to its low cost, stability, and effectiveness, adding chlorine to drinking water is one of the most common treatments to ensure its bacteriological quality (Al-Jasser, 2007). Chlorine inactivates various types of micro-organisms and its residual properties help to prevent micro-organism regrowth during water flow in pipes (Connell, 1997).

Beyond off-flavors development due to chlorination by-products, chlorine flavor by itself constitutes one of the major complaints against tap water. In 1996, chlorine taste was the third most reported taste default of tap water in the US (Suffet et al., 1996). Due to the unpleasant taste of tap water, consumers may prefer bottled water as drinking water, even if bottled drinking water consumption would be associated with a higher economic and ecological cost. (Rodriguez et al., 2004) showed that the perception of tap water quality is closely related to the residual chlorine level: people living near a treatment plant who may receive a higher chlorine level in their tap water were generally less satisfied by tap water quality and perceived more risks associated with it than people living far from the plant. It was reported that, in the US, bottled water drinkers have three main categories for decisions: safety of water; healthfulness of the water; and taste of the water (Mackey et al., 2004). Consumers supplied with tap water containing a residual chlorine level greater than 0.24 mg/L Cl₂ were less satisfied with tap water when compared to consumers receiving lower concentrations (Rodriguez et al., 2004). This value almost coincides with the free chlorine residual (0.2 mg/L) that must be maintained in the distribution system, reducing the likelihood of further contamination (Clark & Coyle, 1990). When taken together, this studies underline that the consumers would reject tap water in safe conditions due the chlorine flavor.
The residual chlorine could be removed using an activated carbon filter at the time of consumption. Activated carbon has already been used to remove chlorine excess of tap water used in food industries (Jaguaribe et al., 2005). Due to its well-developed pore structure, activated carbon in either powder or granules has an excellent adsorbent capacity.

Beyond this concern with chlorine flavor, several studies reported that chlorination of organic matter in fresh water resulted in the formation of disinfection by-products (DBPs) (Richardson, 2003; Rook, 1976), especially trihalomethanes (THMs), which remain a human health concern. Trihalomethanes (THMs) are a group of volatile organic compounds (VOCs) classified as disinfection by-products (DBPs). They were first identified by (Rook, 1976) and are formed during the chlorination of water, when chlorine reacts with naturally occurring organic matter: mainly humic and fulvic acids. Their general formula is CHX₃, where X may be any halogen or a combination of halogens. However, generally speaking this term is used to refer only to those compounds containing either chlorine or bromide, because these are the ones most commonly detected in chlorinated water (chloroform, bromodichloromethane, dibromochloromethane and bromoform). Brominated trihalomethanes are formed when hypochlorous acid oxidizes bromide ion present in water to form hypobromous acid, which subsequently reacts with organic materials to form these compounds (Pavon et al., 2008; Richardson, 2003). Iodinated THMs have been identified in chlorinated drinking water; however, they are not widely measured and are not regulated, even though iodinated compounds may be more toxic than brominated and chlorinated compounds (Richardson, 2003).

The International Agency for Research on Cancer (IARC) has classified chloroform and bromodichloromethane as possible carcinogens for humans (Group 2B) based on limited evidence of carcinogenicity in humans but sufficient evidence of carcinogenicity in experimental animals. Dibromochloromethane and bromoform belong to Group 3 (not classifiable as regards their carcinogenicity to humans), based on inadequate carcinogenicity in humans and inadequate or limited carcinogenicity in experimental animals (Pavon et al., 2008; WHO, 2006). In the case of THMs, approximately equal contributions to total exposure come from four sources: the ingestion of drinking water, inhalation of indoor air, inhalation and dermal exposure during showering or bathing, and the ingestion of foods (WHO, 2006). Trihalomethanes have been detected in different aqueous matrixes: tap water, swimming pool water, distilled water, ultrapure water and even in water that has not been subjected to chlorination processes, such as ground water, mineral water, snow, rain water, sea, and river water. However, the concentrations of these compounds in unchlorinated water tend to be much lower than those usually found in tap water. The presence of these levels of THMs may be due to several causes. In cases in which the chloroform > bromodichloromethane > dibromochloromethane > bromoform pattern is conserved, the THMs are likely to have originated from the infiltration of chlorinated water. The sources of chlorinated water to ground water may include the irrigation of lawns, gardens and parks; leaking drinking water distribution and sewer pipes, and industrial spills, among others.

