Hybrid gravitational microfiltration system for drinking water purification

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Natália Ueda Yamaguchi1*; Silvia Amélia Liwa Abe2; Flávia Vieira da Silva Medeiros3; Angélica Marquetotti Salcedo Vieira2; Rosangela Bergamasco2

1Centro Universitário de Maringá (Unicesumar), Maringá, PR, Brasil
Programa de Pós-Graduação em Tecnologias Limpas
2Universidade Estadual de Maringá (UEM), Maringá, PR, Brasil
Departamento de Engenharia Química
3Universidade Tecnológica Federal do Paraná (UTFPR), Campo Mourão, PR, Brasil
*Corresponding author: e-mail: nataliaueda@hotmail.com, silvia_abe@hotmail.com, flaviavs@gmail.com, amsvieira@uem.br, ro.bergamasco@hotmail.com

ABSTRACT
This study evaluates the application of a polymeric microfiltration membrane in a gravitational filtration module and its combination with granular activated carbon (GAC) impregnated with copper, resulting in a hybrid process. The proposed system would be used to improve the quality of water for human consumption in developing countries. Permeate flux, pH, Escherichia coli removal, color, turbidity and free chlorine removals were evaluated in the applied process. Instrumental techniques, such as N2 adsorption at 77 K, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) analyses were used to characterize the proposed membrane and adsorbent. The GAC ensured higher chlorine removals, as well as higher permeate flux. Furthermore, the GAC impregnated with copper oxide nanoparticles exhibited higher Escherichia coli removal. Therefore, the hybrid gravitational membrane system applying GAC impregnated with copper oxide could be considered as a potential alternative point-of-use treatment to improve the quality of water for human consumption.

Keywords: activated carbon; copper; Escherichia coli; membrane.

Sistema de microfiltração gravitacional híbrido para purificação de água

RESUMO
Neste estudo, uma membrana polimérica combinada com carvão ativado granular (CAG) impregnado com nanopartículas de óxido de cobre foi avaliada em um processo híbrido com membrana. A avaliação do sistema gravitacional proposto visando a melhoria da qualidade da água destinada ao consumo humano em países em desenvolvimento foi realizada avaliando-se o fluxo permeado, pH, remoção de Escherichia coli, cor, turbidez e a remoção de cloro livre. Técnicas instrumentais tais como adsorção de N2 a 77 K, microscopia eletrônica de varredura
Hybrid gravitational microfiltration system …

(MEV), microscopia eletrônica de transmissão (MET) e análises de espectroscopia de raios-x por dispersão em energia (EDX) foram utilizadas para caracterizar o sistema proposto de membrana e adsorvente. O CAG garantiu maiores remoções de cloro, e também maior fluxo permeado. Além disso, o CAG impregnado com nanopartículas de óxido de cobre exibiu maior remoção de *E. coli*. Portanto, o sistema de membrana gravitacional híbrido utilizando CAG impregnado com óxido de cobre pode ser considerado como um tratamento potencial alternativo pontual para melhorar a qualidade da água destinada ao consumo humano.

**Palavras-chave**: carvão ativado; cobre; *Escherichia coli*; membrana.

1. INTRODUCTION

Scientific advancements in water purification can aid the development of new technologies appropriate for different regions of the world. The sheer enormity of the problems that the world is facing due the lack of adequate clean water and sanitation means that much more work is needed to address the challenges faced by developing nations, which suffer a diversity of socio-economical-political-traditional constraints, and require a broader approach incorporating sustainable energy sources and implementing educational and capacity building strategies. Consortiums of governments at all levels, businesses and industries, financial and health organizations, water and environment associations, and educational and research institutions need to focus increased attention on solving these problems. While better water resource management, improved efficiencies, and conservation are vital for moderating demand and improving availability, it is our belief that improving the science and technology of water purification can help to provide cost-effective and robust solutions (Shannon et al., 2008).

In developing countries, centralized drinking water treatment is sometimes deficient, leading to the frequent use of untreated natural water sources such as rivers, lakes, groundwater or rain. These sources are usually unprotected and may contain chemical or microbial pollutants, mainly originated from the absence of appropriate sanitation and thus contaminated by human and animal residues that are either active cases or carriers of disease. Sometimes, even when centralized treatment plants are available, contamination of piped drinking water may occur between the distribution system and the final consumption point (Peter-Varbanets et al., 2009). Also, in rural or informal urban or peri-urban areas there is no centralized water supply. Consequently, decentralized systems are often the only means of improving the quality of water obtained from contaminated sources (Peter-Varbanets et al., 2009).

