Materials Proceedings

Proceeding Paper

Reduced Graphene Oxide Filtration Membranes for Dye Removal—Production and Characterization †

Andreza Lima [1,*], Anthony de Oliveira [1], Luana Demosthenes [1], Talita Sousa [1], Artur Pereira [1], Roberto de Carvalho [2] and Wagner Anacleto [1]

[1] Instituto Militar de Engenharia (IME), Seção de Engenharia de Materiais, Rio de Janeiro 22290-270, Brazil; anthonymatheuss@gmail.com (A.d.O.); eng.luanademosthenes@gmail.com (L.D.); talitagama@gmail.com (T.S.); camposo.artur@gmail.com (A.P.); anacleto@ime.eb.br (W.A.)
[2] Departamento de Engenharia Química e de Materiais, Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio), Rio de Janeiro 22541-041, Brazil; rbcarvalho@puc-rio.br
* Correspondence: andrezamenezeslima@gmail.com

† Presented at the 2nd International Online-Conference on Nanomaterials, 15–30 November 2020; Available online: https://iocn2020.sciforum.net/.

Abstract: Dye removal from manufacturing and textile industry wastewater is one of the biggest challenges in plants. The improper disposal of water with residual dyes can contaminate effluents and fresh water sources. In this work, filtration membranes based on reduced graphene oxide (rGO) were fabricated by the spray coating method, and its capability to remove dyes from water was evaluated. Graphene oxide was prepared by a modified Hummers method and posteriorly reduced with ascorbic acid; a simple and fast spray coating fabrication method was employed to produce stable membranes, which were analyzed in a home-made permeation cell. Raman spectroscopy and scanning electron microscopy (SEM) were able to prove that rGO dispersion was formed by graphene flakes with about 45.9 μm of lateral dimension; X-ray diffraction, SEM and Raman analyses indicate that the spray method was efficient in producing stable and uniform filtration membranes; and UV-vis absorption spectra of feed and permeation solution indicate that rGO membranes were capable in removing dye from water. By the main results, it is possible to affirm that rGO filtration membranes are an efficient, low-cost, scalable and fast way to remove dyes from wastewater.

Keywords: reduced graphene oxide; filtration; membranes; dye removal; SEM

Citation: Lima, A.; de Oliveira, A.; Demosthenes, L.; Sousa, T.; Pereira, A.; de Carvalho, R.; Anacleto, W. Reduced Graphene Oxide Filtration Membranes for Dye Removal—Production and Characterization. *Mater. Proc.* **2021**, *4*, 29. https://doi.org/10.3390/IOCN2020-07892

Academic Editors: Ana María Díez-Pascual, Antonio Di Bartolomeo and Guanying Chen

Published: 11 November 2020

1. Introduction

Dyes are widely used in various industrial segments, resulting in wastewater containing dyes as one of the most common discards in textiles, paper, cosmetics and other plants. The improper disposal of this material in affluents can contaminate water sources and soil, being very dangerous to humans, animals and the environment [1–3].

Coagulation and biodegradation are already used to remove dyes from wastewater, but they have a series of disadvantages, such as complexity, limited effect and the possibility of producing carcinogenic substances. Membrane separation technology is being widely studied for this application because it is simple, versatile, energy saving, cost-effective and able to remove pollutants with different sizes [4,5].

The membrane-based separation and purification process can also be used for metal ions, salts, oil, coliform and proteins removal, bacterial rejection and antifouling templates. It is also possible to produce membranes with double function, which can be applied to remove two types of pollutants [6,7].

Graphene and other carbon materials can be used to produce membranes due to their chemical structure and physical properties. For example, graphene oxide (GO) is applied as a membrane material since it has good mechanical stability, oxygen-containing groups and surface area. In contrast, its instability in water and low flux are some of the disadvantages in selecting this material [8].

Carbon nanotubes and other nanomaterials can be used to enhance the stability of GO. Applying reduced graphene oxide (rGO) dispersions to produce membranes could also be an alternative. The hydrophobic areas between layers of reduced material are responsible for generating low-friction flow of water, contributing to the elimination of impurities. Furthermore, the π-conjugated rGO structure presents the advantage of attracting pollutants with benzene rings [9].

In this work, a simple and effective method is described to remove dyes from wastewater with rGO-based filtration membranes, which can be produced and employed in large scale for water treatment in industries.