Adsorption in carbonaceous materials, as carbon nanotubes and carbon spheres was reported as an effective technique in removing THM from water (Lu et al., 2005; Morawski et al., 2000). However, the authors did not consider the application of simpler and cheaper technology, as granular activated carbon.
(Amy et al., 1990) found that the majority of THM formation potential is presented by small to medium organic compounds with a specific ultraviolet absorbance (SUVA) values less than 3.0. The SUVA parameter represents the ratio $\text{UV}_{254}/\text{DOC}$ and constitutes an indicator of carbon aromacity in water (Uyak et al., 2008).

Numerous research studies involving microfiltration (MF) and ultrafiltration (UF) of surface waters in rivers and lakes have proved that NOM is the main source of fouling during membrane processes (Uyak et al., 2008). The application of activated carbon (AC) in conjunction with MF/UF membranes is a promising technology for the removal of organic compounds in drinking water treatment, which incorporates the adsorption capabilities of activated carbon and the microorganism and particle removal ability of the MF/UF membranes (Tsujimoto et al., 1998; Yuasa, 1998). (Ravanchi & Kargari, 2009) highlighted the importance to propose innovative integrated membrane processes in order to became this process more commercial.

Moreover, nanofiltration membranes also showed potential in removing THMs from drinking water (Uyak et al., 2008). The application of nanofiltration and reverse osmosis in drinking water treatment is increasing in developed countries (Clever et al., 2000). However, their application in developing countries is still limited due the high costs of the membranes and pumping (Glucina et al., 2000).

Alternatively, microfiltration membrane processes can be designed to operate with gravity as the driving force, in simple systems that could be operated by non-trained people. Besides this, gravitational systems present the following advantages: energy saving, once pumps are not necessary; simpler tubing is required because it operates at low pressures. However, this kind of researched is scarce in the scientific literature (Peter-Varbanets et al., 2009).

In this way, the objective of this publication is to show the efficiency of a microfiltration membrane working alone and associated with activated carbon for removing THM and their precursors from tap water in a gravitational module.

2. Process configuration

2.1 Materials

Acetate cellulose microfiltration membrane (pore diameter=3.0 µm) was purchased from ADVANTEC/MFS (Japan). Commercial Granular Activated Carbon (GAC) 20x40 mesh made from coconut was supplied by BAHIACARBON (Brazil). Table 1 presents the textural characteristics of this activated carbon.

<table>
<thead>
<tr>
<th>Surface area (m² g⁻¹)</th>
<th>Micropore area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>715.46</td>
<td>677.77</td>
<td>0.3856</td>
<td>20.04</td>
</tr>
</tbody>
</table>

Table 1. Textural characteristics of the activated carbon used in this work.

Filtration tests were carried out with the membrane working alone and with GAC as a pretreatment. The gravitational module used in this study (Fig. 1) operated exclusively with gravity as driven force, which produced a pressure of approximately 0.36 bar, due the position of the lung tank in relation to the filtration module.
The filtration module was composed of two parts: a flat-sheet membrane cell made of stainless steel and an acrylic cartridge to support the activated carbon. The effective membrane was 103 cm$^2$ and the activated carbon bed was 20 cm high. In each experiment, a new membrane was used, rinsed with ultrapure water and compacted by filtering ultrapure water during 2 h before starting a filtration test.

