Disciplinarum Scientia. Série: Naturais e Tecnológicas, Santa Maria, v. 17, n. 3, p. 417-428, 2016.
Recebido em: 10.10.2016. Aprovado em: 07.12.2016.

ISSN 2176-462X

SYNTHESIS AND CHARACTERIZATION OF A NANOFILTER WITH CARBON NANOTUBES FOR THE REMOVAL OF WATER CONTAMINANTS[1]

SÍNTESE E CARACTERIZAÇÃO DE UM NANOFILTRO COM NANOTUBOS DE CARBONO PARA A REMOÇÃO DE CONTAMINANTES NA ÁGUA

Robson Dalla Nora[2], Daiene Dorfey[3], Sergio Roberto Mortari[4],
Fernando Machado Machado[4], Tiago Moreno Volkmer[4] and Alexandre Swarowsky[5]

ABSTRACT

The interest in nanotechnology as a mitigation tool of environmental problems, specifically the nanofiltration, is noticeable for the treatment of drinking water and wastewater. The aim of this work was to prepare and characterize Multiple Walls Nanotubes Nanofilters (MWNT), composed by polyethylene glycol (PEG), chitosan and sodium sodium sulfate (SDS) to remove contaminants in water. Different proportions of PEG 6000 K, chitosan and MWNT/SDS solution were studied to obtain the desired permeability. The nanofilter was characterized by scanning electron microscopy, Raman spectroscopy; its pore size and porosity was determined by the nitrogen adsorption method. The results showed that the produced nanofilter has a pore size average 384 nm to 493 nm and lower permeability.

Keywords: benzothiophene, chitosan, water treatment.

RESUMO

O interesse em nanotecnologia como uma ferramenta de mitigação de problemas ambientais, especificamente a nanofiltração, é notável para o tratamento de água potável e de águas residuais. O objetivo deste trabalho foi a preparação e caracterização de um nanofiltro com nanotubos de carbono de paredes múltiplas compostas por polietileno glicol, quitosana e sulfato de sódio dodecil para remover os contaminantes na água. Parâmetros tais como o teor de polietileno glicol 6000 K, quitosano e MWNT/dodecilsulfato de sódio (SDS) foram analisados para se obter a permeabilidade desejada. O nanofiltro foi caracterizado por microscopia eletrônica de varredura, espectroscopia Raman; seu tamanho de poro e porosidade foi determinada pelo método de adsorção de nitrogênio. Os resultados mostraram que o nanofiltro produzido tem um tamanho médio de poro de 384 nm a 493 nm e baixa permeabilidade.

Palavras-chave: *benzotiofeno, quitosana, tratamento de água.*

---

[1] Scientific Initiation Work.

[2] Academic of Sanitary and Environmental Engineering - Centro Universitário Franciscano. E-mail: dallanorarobe@gmail.com

[3] Student of the Nanoscience Graduate Program - Centro Universitário Franciscano. E-mail: daienedorfey11@gmail.com

[4] Professors Collaborator - Centro Universitário Franciscano. E-mails: mortari@unifra.br; fernando.machado@hotmail.com.br; tiagovolkmer@gmail.com

[5] Adviser. Centro Universitário Franciscano. E-mail: alexandre@unifra.br

INTRODUCTION

Due to the rapid economic, agricultural and industrial growth in recent decades in a disorderly way and without environmental planning, contamination of the surface and groundwater has been an issue. Consequently, raw water and wastewater may contain particles in the size of micrometers to nanometers, in addition to other dissolved contaminants (LI, 2014; LUO et al., 2014; MEFFE; BUSTAMANTE, 2014; ROBLES-MOLINA et al., 2014). Given this current environment, whether or not altered by human activities, the lentic and lotic water resources used for human consumption require conventional treatment methods that fit the standards of drinking water quality. However, with the advancement of technology, these methods could be improved or replaced with the introduction of non-conventional methods, such as nanotechnology.