2. Materials and Methods

2.1. Preparation of GO and rGO Dispersions

The graphene oxide (GO) dispersion was produced by a modified Hummers method [10], promoting intercalation and oxidation in graphite flakes by mixing sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4) and potassium permanganate ($KMnO_4$), followed by exfoliation with washing/centrifugation steps. rGO was produced from GO dispersion, adding ascorbic acid as a reducing agent, ammonium hydroxide (NH_4OH) and polystyrene sulfonate (PSS), while heating at 80 °C for 3 days, also followed by washing/centrifugation steps [11].

2.2. Preparation of rGO Filtration Membranes

Cellulose acetate (CA) membranes, with 0.2 μm pore size and 25 mm diameter, were used as substrates to deposit graphene. rGO dispersions were elected to produce filtration membranes (FM) because of their hydrophobic character, which can improve the water flux and the stability of the membrane [12]. rGO filtration membranes were produced in home-made spray coating deposition equipment with a Steula BC 66-08 airbrush with a nozzle of 0.8 mm, rGO dispersions with 1.0 mg/mL of concentration, 20 psi of nitrogen as carrier gas, a substrate temperature of 90 °C, 1 s of layer deposition, 30 s of drying time between depositions and variable numbers of layers: 40 (named as 40-ly rGO FM), 60 (60-ly rGO FM), 80 (80-ly rGO FM) and 100 (100-ly rGO FM).

2.3. Characterization

rGO dispersion was characterized by Raman spectroscopy, using a NT-MDT NTEGRA spectrometer, with 473 nm of laser wavelength and a radiation time of 100 s, and SEM analysis in QUANTA FEG FEI equipment, with magnifications ranging from 500× to 5000×, a voltage of 2 kV, spot size 4.5 to 5.0 and working distance from 4.7 to 8.3 mm. The lateral dimension of rGO flakes was obtained by measuring with xT microscope control software help.

Filtration membranes were characterized by the following techniques: X-ray diffraction (XRD), with X'Pert MRD PANalytical equipment, cobalt source, 40 kV and 40 mA of voltage and current; Raman spectroscopy, with the same equipment and parameters used for rGO and SEM, also in QUANTA FEG FEI, with a voltage of 5 kV, spot size 3 to 5 and working distance from 11.2 to 14.0 mm.

2.4. Evaluation of Dye Removal

The capability of dye removal of rGO filtration membranes was evaluated using a home-made permeation cell (Figure 1b), with 2 bar of Ni. Pure water flux was evaluated during 1 h before the analysis of dye wastewater. CA substrate and rGO filtration membranes with 40, 60, 80 and 100 layers were tested. Additionally, 20 ppm-aniline aqueous solution was used as feed solution, simulating a wastewater.

UV-vis absorption spectra of feed and permeation solution were made with a CARY 5000 spectrophotometer, from VARIAN. The analyses were obtained for wavelengths from 400 nm to 800 nm.

(**a**) (**b**)

Figure 1. (**a**) Permeation system; (**b**) Permeation cell.

3. Results and Discussion

3.1. rGO Dispersion Characterization

Figure 2 exhibits the Raman spectra of rGO dispersion used to produce the filtration membranes. It is possible to notice the arising of D band (1370 cm^{-1}), which is associated with sp^3 hybridized carbon atoms, corresponding to structural imperfections of graphene sheets and disorder due to oxidation. A strong G band (1590 cm^{-1}) is also observed, related to sp^2 hybridized carbon and tangential vibration, responsible for identifying graphene structure [13,14]. In 2705 cm^{-1}, a weak peak belonging to the 2D band is noticed; this band is always observed in carbon materials and is related to the numbers of graphene layers of the rGO [15].