Among these systems, membrane separation processes are suitable for water treatment since they can remove bacteria, viruses, turbidity and color (Bergamasco et al., 2011b). However, most membrane processes are pressure-driven and require pumps and high energy consumption. Because of the high cost of constructing large pressure vessels with the proper wetted surfaces for corrosion resistance, pressure filters are typically used for small- and medium-size capacity water reverse osmosis plants. Gravity filters are used for all sizes of water reverse osmosis in water treatment plants but have found wider applications for large and medium-size facilities (Voutchkov, 2010). Other researchers have reported that the disadvantages of membrane water treatment are fouling and plugging. Its occurrence leads to a decline in membrane permeability and reduced flux (Kim et al., 2009).

Integration of a pretreatment with a membrane filtration process has been employed to reduce membrane fouling and to improve the removal of certain contaminants. It is reported that the combination of activated carbon with membrane filtration increased the obtained volume of filtrated water and prolonged the continuous filtration time by mitigating membrane fouling (Ajmani et al., 2012; Kim et al., 2009; Silva et al., 2012).

Moreover, it is well known that activated carbon shows strong adsorbability of several kinds of organic pollutants, trace heavy metal ions and some nonmetal ions due to its...
microporous structure and immense specific surface. If copper can be loaded on the surface of activated carbon with high specific surface area, it may enlarge the reaction area between copper and ions/organic molecules and effectively improve the efficiency of the adsorbent (Deveci et al., 2006; Liu et al., 2011; Zhao et al., 2010). In addition, copper presents bactericidal properties, as reported in some studies (Castro et al., 2010; Moritz e Geszke-Moritz, 2013). They have reported Cu-textiles and composite materials presenting antiviral, algicide and fungicide properties. Copper-impregnated materials have been reported to be effective against *E. coli*, *Staphylococcus aureus* and the fungi *Candida albicans* and were also effective against other infections, besides being safe to humans (as demonstrated by the widespread and prolonged use by women of copper intrauterine devices) and not causing skin irritation when externally applied (Borkow e Gabbay, 2004; Castro et al., 2010).

The main objective of the study was to propose a simple module that ensures water quality for human consumption in a simple and inexpensive household filter destined for developing countries.

2. MATERIALS AND METHODS

2.1. Activated carbon modification

This study used commercial GAC 16 x 52 mesh obtained from oil palm shell supplied by BAHICARBON (Brazil). Copper oxide nanoparticles were impregnated on the porous GAC using a wet technique. 150 g of GAC were added to 150 ml of an aqueous solution of copper sulfate in order to obtain 0.5 or 1.0 wt.% of Cu loading. The solution was stirred in a rotary evaporator system for 24 h at 60°C and 20 rpm. Afterwards, it was dried at 80°C in a vacuum system in the same equipment. The samples were successively calcined at 350°C for 5 h (Bergamasco et al., 2010). Samples with 0.5 and 1.0 wt.% of Cu loading were named GAC/Cu05 and GAC/Cu10, respectively.

2.2. Characterization

GAC pore characteristics (surface area, pore volume and average pore size) were measured in a Quantachrome Autosorb Automated Gas Sorption System (Florida, USA). BET specific surface areas were determined by N₂ adsorption-desorption isotherms at 77 K. Micropore area was determined by means of the t-method of Halsey and mesopore area, volume, average pore diameter using Barrett-Joyner-Halenda method (BJH). Volume and average pore diameter of micropores were calculated using Horvath-Kawazoe method (HK).

The surface morphology and composition of new membrane and GAC before use were studied using a scanning electron microscope (SEM) FEI (Model Nova 200 NanoSEM), energy dispersive X-ray spectroscopy (EDX). The morphology of copper oxide nanoparticles was also analyzed by transmission electron microscopy (TEM).

2.3. Hybrid membrane gravitational system

Figure 1 shows the gravitational filtration module used in this study, which was proposed in a previous study (Silva et al., 2012).