The interest in nanotechnology as a mitigation tool of environmental problems, specifically the nanofiltration, is noticeable for the treatment of drinking water and wastewater (ALI et al., 2014; CHAKRABART; THAKUR; SHAHI, 2013; JEONG; YANG; YOUK, 2007; MOSTAFAVI; MEHRNIA; RASHIDI, 2009; SARI; CHELLAM, 2013). Based on modern technology, current research focuses objectively on nanoadsorbent, nanoadsorbent base metal, zeolite, polymeric nanoadsorbent and nanoadsorbent mainly based on the carbon nanotubes (GEHRKE; GEISER; SOMBORN-SCHULZ, 2015).

It stands out that carbon nanotubes (CNT) can remove pollutants, such as pharmaceuticals antibiotics, viruses (MOSTAFAVI; MEHRNIA; RASHIDI, 2009), microcystin (YAN et al., 2006), natural organic matter (HYUNG; KIM, 2008), phenol (WISNIEWSKI et al., 2012) and pesticides (BROOKS; LIM; KILDUFF, 2012; MADAENI et al., 2012a; RIKHTEHGARAN; LOHRASEBI, 2015). CNT are characterized by one or more graphene sheets rolled up in a concentric manner, with nanometric dimensions hollow inner cavity (JOURNENTE; BERNIER, 1998). Due to its structural, mechanical and unique electrical characteristics, these are the objects of study for various applications in many fields of interest (OLIVEIRA, 2009; RAO et al., 2001). In order to increase sensitivity, or affinity, various chemicals such as metals, metal oxides, organic molecules, and polymers can modify the surface of the CNT. In addition to the CNT, the adsorption can be carried out using additives such as dodecyl sulfate surfactant (MADAENI et al., 2012b; ONESIPPE; LAGERGE, 2008) and polymers such as chitosan and polyethylene glycol (ONESIPPE; LAGERGE, 2008; REIAD et al., 2012).

Therefore, the main objective of this work was to prepare and characterizeof the Carbon Nanotube nanofilter composed by multiple walls (MWNT), polyethylene glycol, chitosan and dodecil sodium sulfate to remove contaminants in water.

MATERIALS AND METHODS

MATERIALS

To manufacture the nanofilter, the following materials were used: 1. chitosan (Poly D-Glucosamine) low molecular weight, 75-85% of desacetilization (Sigma Aldrich - Brazil); 2. Polyethylene Glycol 6000 K; 3. Sodium hydroxide (NaOH) 4. Glacial Acetic Acid PA (C2H4O2) all supplied by Vetec Fine Chemicals Ltd. - Brazil; 5. Sodium Dodecyl Sulfate (NaC12H25SO4 (SDS)) (Fluka, 99%); 6. MWNT supplied by the Nanoamor Company (USA) with 95% purity and an outer diameter of 60-100 nm. All solutions were prepared using distilled water (pH 7) and each experiment was carried out three times.

FUNCIONALIZATION OF MWNT WITH SODIUM DODECYL SULFATE

To functionalize the multiple wall carbon nanotubes 0.5 g of SDS were added into 100 mL of distilled water in a 250 mL beaker. Then, the solution was placed in a Bath Ultrasound USC - 3300 (Unique Ultra Cleaner) for 5 min. After that, 0.1 g of MWNT was added and heated at 30 °C for 3 h.

NANOFILTER PREPARATION

To prepare the nanofilters, 1.0 g of chitosan and 1.0 g of Polyethylene Glycol (PEG) 6000 K were added to 35 mL of distilled water in a 250 mL beaker. The 1:1 proportion between chitosan and PEG were was choose after some experimental tests to obtain the desired permeability. The solution was placed in a hot plate (70 °C) with magnetic stirring for 20 min and then 2 mL of Glacial Acetic Acid were added. After 30 min, 15 mL of MWNT / SDS solution were added and for the suspension was kept stirring for 90 min for a better homogenization. The suspension volume was strictly controlled to obtain standardized thickness nanofilters. The chitosan gel was placed in petri dishes and dried at 60 °C for 36 h. After being completely dry, the nanofilters were detached from the plates and left for 48h in a solution of 1 mol L^{-1} NaOH for stabilization.

CHARACTERIZATION OF THE NANOFILTER

The porous nanofilters were characterized by different techniques, which allow two parameters: one related to the morphology of the nanofilter (pore size, effective thickness and surface porosity) and the other as the permeability and selectivity of the nanofilter (retention curve and flow permeate) (HABERT; BORGES; NOBREGA, 2006).