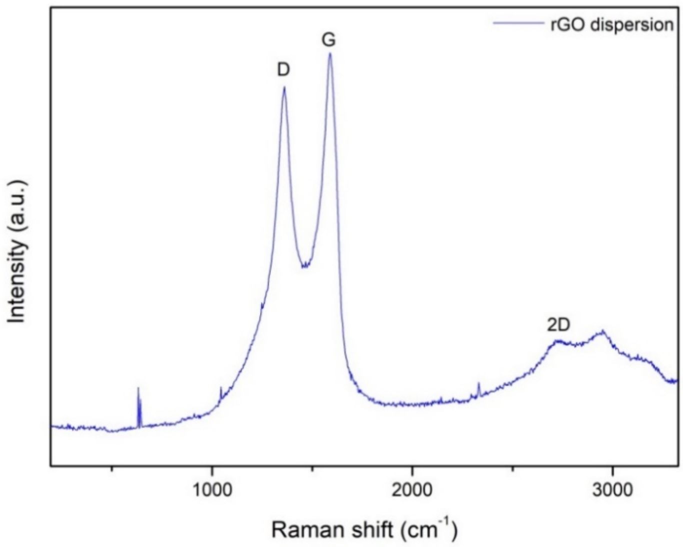
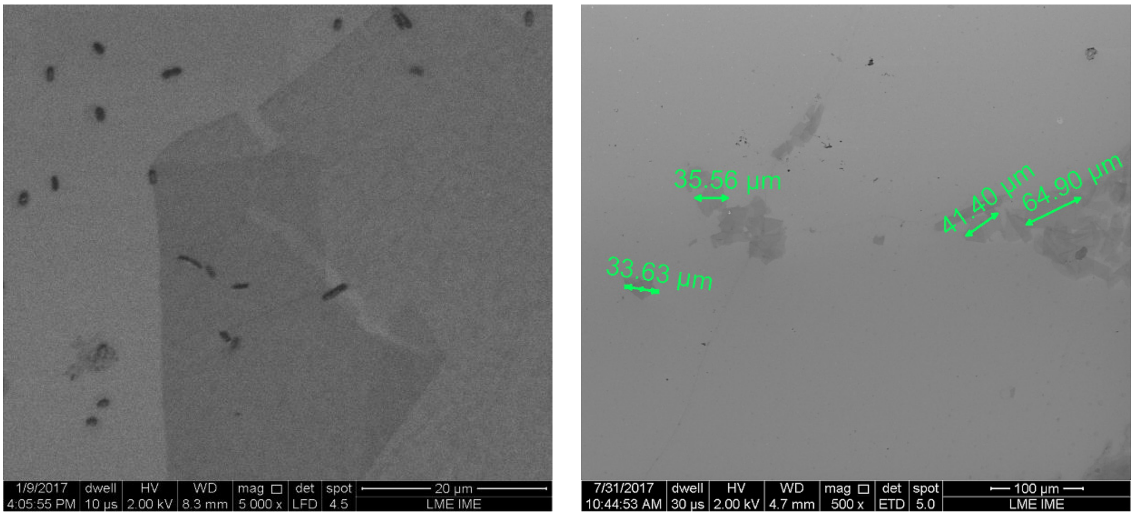


Figure 2. Raman spectra of reduced graphene oxide (rGO) dispersion.

The SEM micrographs for rGO flakes can be observed in Figure 3. It is possible to notice morphological characteristics such as thin sheets, folds and veins. The lateral dimension of 50 flakes was also studied, reaching an average value of 45.9 ± 26.6 µm; this characteristic is very interesting since large GO and rGO sheet size can directly affect permeability, salt rejection and other properties. For example, large GO sheets are more successful in eliminating salt from water than medium and small sizes [16].



(**a**) (**b**)

Figure 3. SEM micrographs for (**a**) rGO; (**b**) rGO with measurements.

3.2. rGO Filtration Membranes Characterization

As evidenced from XRD diffractograms in Figure 4, the CA substrate presents an amorphous halo at 2θ = 7.2° and rGO filtration membranes have peaks at 2θ = 7.8° and 8.2°, which were related to (002) crystal plane of GO [17–19].