2.2 Raw water

The raw water used in this study was prepared using finished water of Pirapó River water (PRW), located in Maringá-Brazil. Quality parameters of this water are summarized in Table 2.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg/L)</td>
<td>1.89</td>
</tr>
<tr>
<td>$UV_{254}$ (L/cm)</td>
<td>0.032</td>
</tr>
<tr>
<td>SUVA (L/mg m)</td>
<td>1.69</td>
</tr>
<tr>
<td>Color (UC)</td>
<td>1.0</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.67</td>
</tr>
<tr>
<td>pH</td>
<td>7.26</td>
</tr>
</tbody>
</table>

Table 2. Finished Pirapó River water (PRW) quality parameters

Two different types of water were prepared, and the details of each preparation are given below:

a. Chlorinated water

Chlorinated water samples were obtained by adding sodium hypochlorite (NaOCl $\sim$2.5%, commercial grade) to tap water (PRW) in order to adjust the chlorine concentration to 2.0
mg/L, the limit regulated by Brazilian Government. The removal of chlorine, DOC, UV$_{254}$ and SUVA were evaluated using the chlorinated water.

b. Water containing THMs

Trihalomethanes mix at 2000 µg/L, produced by Supelco was diluted to 10 mg/L, and this final solution was used to adjust the THMs concentration in tap water (PRW), in order to maintain the total THMs concentration around 120 µg/L, slightly higher than the limit regulated by the Brazilian Government of 100 µg/L.

2.3 Analytical methods

Dissolved organic carbon (DOC) measurements were performed with a HACH DR2010 spectrophotometer, using the low range direct method. Besides, UV$_{254}$ absorbance measurements were conducted in accordance with Standard Methods by a HACH DR 2010 UV spectrophotometer at a wavelength of 254 nm. Water samples for DOC and UV$_{254}$ measurements were first filtered through a pre-washed 0.45 µm membrane filter to remove turbidity, which can interfere in these measurements, and distilled ultra filtered water was used as the background correction on the spectrophotometer.

Chlorine measurements were performed with a HACH DR/2010 spectrophotometer, using the DPD method for free chlorine determination, according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1998). The samples were collected and immediately analyzed, using the HACH DPD free chlorine reagent.

THM concentrations were determined by Gas chromatography–mass spectrometry (GC-MS). For determination of THM was used in a chromatograph GC-MS with mass detector DSQ II with autosampler from Thermo triplus Red Space. The recovery of THMs was optimized using excess of KCl (4g per 12 mL of sample), according to Caro et al. (2007).

2.4 Flux and resistance measurements

Firstly, the permeated flux of deionized water was measured during 120 min in a clean membrane using new and clean membrane.

After the tests with raw water, final flux with deionized water was determined, also during 120 min. At the end of this measurement, the membrane was removed from the experimental module (Fig. 1) and mechanically cleaned in order to remove the cake formed on the membrane surface. After that, a new flux measurement with deionized water was done.

Resistances due to different fouling mechanisms were determined in order to investigate the fouling behavior. Resistances were calculated following the resistance-in-series model adapted from (A.I. Schafer, 2005) as presented in equation (1):

$$ J = \frac{\Delta P}{\eta (R_m + R_p + R_f)} \quad (1) $$

where $J$ is permeate flux [kg m$^{-2}$ s$^{-1}$], $\Delta P$ is trans-membrane pressure [kg m$^{-1}$ s$^{-2}$], $\eta$ is dynamic viscosity [kg m$^{-1}$ s$^{-1}$], and $R$ denotes a resistance [m$^2$ kg$^{-1}$]: $R_m$ is membrane
hydraulic resistance, $R_p$ is resistance due to pore blocking, and $R_c$ is resistance due to cake formation.

Each resistance was experimentally measured in the gravitational system with and without GAC pretreatment. Membrane hydraulic resistance, $R_m$, was determined measuring the flux of deionized water through a clean membrane sheet. In this case, the others resistances are equals to zero.