Morphology

Scanning electron microscopy (SEM)

The morphology of the upper surface of the nanofilter was studied through a scanning electron microscope, JEOL JSM 6060, with an acceleration voltage of 15 to 20 kV and magnification ranging from 100 to 30000 times. The nanofilter was immersed in ethanol and n-hexane for 24 hours followed by drying at 25 °C for 30 min, followed by drying at 60 °C for 30min, and this procedure is necessary to avoid the collapse of the porous surface due to the high surface tension of water. The treated sample was placed on a sample holder and coated with gold to provide the electrical conductivity of the filter.

Raman spectroscopy

It A Renishaw inVia Raman Spectometer was used to analyse the nanofilters (). The experiments analyzed at room temperature, and the scan range was 0-3100 cm^{-1} using a laser of 514 nm wavelength. Five samples were prepared, namely, 5 nanofilters were dried at 60°C and ground.

Texture property

The analysis of the surface area and porosity was made by a volumetric adsorption analyzer, i.e. Nova 1000 (Quantachrome Instruments). The specific surface area was determined by the method of Brunauer, Emmett and Teller (BET) (BRUNAUER; EMMETT; TELLER, 1938), and volume and average pore diameter were obtained by using the method of Barrett, Joyner and Halenda (BJH) (BARRETT; JOYNER; HALENDA, 1951).

Flow permeated

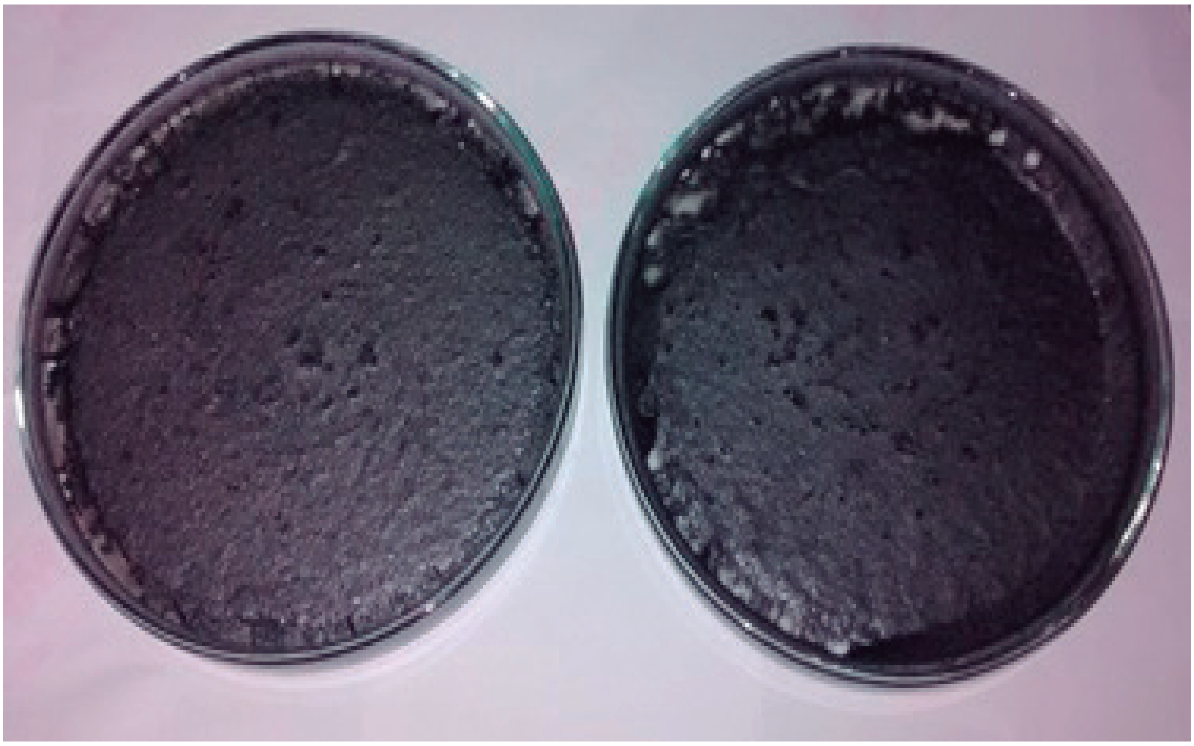
Four circular nanofilters (diameter = 47mm) were prepared for this study. Initially, each nanofilter was coupled to the holder and 5 mL of distilled water were added. Time was recorded for any water to be filtered and repeated 4 times for each nanofilter. The water permeate flux (Jp) was measured under a suction pressure of 0.5 atm. This value is defined as Jp ($L\ m^{-2}\ h^{-1}$) = Flow ($L\ s^{-1}$) x 3600 ($s\ h^{-1}$) / nanofilter area (m^2).