The cellulose acetate microfiltration membrane (pore diameter = 3.0 μm) was purchased from ADVANTEC (Japan). GAC impregnated with copper oxide nanoparticles was placed in the filtration module, before the flat membrane, as a pre-treatment in a packed-bed filter resulting in a hybrid gravitational system as shown in Figure 1A. This filter was obtained by packing 150 g of GAC in a 20-cm high acrylic cartridge. Additional tests were carried out to compare the effects of GAC pretreatment with the unitary process, which was the process using membrane alone, illustrated in Figure 1B. All process conditions evaluated in the gravitational system are given in Table 1.
Each process system was evaluated performing 5 steps according to previous studies (Bergamasco et al., 2011a; Silva et al., 2012): (1) determination of the initial permeate flux with deionized water with a clean membrane, (2) filtration of deionized water contaminated with *E. coli* with an approximate concentration of 1x10⁵ CFU mL⁻¹ (3) four subsequent filtrations of tap water during 120 min totaling 480 min of filtration, (3) second filtration of water artificially contaminated with *E. coli*, as described in step 2. This test was carried out to evaluate the final *E. coli* removal, after tap water filtration (5) determination of final permeate flux of deionized water with dirty membrane.

2.4. Water samples and analysis

Tests of *Escherichia coli* and chlorine removal, color, turbidity, pH variation, flux and total volume of filtrated tap water were performed to characterize the filtration system efficiency. All procedures were carried out according to Standard Methods for the examination of water and wastewater (APHA et al., 2012). Two types of water were used, deionized water artificially contaminated with *E. coli* and tap water. The characteristics of tap water used in this study are presented in Table 2.
Table 2. Characteristics of tap water.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color (HU)</td>
<td>0</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.09 - 1.21</td>
</tr>
<tr>
<td>Free Chlorine (mg L⁻¹)</td>
<td>0.02 - 0.63</td>
</tr>
<tr>
<td>pH</td>
<td>6.86 - 7.51</td>
</tr>
</tbody>
</table>

Removal of color, turbidity, free chlorine and pH variation were also measured during filtration. Color and free chlorine were measured with a HACH DR/4000 spectrophotometer and turbidity was measured using a HACH 2100N.

After the filtration of contaminated water, *E. coli* removal was evaluated using the membrane filter technique for members of the coliform group, as described in the Standard methods for the examination of water and wastewater (APHA et al., 2012).

3. RESULTS AND DISCUSSION

3.1. Materials characterization

SEM images of a new membrane and GAC before use are shown in Figure 2.

![SEM images of evaluated membrane (A) and GAC (B).](image)

Wide (2 – 10 μm) and irregular pores are observed in Figure 2A from SEM membrane micrographs. GAC micrographs also showed wide macropores with a flat morphology surface in Figure 2B. Similar micrographs were reported by other authors (Jia and Lua, 2008; Ngarmkam et al., 2011).

From the EDX results for GAC and GAC impregnated with copper oxide, it was determined that the GAC composition is carbon and silica. The presence of silica in activated carbon was also reported by others authors (Giri et al., 2012; Haro et al., 2012). Regarding impregnated samples, EDX analysis confirms the presence of copper. Also, the EDX spectrum of GAC did not show the presence of oxygen, although the presence of oxygen is noticeable in impregnated samples. These results indicate the presence of copper oxide nanoparticles in activated carbon (Ruparelia et al., 2008).

Figure 3 presents the result of TEM analysis of GAC impregnated with copper oxide nanoparticles.
The presence of copper was confirmed again, with arrows indicating copper oxide nanoparticles in GAC matrix of regular spherical sizes of approximately 20 nm. Similar results were obtained by other authors using carbon matrix and copper (Khare et al., 2014; Singh et al., 2013).

The results of textural GAC characterization are presented in Table 3.

Table 3. Textural characteristics of the activated carbon used in this study.