The sum of resistances due to pore blocking and cake formation ($R_p + R_c$) was determined measuring the flux of deionized water with the fouled membrane, i.e. with the membrane that was used for raw water filtrations without clean procedures.

After mechanical cleaning, the flux measurements was carried out in order to obtain the resistance due to pore blocking, $R_p$.

Membrane fouling percentage ($%F$) was calculated according to equation (2), as proposed by (Balakrishnan et al., 2001). This percentage represents the drop in deionized water flux after the tests of filtration with raw water.

$$%F = \frac{(J_i - J_f)}{J_i} \times 100$$ \hspace{1cm} (2)

where $%F$ is membrane fouling percentage, and $J_i$ and $J_f$ are deionized water fluxes in clean and fouled membranes, respectively.

3. Process performance

3.1 Flux measurements with raw water

In general, the application of activated carbon as pretreatment to micro/ultrafiltration membranes affects the permeate flux of membranes and improves the removal of several parameters that may cause fouling (Fabris et al., 2007; Kim & Gai, 2008). However, there is a lack of information in the literature about this application in gravitational systems.

The permeate fluxes of the membrane operating alone and with activated carbon as pretreatment were determined during the evaluation of chlorine and THM removals from tap water in the gravitational module. Considering that the observed values of permeate fluxes were almost equals in both assays, Fig. 2 illustrates the average values of both assays during the 480 min of operation. The membrane working alone is referred as M3 and the membrane working with activated carbon as pretreatment is referred as M3C.

The permeate flux increased when using activated carbon as pretreatment. In the first 50 minutes of operation, it is observed a permeate flux between 2000 and 400 kg h$^{-1}$ m$^{-2}$ to the membrane M3 (without GAC pretreatment) and between 3000 and 700 kg h$^{-1}$ m$^{-2}$ to the membrane M3C (with GAC pretreatment). After 50 min of operation, the permeate flux was around 200 and 300 kg h$^{-1}$ m$^{-2}$ to the membranes M3 and M3C, respectively. However, in the last 100 minutes of operation, it is observed that the permeate flux was around 100 kg h$^{-1}$ m$^{-2}$ to the membrane M3, and around 200 kg h$^{-1}$ m$^{-2}$ to the membrane M3C. The better performance of the membrane M3C in comparison to the membrane M3 is probably due to the adsorption of organic matter in the activated carbon surface, which mitigates fouling effects (Kim & Gai, 2008).
Fig. 2. Permeate fluxes of tap water to the membranes with and without GAC as pretreatment (M3C and M3, respectively).

Fig. 3 presents the results of total resistance against time to the 3.0 µm membrane working alone and associated with activated carbon, calculated using Equation 1. Total resistance is referred as the sum of $R_m$, $R_p$, and $R_c$.

It is possible to notice from Fig. 3 that the application of GAC as pretreatment reduced the total resistance of the membrane during the operation with tap water. This decrease in the total resistance is probable the main cause of the flux increase observed during the filtration with GAC as pretreatment.
3.2 DOC and UV$_{254}$ rejection capacity

Figs. 4 and 5 present the reduction in DOC and UV$_{254}$ compounds, respectively, after microfiltrations of tap water with and without GAC pretreatment.

DOC rejection by the process with the membrane working alone (M3) was between 50 and 70% (Fig. 4) during the complete experiment. The range presented by UV$_{254}$ rejection was between 35 and 55% (Fig. 5). These results are comparable to previous results found to nanofiltration membranes (Alborzfar et al., 1998), with the advantage of using microfiltration and a gravitational system, much more cheaper than a nanofiltration system using pumps.

Fig. 4. DOC rejection in tap water after microfiltrations with the membrane working alone (M3) and with GAC as pretreatment (M3C).