RESULTS AND DISCUSSION

NANOFILTERS

As presented in figure 1, an image of the produced nanofilter is shown. It was visually found two surfaces: a rough and a smooth top surface, and the bottom surface mainly due to the mold.

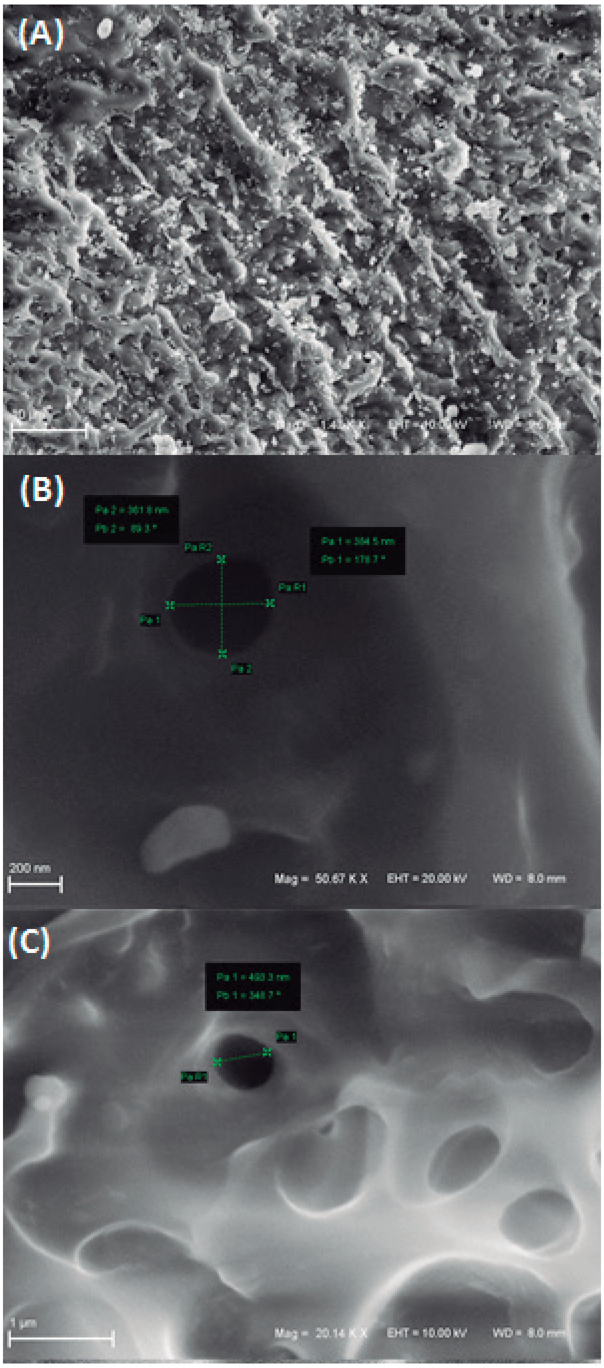
Figure 1 - Image produced nanofilter in this work.



Source: author.

In figure 2 (A), it is shown the photomicrograph of the top surface of the nanofilter obtained by SEM. The surface of the nanofilter was visually rough. The existence of pores is shown with an image magnified, as shown in figure 2 (B) and figure 2 (C). The pore size of the nanofilter is found around 384 nm and 493 nm. Accordingly, depending on what is intended to retain the nanofilter can act on absorption or adsorption, and it will depend on the size of the contaminant molecule.

Figure 2 - SEM photomicrographs of the nanofilter manufactured
(A) Photomicrograph of the upper surface, (B) and (C) Photomicrographs pore size.