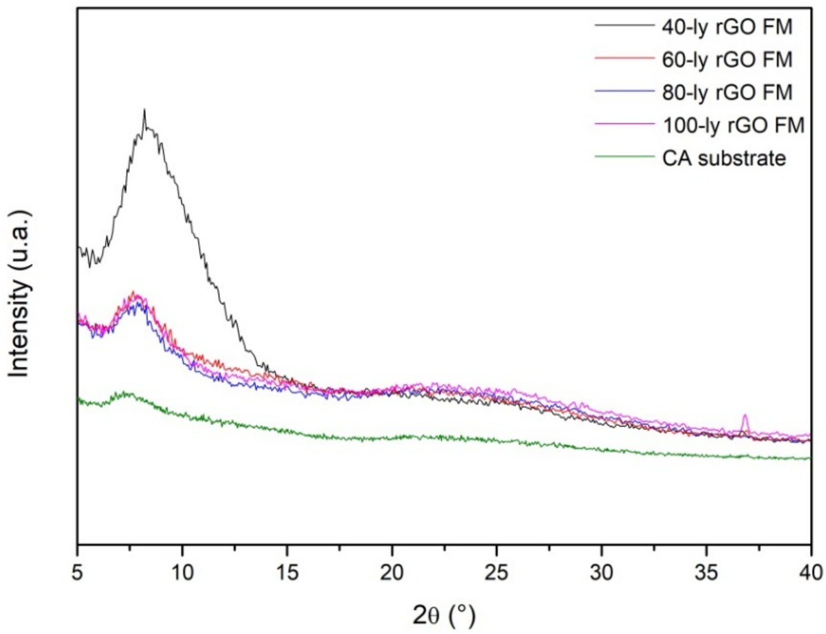


Figure 4. XRD patterns for cellulose acetate (CA) substrate and rGO filtration membranes (FM) with different number of layers (ly).

Figure 5 reveals the Raman spectra for the CA substrate and an rGO filtration membrane. It is possible to observe that the substrate has bands near the region of the bands corresponding to rGO, and elevations in the Raman shift correlated to the D (1368 cm^{-1}) and 2D (2737 cm^{-1}) bands in filtration membrane spectra are not clear, but the presence of the G band (1584 cm^{-1}) is evident, proving that the deposition method was efficient [19,20].

The other bands that occur in rGO filtration membrane Raman spectra are related to the CA substrate, as it can be proved by comparing both spectra.

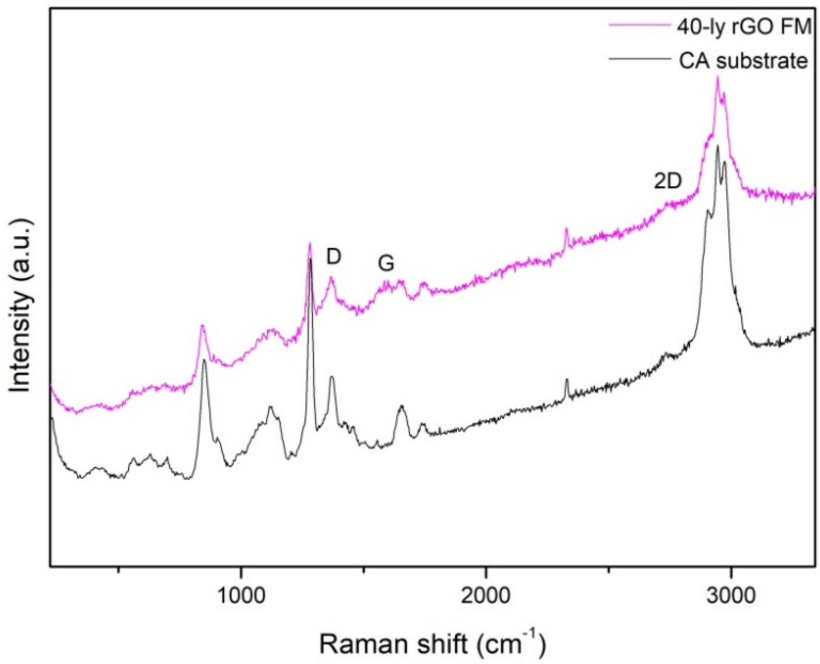
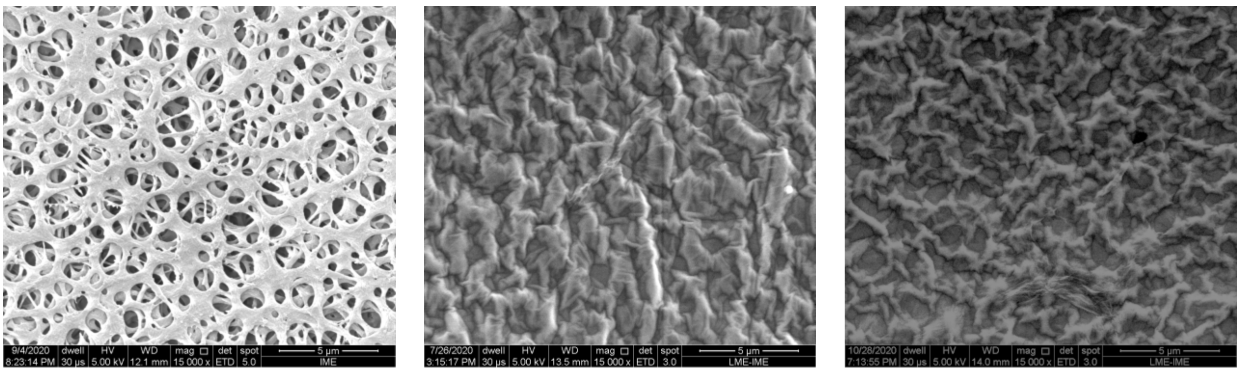
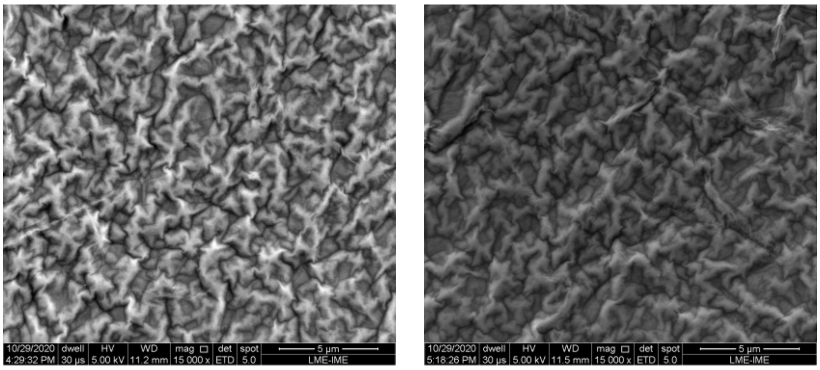