<table>
<thead>
<tr>
<th></th>
<th>Area (m² g⁻¹)</th>
<th>Volume (cm³ g⁻¹)</th>
<th>Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET</td>
<td>Micro</td>
<td>Meso</td>
</tr>
<tr>
<td>GAC</td>
<td>824</td>
<td>745</td>
<td>28</td>
</tr>
<tr>
<td>GAG/Cu05</td>
<td>792</td>
<td>727</td>
<td>16</td>
</tr>
<tr>
<td>GAC/Cu10</td>
<td>758</td>
<td>696</td>
<td>20</td>
</tr>
</tbody>
</table>

GAC used in this study showed a predominantly microporous characteristic by N₂ adsorption-desorption analysis. Comparing BET area from GAC and GAC/Cu samples, a decrease in this parameter was observed in impregnated samples as well as in the volume of micropores and mesopores. These results indicate that the impregnation of copper oxide lead to the lowering of their surface pores and volume. These phenomena are caused because pore blocking is a result of copper and carbon matrix interaction (Goscianska et al., 2012).

Both the volumes of micropores and mesopores were reduced after modifications, suggesting that copper oxide nanoparticles are located in both mesopores and micropores (Bandosz e Petit, 2009).

3.2. Gravitational System Evaluation

Figure 4 presents of all the evaluated parameters after the filtration of tap water through the filtration system and the initial and final flux for all the processes studied.
Discontinuities were observed, since the filtration was carried out in four sequential steps of 120 min each, comprising 480 min. Moreover, Figure 4B revealed a higher flux in hybrid system with GAC not impregnated with copper nanoparticles. These results showed that the flux obtained in the system filtration with GAC is greater than the one in system filtration without GAC, and that the flux decay is faster in the process without GAC. Thus, GAC ensured a higher flux and lower membrane fouling. This is possibly the result of the reduction of contaminants loaded onto the membrane due the adsorption of contaminants on the GAC (Kim et al., 2009).

Textural analysis showed that GAC impregnated with copper nanoparticles has smaller specific area due to pore blocking, thus presenting decreased adsorbent rate when compared with GAC without copper impregnation. Consequently, GAC without copper impregnation seems to decrease membrane fouling more efficiently and increases water flux. To confirm that theory, more specific adsorption studies with the GAC and GAC impregnated with copper nanoparticles must be done.

All samples showed the same color 0 HU. As this parameter seemed unvarying, the conclusion that can be drawn with this result is that the hybrid gravitational filtration system did not add color to the filtered water in any of the studied systems. According to Figure 4D,
the filtered water presented a pH close to neutrality, as well as tap water. Therefore, the filtration system did not change the pH, even though it is known that activated carbon causes pH raise during water treatment (Farmer et al., 1996). This result can be explained by the rapid filtration system with low hydraulic retention time, which does not allow high contact time.

The percentage of removal of turbidity showed an extensive range, from 25 to 82%. However, the turbidity of tap water was not lowered by the filtration system; it is notable that turbidity values are higher when hybrid systems are used. This may be due to the fact that fine particles of GAG are solubilized. The hybrid filtration system with activated carbon significantly increased chlorine removal, higher than 90% in all collected samples, while the filtration system for the unitary process without GAC showed low chlorine removals, confirming that microfiltration itself does not remove some water contaminants and that activated carbon can be used as a combined technology to improve water quality (Kim et al., 2009).

Regarding the final E. coli removal presented in Figure 4F, all filtration systems obtained a 99.99% of final E. coli removal, perhaps due the membrane fouling after tap water filtration. Initial E. coli removal, however, was noticeably increased in hybrid filtration systems according to the increase in copper concentration. Copper with 1.0 wt.% concentration was the only filtration system that exhibited bactericidal efficiency of 99.99%, as observed in the initial assay. The bactericidal effect was expected owing to the presence of copper nanoparticles, confirmed by TEM analysis (Figure 3), and according to the experimental results obtained by many authors in studies of the antibacterial effect of copper nanoparticles (Ruparelia et al., 2008).

4. CONCLUSIONS

The results of this study showed that is possible to enhance the quality of tap water in a hybrid gravitational membrane system, driven without requiring an external energy supply, such as pumps. GAC ensured higher chlorine removals, as well as higher initial permeate fluxes. GAC impregnated with copper also increased bactericidal efficiency. Therefore, the hybrid gravitational membrane system, using GAC impregnated with 1 wt.% of copper, could be considered as an alternative and inexpensive point-of-use treatment of water destined for human consumption in emerging countries.

5. ACKNOWLEDGMENTS

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6. REFERENCES