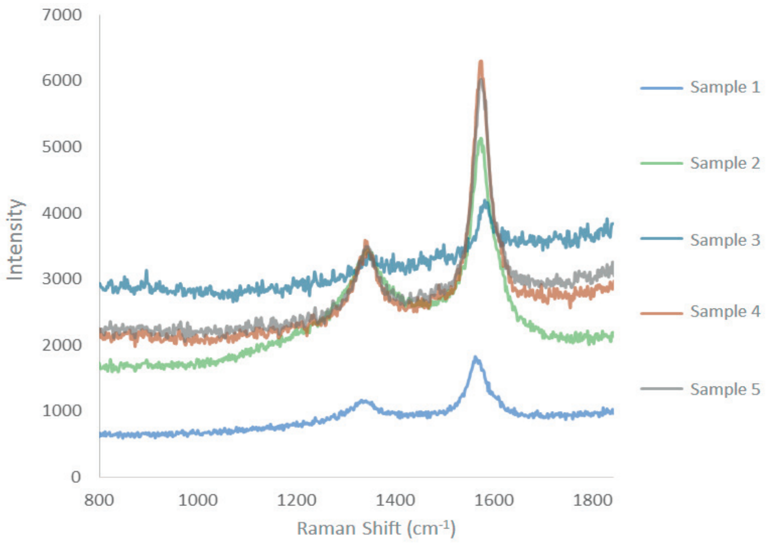


Source: author.

The obtained nanofilter maintains the carbon nanotubes and the results are shown in figure 3. In the spectra of samples measured by Raman spectroscopy, which allows analyzing the vibrational properties of a molecule or solid, it can be seen, in the two samples, two peaks around 1357 cm^{-1}, which is the Band D (derived mode of structural disorder and only appears due to the breakdown of the translational symmetry of the nanotube) (FERRARI; ROBERTSON, 2000; SOUZA-FILHO; FAGAN, 2007) and 1576 cm^{-1}, which is the peak G (G band originates from basically the from the symmetry breaking of the tangential vibration when the graphene sheet is folded to form a cylindrical tube) (JORIO et al., 2003).

Furthermore, in figure 3, it was found that the intensity of the D band is lower than the intensity of the G band in both samples. This indicates the presence of multi-walled carbon nanotubes in the sample, plus a small amount of amorphous carbon, polyhedral shells or carbon nanofibers (FLAHAUT; LAURENT; PEIGNEY, 2005; KATAURA et al., 2000).

Figure 3 - Spectrum Raman of the nanofilters samples.

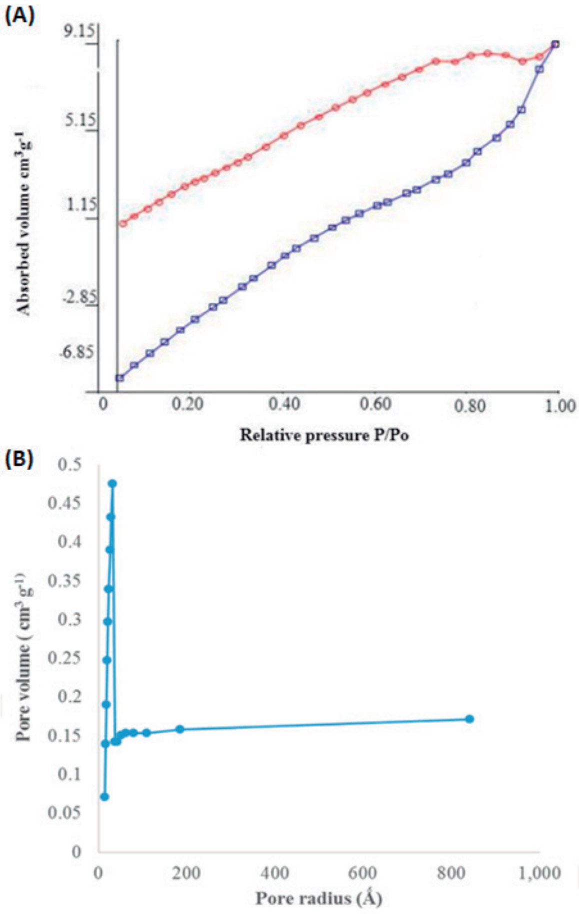


Source: author.