Fig. 5. UV$_{254}$ rejection of in tap water after microfiltrations with the membrane working alone (M3) and with GAC as pretreatment (M3C).
Besides this, M3C presented a removal of 70 to 95% to DOC (Fig. 4) and a removal of 55 to 70% to UV254 (Fig. 5). The application of activated carbon as pretreatment significantly increased the removal of dissolved organic matter, as reported before (Bao et al., 1999).

### 3.3 Chlorine rejection capacity of the evaluated systems

Fig. 6 shows the rejection performances of free chlorine, in the initial concentration of 2 mg/L, by the two studied systems, M3 and M3C, in the gravitational module.

![Chlorine rejection in tap water after microfiltrations with the membrane working alone (M3) and with GAC as pretreatment (M3C).](image)

Chlorine rejection increased gradually to the membrane working alone (M3), from 70% in the first minutes of operation to 100% after 270 min. It probably happened due to a formation of a cake fouling layer on the surface of the membrane, which improved the removal rate of contaminants (Kim & Gai, 2008).

In contrast to M3, the chlorine rejection of the system using activated carbon as pretreatment (M3C) was of 100% during the complete experiment. (Jaguaribe et al., 2005) reported that, due to its well-developed pore structure, coconut shells activated carbon (working alone) reduces around 40% of free chlorine presented in water.

### 3.4 THM rejection capacity of the evaluated systems

Total THM and its four compounds were chosen to evaluate the change in permeate concentration over the course of filtration tests using the membrane working alone (M3) and using activated carbon as pretreatment to the membrane (M3C). Fig. 7 illustrates the total THM rejection capacity of M3 and M3C processes.

Total THM rejection of M3 process was approximately equals to 74% during the complete experiment, which could be considered a suitable result, since similar results were obtained when using nanofiltration membranes at higher pressures (Uyak et al., 2008), and considering the fact that M3 is a microfiltration membrane operating only by gravity.
Moreover, M3C process presented a removal of 93 to 99% of THM compounds due to the considerable adsorption capacity of activated carbon toward various pollutants, especially THM, as reported before (Razvigorova et al., 1998).

Fig. 8 shows the rejection performances of three species of THM by the two studied systems, M3 and M3C during the 480 min of filtration. The THM species are chloroform (CFM), bromodichloromethane (BDCM) and dibromochloromethane (DBCM). Since bromoform (BFM) was not detected in the tested water, hence, three species were taken in account.

Fig. 7. Total THM rejection in tap water after microfiltrations with the membrane working alone (M3) and with GAC as pretreatment (M3C).

The selected microfiltration membrane working alone (M3) was effective in removing the THM compounds during the 480 min of filtration. It was depicted in Fig. 8 that the rejection efficiencies of CFM were found to be around 65 and 70% during the 480 min of operation. Moreover, the rejection efficiencies of BDCM and DBCM were practically 100%. As observed in previous similar studies (Uyak et al., 2008), the removal efficiency of M3 process was increased with increasing the molecular weight of THM species. As bromine atom replace the chlorine atoms, greatly increasing the molecular weight, resulted in higher removal efficiency. The higher removal efficiency of BDCM and DBCM was attributed to higher molecular weight and brominating characteristics (Uyak et al., 2008).

For the system using activated carbon as pretreatment to the microfiltration membrane (M3C), Fig. 8 illustrates the removal of CFM to be around 99% in the first minutes of operation and around 94% after 100 minutes. The rejection rates of BDCM and DBCM were also around 100%. The application of activated carbon as pretreatment enhanced the THM compounds removal, and this fact is especially notable to CFM, once the rejection rates of BDCM and DBCM were considerably high also when the gravitational module operated only with the microfiltration membrane (M3). It was found in the literature that magnitude of adsorption of these chlorinated compounds was in the following order: BDCM>DBCM>CFM. The molecules containing bromine were adsorbed with highest efficiency compared to the remainder of lower radius (chlorine). It means that not only the size of pores determines the adsorption but also surface chemical character may influence it (Razvigorova et al., 1998).
3.5 Flux and resistance measurements

Fig. 9 illustrates the permeate flux values measured with deionized water to the membrane with and without the GAC pretreatment before and after the filtrations with tap water.