Figure 5. Raman spectra of CA substrate and 40-ly rGO FM.

SEM micrographs (Figure 6) indicate that the spray coating method was efficient in depositing graphene flakes on the substrate surface. In Figure 6a, it is possible to note the uniform surface with pores from the commercial CA substrate, whereas in as-prepared rGO filtration membrane samples, the micrographs acquire a rough aspect, characteristic of an accumulation of graphene, even making it feasible to see some flakes. The morphology observed in the rGO membranes produced in this work is very similar to GO and rGO composite membranes produced by other authors [12,21,22].



(**a**) (**b**) (**c**)



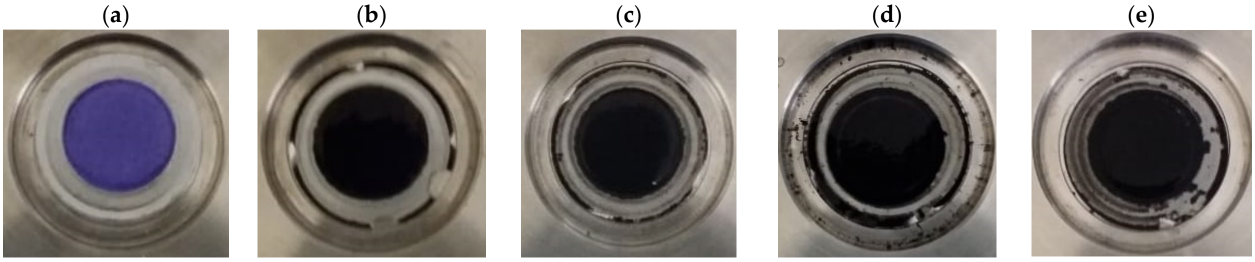
(**d**) (**e**)

Figure 6. SEM micrographs for: (**a**) CA substrate; (**b**) 40-ly rGO FM; (**c**) 60-ly rGO FM; (**d**) 80-ly rGO FM; (**e**) 100-ly rGO FM.

3.3. Dye Removal Evaluation

The appearance of the CA substrate and rGO filtration membranes, before and after the permeation test, can be observed in Figure 7. It is possible to detect that in the area of interest, none of the rGO filtration membranes suffered significant damage during tests, indicating that the studied membranes were stable.

(**a**) (**b**) (**c**) (**d**) (**e**)



(**f**) (**g**) (**h**) (**i**) (**j**)

Figure 7. Filtration membranes: (**a**) CA substrate; (**b**) 40-ly rGO FM; (**c**) 60-ly rGO FM; (**d**) 80-ly rGO FM ; (**e**) 100-ly rGO FM before permeation test; (**f**) CA substrate; (**g**) 40-ly rGO FM; (**h**) 60-ly rGO FM; (**i**) 80-ly rGO FM; (**j**) 100-ly rGO FM after permeation test.