BJH AND BET

In figure 4 (a), it is shown the results of BET testing for a sample of the nanofilter. The isotherms observed for the sample exhibit similarity with the type IV according to the IUPAC classification (HATTORI; KANEKO; OHBA, 2013) for the six kinds of gas adsorption isotherm, mesopores characteristics bodies. Figure 4 (b) shows the pore size distribution, and the average pore radius is 15,548 Ǻ. According to data obtained from the BJH adsorption, pore volume was 0.013 cm^3g^{-1} and surface area was 10,089 m^2 g^{-1}.

Figure 4 - Isotherms curve of adsorption and desorption (A). Distribution of the nanofilter pore size (B).



Source: author.

PERMEATED FLOW

The data obtained from the water permeate flow was about 7,5 x 10^{-5} m^3 m^{-2} s^{-1}, which can be attributed to the smaller pore size and, therefore, lower permeability. However, the flow is dependent on the pressure applied, the higher the pressure will flow (MOSTAFAVI; MEHRNIA; RASHIDI, 2009). Similar results have been found (15 L/dia) and show that the nanofilter has potentiality to be applied in water treatment systems (MPENYANA-MONYATSI et al., 2016).

CONCLUSION

Chitosan, polyethylene glycol and sodium dodecyl sulfate were used for the fabrication of a nanofilter constructed by MWNT. The filter was characterized by the nanofilter pore size average in the region of nanometers. The results showed that the product nanofilter has low permeability, average pore radius 15 Ǻ, and nanotubes are maintained after the manufacturing process. Research still needs to be done to understand what and how this filter can retain different substances.

REFERENCES

ALI, Md. E. et al. Carbon nanotube membranes for water purification: A bright future in water desalination. **Desalination**, v. 336, p. 97-109, 2014.

BARRETT, E. P.; JOYNER, L. G.; HALENDA, P. P. The determination of pore volume and area distributions in porous substances. I. computations from nitrogen isotherms. **Journal of the American Chemical Society**, v. 73, p. 373-380, 1951.

BROOKS, A. J.; LIM, H. N.; KILDUFF J. E. Adsorption uptake of synthetic organic chemicals by carbon nanotubes and activated carbons. **Nanotechnology**, v. 23, n. 29, p. 294008, 2012.

BRUNAUER, S.; EMMETT, P. H.; TELLER, E. Adsorption of gases in multimolecular layers. **Journal of the American Chemical Society**, v. 60, p. 309-319, 1938.

CHAKRABARTY, T.; THAKUR, A. K.; SHAHI, V. K. Functionalized chitosan based nano-filter membranes for pH-controlled separation of amino acids. **Separation and Purification Technology**, v. 108, p. 57-64, 2013.

FERRARI, A. C.; ROBERTSON, J. Interpretation of Raman Spectra of disordered and amorphous carbon. **Physical Review B**, v. 61, p. 14095-14107, 2000.

FLAHAUT, E.; LAURENT, C. H.; PEIGNEY, A. Catalytic CVD synthesis of double and triple-walled carbon nanotubes by the control of the catalyst preparation. **Carbon**, v. 43, p. 375-383, 2005.

GEHRKE, I.; GEISER, A.; SOMBORN-SCHULZ, A. Innovations in nanotechnology for water treatment. **Nanotechnology, Science and Applications**, v. 8, p. 1-17, 2015.

HATTORI, Y.; KANEKO, K.; OHBA, T. Adsorption Properties. In: POEPPELMEIER, J. R. (Ed.). **Comprehensive Inorganic Chemistry II**. 2. ed. Amsterdam: Elsevier, 2013. p. 25-44.

HABERT, A., C; BORGES, C.P.; NÓBREGA, R. **Processos de Separação com Membranas**. Rio de Janeiro: E-papers Serviços Editoriais Ltda, 2006. 180p.

HYUNG, H.; KIM, J. H. Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: Effect of NOM characteristics and water quality parameters. **Environmental Science and Technology**, v. 42, n. 12, p. 4416-4421, 2008.

JEONG, E. H.; YANG, J.; YOUK, J. H. Preparation of polyurethane cationomer nanofiber mats for use in antimicrobial nanofilter applications. **Materials Letters**, v. Issue 18, p. 3991-3994, 2007.