The association with activated carbon significantly improved the performance of the 3.0 µm membrane in relation to the initial and final flux values. The initial flux to the carbon+membrane system was approximately 2700 kg m\(^{-2}\) h\(^{-1}\), while the membrane working alone presented initial flux around 2000 kg m\(^{-2}\) h\(^{-1}\).

Considering final flux values, the membrane associated with GAC achieved values around 222 kg m\(^{-2}\) h\(^{-1}\) and the membrane working alone presented values not higher than 60 kg m\(^{-2}\) h\(^{-1}\). These results could be related to the adsorption of organic matter by the activated carbon (Choo & Kang, 2010).
Fig. 9. Initial and final flux values of deionized water to the membrane with and without GAC as pretreatment (M3C and M3, respectively).

Table 3 shows the results of resistances and fouling percentage to the 3.0 µm membrane working alone and associated with activated carbon.

<table>
<thead>
<tr>
<th>Process</th>
<th>R_m \times 10^8 (m^{-1})</th>
<th>R_c \times 10^8 (m^{-1})</th>
<th>R_p \times 10^8 (m^{-1})</th>
<th>R_t \times 10^8 (m^{-1})</th>
<th>%F</th>
</tr>
</thead>
<tbody>
<tr>
<td>M3</td>
<td>0.141</td>
<td>1.31</td>
<td>4.17</td>
<td>5.621</td>
<td>97.3</td>
</tr>
<tr>
<td>M3C</td>
<td>-</td>
<td>1.13</td>
<td>0.156</td>
<td>1.395</td>
<td>91.9</td>
</tr>
</tbody>
</table>

Table 3. Results of resistance and fouling percentage.

It was observed a considerable decrease in the $R_c$, $R_p$, and $R_t$ values when GAC was applied as pretreatment, indicating that the activated carbon reduced the fouling due the cake formation ($R_c$) and pore blocking ($R_p$). These results are in accordance with the previous reports (Kim & Gai, 2008). The hydraulic membrane resistance ($R_m$) was not determined to the membrane working with GAC as pretreatment because it is considered an inherent property of the membrane.

It was also observed a decrease in the fouling percentage with the application of activated carbon as pretreatment to the 3.0 µm membrane, which could also be expected, according to previous reports in the literature (Choo & Kang, 2010).

4. Conclusions

Microfiltration and its association with activated carbon are technologies that have potential for use in drinking water treatment. The conclusions that can be drawn from the results of this experimental investigation are as follows:

- Experimental results show that the microfiltration membrane evaluated in this study was effective in removing DOC, $\text{UV}_{254}$, chlorine, CFM, BDCM, and DBCM compounds. Further, brominated THM compounds were removed more significantly than chlorinated THM ones. The higher removal efficiency of DBCM was attributed to higher molecular weight and brominating characteristics.

- The application of activated carbon as pretreatment increased the permeate flux and also increased the rejection efficiency of DOC, $\text{UV}_{254}$, chlorine, CFM, BDCM, and DBCM compounds. It was attributed to the chemical interaction that probably happens between activated carbon surface and the studied compounds.
The system using activated carbon and microfiltration membrane (M3C) applied in a gravitational module is a promising alternative to improve drinking water quality, due to its efficiency, simplicity and low cost.

5. Acknowledgments
The authors acknowledge the financial support of the CNPq and the FAPEMIG.

6. References


This book attempts to cover various issues of water quality in the fields of Hydroecology and Hydrobiology and present various Water Treatment Technologies. Sustainable choices of water use that prevent water quality problems aiming at the protection of available water resources and the enhancement of the aquatic ecosystems should be our main target.

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