Figure 8 exhibits the UV-vis absorption spectra for feed and permeated solutions. Comparing the curves related to 20 ppm-aniline feed solution and CA substrate permeation solution; it is observed that the CA substrate has the capability to filtrate some part of the dye, but not a significant amount. The rGO film deposited over the CA substrate successfully eliminated dye from the feed solution in the samples with 40, 60 and 80 layers.

The permeation tests of the filtration membrane with 100 layers of rGO resulted in a light brown permeated solution, which indicates that some part of graphene detached off the membrane, mixing in the permeated water, even if the appearance of the membrane (Figure 7j) does not show a significant failure in rGO film surface. This can be confirmed by analyzing Figure 9, which shows the comparison among samples and emphasizes the distinction of 100-ly rGO FM permeated solution. The analysis of the results indicates that more than 80 layers of deposited rGO can be excessive and prejudicial to the filtration process.

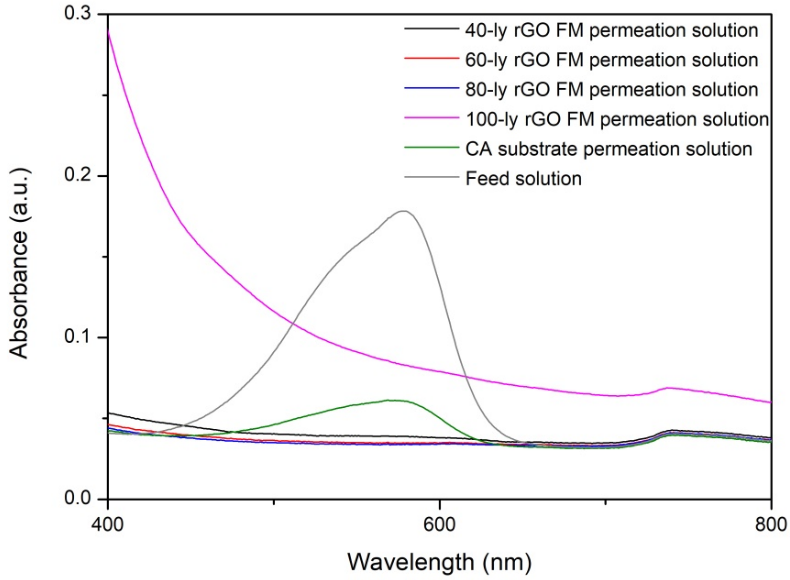


Figure 8. UV-vis absorption spectra for feed and permeation solutions.

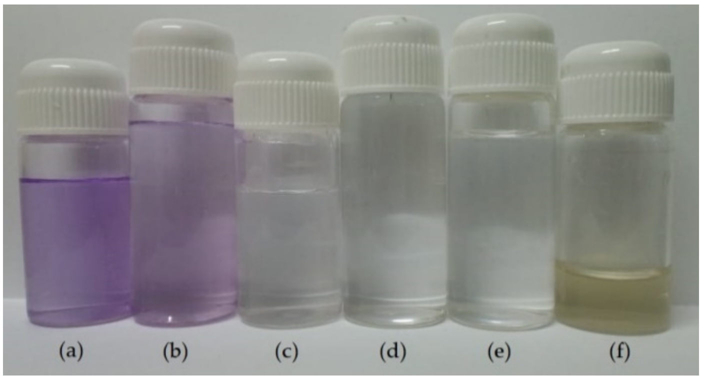


Figure 9. (**a**) Feed solution; permeation solutions: (**b**) CA substrate; (**c**) 40-ly rGO FM; (**d**) 60-ly rGO FM; (**e**) 80-ly rGO FM; (**f**) 100-ly rGO FM.

4. Conclusions

In conclusion, it is possible to state that:

(i) The rGO dispersion was successfully produced and has lateral size and properties suitable for an application as a filtration membrane;
(ii) The spray coating method produced uniform and stable rGO membranes;
(iii) The permeation test proves that rGO filtration membranes can be used to eliminate dyes from manufacturing and textile industry wastewater as a simple, low-cost and scalable method.