JORIO, A. et al. Characterizing carbono nanotube samples with resonance Raman scattering. **New Journal of Physics**, v. 5, p. 1-17, 2003.

JOURNENTE, C.; BERNIER, P. Production of carbon nanotubes. **Applied Physics A**, v. 67, p. 1-9, 1998.

KATAURA, H. et al. Diameter control of single-walled carbon nanotubes. **Carbon**, v. 38, p. 1691-1697, 2000.

LI, W. C. Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. **Environmental Pollution**, v. 187, p. 193-201, 2014.

LUO, Y. et al. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. **Science of the Total Environment**, v. 473-474, p. 619-664, 2014.

MADAENI, S. S. et al. Fabrication of cellulose acetate/sodium dodecyl sulfate nanofiltration membrane: Characterization and performance in rejection of pesticides. **Desalination**, v. 290, p. 99-106, 2012a.

MADAENI, S. S. et al. Fabrication of cellulose acetate/sodium dodecyl sulfate nanofiltration membrane: Characterization and performance in rejection of pesticides. **Desalination**, v. 290, p. 99-106, 2012b.

MEFFE, R.; BUSTAMANTE, I. Emerging organic contaminants in surface water and groundwater: A first overview of the situation in Italy. **Science of The Total Environment**, v. 481, p. 280-295, 2014.

MOSTAFAVI, S. T.; MEHRNIA, M. R.; RASHIDI, A. M. Preparation of nanofilter from carbon nanotubes for application in virus removal from water. **Desalination**, v. 238, Issues 1-3, p. 271-280, 2009.

MPENYANA-MONYATSI, L. et al. The effects of material loading and flow rate on the disinfection of pathogenic microorganisms using cation resin-silver nanoparticle filter system. **Physics and Chemistry of the Earth Parts A/B/C**, 2016. Disponível em: <https://goo.gl/iHxQ84>

OLIVEIRA, B. L. **Síntese de nanotubos de carbono por deposição química de vapor empregando Fe/CaCO3 e Fe/NTC como catalisador**. 2009. 117f. Dissertação (Mestrado em Engenharia Química) - Universidade Federal do Rio de Janeiro, Rio de Janeiro, 2009.

ONESIPPE, C.; LAGERGE, S. Study of the complex formation between sodium dodecyl sulfate and hydrophobically modified chitosan. **Carbohydrate Polymers**, v. 74, Issue 3, p. 648-658, 2008.

RAO, C. N. R. et al. Nanotubes. **ChemPhysChem**, v. 2, Issue 2, p. 78-105, 2001.

REIAD, N. A. et al. A. Adsorptive removal of iron and manganese ions from aqueous solutions with microporous chitosan/polyethylene glycol blend membrane. **Journal of Environmental Sciences**, v. 24, Issue 8, p. 1425-1432, 2012.

RIKHTEHGARAN, S.; LOHRASEBI, A. Water desalination by a designed nanofilter of graphene-charged carbon nanotube: A molecular dynamics study. **Desalination**, v. 365, p. 176-181, 2015.

ROBLES-MOLINA, J. et al. Monitoring of selected priority and emerging contaminants in the Guadalquivir River and other related surface waters in the province of Jaén, South East Spain. **Science of The Total Environment**, v. 479-480, p. 247-257, 2014.

SARI, M. A.; CHELLAM, S. Surface water nanofiltration incorporating (electro) coagulation-microfiltration pretreatment: Fouling control and membrane characterization. **Journal of Membrane Science**, v. 437, p. 249-256, 2013.

SOUZA-FILHO, A. G.; FAGAN, S. F. Funcionalização de nanotubos de carbono. **Química Nova**, v. 30, p. 1695-1703, 2007.

WISNIEWSKI, M. et al. Removal of internal caps during hydrothermal treatment of bamboo-like carbon nanotubes and application of tubes in phenol adsorption. **Journal of Colloid and Interface Science**, v. 381, n. 1, p. 36-42, 2012.

YAN, H. et al. Adsorption of microcystins by carbon nanotubes. **Chemosphere**, v. 2, n. 1, p. 142-144, 2006.