Author Contributions: Conceptualization, A.L. and W.A.; methodology, A.d.O.; software, A.L.; validation, A.d.O., R.d.C. and W.A.; formal analysis, A.L.; investigation, A.L.; resources, R.d.C. and W.A.; data curation, A.L., L.D. and T.S.; writing—original draft preparation, A.L.; writing—review and editing, A.L., L.D., T.S., A.P. and W.A.; visualization, W.A.; supervision, W.A. and R.d.C.; project administration, A.L.; funding acquisition, W.A. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) grant by the Brazilian government (No. 403140/2019-6).

Acknowledgments: The authors thank Nacional de Grafite Company for providing the graphite used in this study, Laboratório de Revestimentos Protetores e Materiais Nanoestruturados (PUC-

Rio) for the contribution to the Raman analysis and Anderson Menezes Lima for the help in the assembly of the spray deposition system.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Yan, X.; Tao, W.; Cheng, S.; Ma, C.; Zhang, Y.; Sun, Y.; Kong, X. Layer-by-layer assembly of bio-inspired borate/graphene oxide membranes for dye removal. *Chemosphere* **2020**, *256*, 127118–127127, doi:10.1016/j.chemosphere.2020.127118.
2. Ariaeenejad, S.; Motamedi, E.; Salekdeh, G.H. Application of the immobilized enzyme on magnetic graphene oxide nano-carrier as a versatile bi-functional tool for efficient removal of dye from water. *Bioresour. Technol*. **2021**, *319*, 124228–124237, doi:10.1016/j.biortech.2020.124228.
3. Zhu, M.; Liu, Y.; Chen, M.; Gan, D.; Wang, M.; Zeng, H.; Liao, M.; Chen, J.; Tu, W.; Niu, W. Ultrahigh flux of graphene oxide membrane modified with orientated growth of MOFs for rejection of dyes and oil-water separation. *Chin. Chem. Lett.* **2020**, doi:10.1016/j.cclet.2020.04.011.
4. Hou, J.; Chen, Y.; Shi, W.; Bao, C.; Hu, X. Graphene oxide/methylene blue composite membrane for dyes separation: Formation mechanism and separation performance. *Appl. Surf. Sci.* **2020**, *505*, 144145–144157, doi:10.1016/j.apsusc.2019.144145.
5. Lin, C.; Tung, K.; Lin, Y.; Dong, C.; Chen, C.; Wu, C. Fabrication and modification of forward osmosis membranes by using graphene oxide for dye rejection and sludge concentration. *Process. Saf. Environ.* **2020**, *144*, 225–235, doi:10.1016/j.psep.2020.07.007.
6. Sundaran, S.P.; Reshmi, C.R.; Sagitha, P.; Manaf, O.; Sujith, A. Multifunctional graphene oxide loaded nanofibrous membrane for removal of dyes and coliform from water. *J. Environ. Manag.* **2019**, *240*, 494–503, doi:10.1016/j.jenvman.2019.03.105.
7. Vantanpour, V.; Khadem, S.S.M.; Dehqan, A.; Al-Naqshabandi, M.A.; Ganjali, M.R.; Hassani, S.S.; Rashid, M.R.; Saeb, M.R.; Dizge, N. Efficient removal of dyes and proteins by nitrogen-doped porous graphene blended polyethersulfone nanocomposite membranes. *Chemosphere* **2020**, *263*, 127892–127902, doi:10.1016/j.chemosphere.2020.127892.
8. Zeng, H.; Yu, Z.; Shao, L.; Li, X.; Zhu, M.; Liu, Y.; Feng, X.; Zhu, X. Ag_2CO_3@UiO-66-NH_2 embedding graphene oxide sheets photocatalytic membrane for enhancing the removal performance of Cr(VI) and dyes based on filtration. *Desalination* **2020**, *491*, 114558–114569, doi:10.1016/j.desal.2020.114558.
9. Sheng, J.; Yin, H.; Qian, F.; Huang, H.; Gao, S.; Wang, J. Reduced graphene oxide-based composite membranes for in-situ catalytic oxidation of sulfamethoxazole operated in membrane filtration. *Sep. Purif. Technol.* **2020**, *236*, 116275–116284, doi:10.1016/j.seppur.2019.116275.
10. Faria, G.S.; Lima, A.M.; Brandão, L.P.; Costa, A.P.; Nardecchia, S.; Ribeiro, A.A.; Pinheiro, W.A. produção e caracterização de óxido de grafeno e óxido de grafeno reduzido com diferentes tempos de oxidação. *Rev. Matéria*. **2017**, *22*, e11918, doi:10.1590/S1517-707620170005.0254.
11. Rourke, J.P.; Pandey, P.A.; Moore, J.J.; Bates, M.; Kinloch, I.A.; Young, R.J.; Wilson, N.R. The real graphene oxide revealed: Stripping the oxidative debris from the graphene-like sheets. *Angew. Chem. Int. Ed.* **2011**, *50*, 3173–3177, doi:10.1002/anie.201007520.
12. Ma, J.; Tang, X.; He, Y.; Fan, Y.; Chen, J.; HaoYu. Robust stable MoS_2/GO filtration membrane for effective removal of dyes and salts from water with enhanced permeability. *Desalination* **2020**, *480*, 114328–114338, doi:10.1016/j.desal.2020.114328.
13. Pruna, A.; Pullini, D.; Busquets, D. Influence os synthesis conditions on properties of green-reduced graphene oxide. *J. Nanopart. Res*. **2013**, *15*, 1605–1616, doi:10.1007/s11051-013-1605-6.
14. Tung, T.T.; Alotaibi, F.; Nine, M.J.; Silva, R.; Tran, D.N.; Janowska, I.; Losic, D. Engineering of highly conductive and ultra-thin nitrogen-doped graphene films by combined methods of microwave irradiation, ultrasonic spraying and thermal annealing. *Chem. Eng. J.* **2018**, *338*, 764–773, doi:10.1016/j.cej.2018.01.085.
15. Xu, H.; Ma, L.; Jin, Z. Nitrogen-doped graphene: Synthesis, characterizations and energy applications. *J. Energy Chem.* **2018**, *27*, 146–160, doi:10.1016/j.jechem.2017.12.006.
16. Gogoi, A.; Konch, T.J.; Raidongia, K.; Reddy, K.A. Water and salt dynamics in multilayer graphene oxide (GO) membrane: Role of lateral sheet dimensions. *J. Membr. Sci.* **2018**, *563*, 785–793, doi:10.1016/j.memsci.2018.06.031.
17. Li, J.; Hu, M.; Pei, H.; Ma, X.; Yan, F.; Dlamini, D.S.; Cui, Z.; He, B.; Li, J.; Matsuyama, H. Improved water permeability and structural stability in a polysulfone-grafted oxide composite membrane used for dye separation. *J. Membr. Sci.* **2020**, *595*, 117547–117558, doi:10.1016/j.memsci.2019.117547.
18. Zhang, R.; Ma, Y.; Lan, W.; Sameen, D.; Ahmed, S.; Dai, J.; Qin, W.; Li, S.; Liu, Y. Enhanced photocatalytic degradation of organic dyes by ultrasonic-assisted electrospray TiO_2/Graphene oxide on polyacrylonitrile/β-cyclodextrin nanofibrous membranes. *Ultrason. Sonochem.* **2021**, *70*, 105343–105361, doi:10.1016/j.ultsonch.2020.105343.
19. Hassanpour, A.; Nahar, S.; Tong, X.; Zhang, G.; Gauthier, M.A.; Sun, S. Photocatalytic interlayer spacing adjustment of a graphene oxide/zinc oxide hybrid membrane for efficient water filtration. *Desalination* **2020**, *475*, 114174–114182, doi:10.1016/j.desal.2019.114174.
20. Fan, X.; Cai, C.; Gao, J.; Han, X.; Li, J. Hydrothermal reduced graphene oxide membranes for dyes removing. *Sep. Purif. Technol.* **2020**, *241*, 116730–116738, doi:10.1016/j.seppur.2020.116730.

21. Homem, N.C.; Beluci, N.C.L.; Amorim, S.; Reis, R.; Vieira, A.M.S.; Vieira, M.F.; Bergamasco, R.; Amorim, M.T.P. Surface modification of a polyethersulfone microfiltration membrane with graphene oxide for reactive dyes removal. *Appl. Surf. Sci.* **2019**, *486*, 499–507, doi:10.1016/j.apsusc.2019.04.276.
22. Liu, P.; Zhu, C.; Mathew, A.P. Mechanically robust high flux graphene oxide—Nanocellulose membranes for dye removal from water. *J. Hazard. Mater.* **2019**, *371*, 484–493, doi:10.1016/j.jhazmat.2019.03.009.