IOCN 2020


**MILITARY INSTITUTE OF ENGINEERING**
**INSTITUTO MILITAR DE ENGENHARIA - IME**
Department of Materials Engineering


# Reduced graphene oxide filtration membranes for dye removal – production and characterization


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**2nd International Online-Conference on Nanomaterials**
**IOCN 2020**

# Schedule

- Introduction
- Materials and Methods
- Results and Discussion
- Conclusions
- References
- Acknowledments

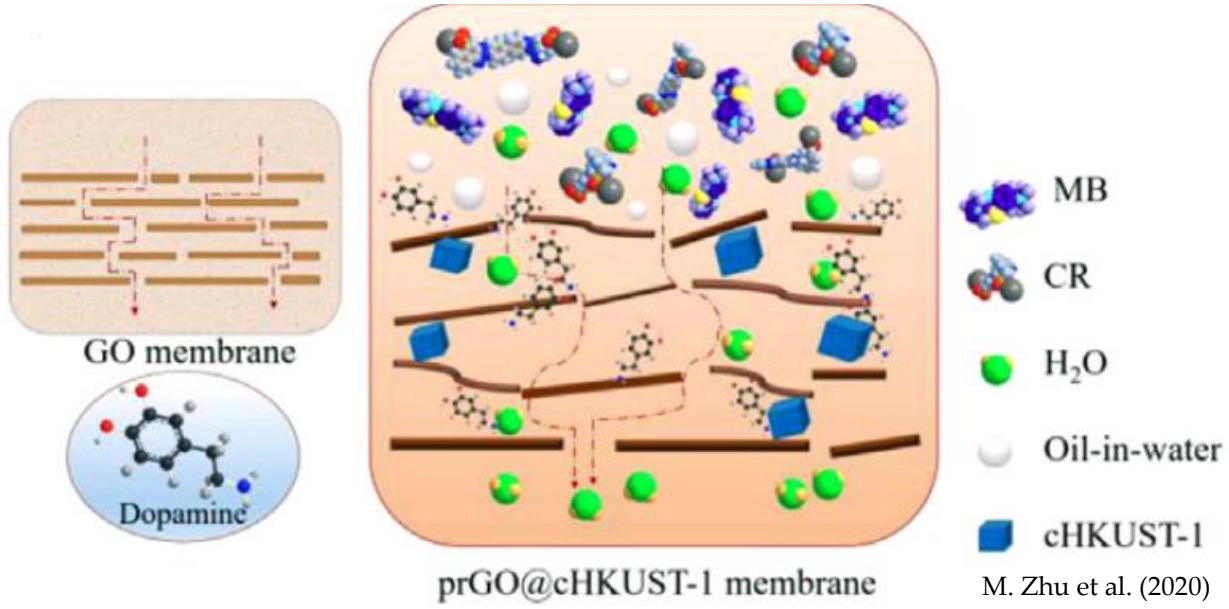
# Introduction

- Dyes are widely used in various industries segments. The improper disposal of this material in affluents can contaminate water sources and soil, being very dangerous to humans, animals and the environment .

- Graphene and others carbon materials can be used to produce membranes due to their chemical structure and physical properties.

- Graphene oxide (GO) is applied as a membrane material since his good mechanical stability, oxygen-containing groups and surface area. In contrast, the instability in water and low flux are some of the disadvantages in select this material.

- In reduced graphene oxide (rGO), hydrophobic areas between layers are responsible to generate low-friction flow of water, contributing to elimination of impurities. Furthermore, the π-conjugated rGO's structure presents the advantage to attract pollutants with benzene rings




M. Zhu et al. (2020)

**Figure 1** – Example of mechanism of dyes and oil-water emulsion separation in a GO membrane.

# Materials and Methods

- Preparation of GO and rGO

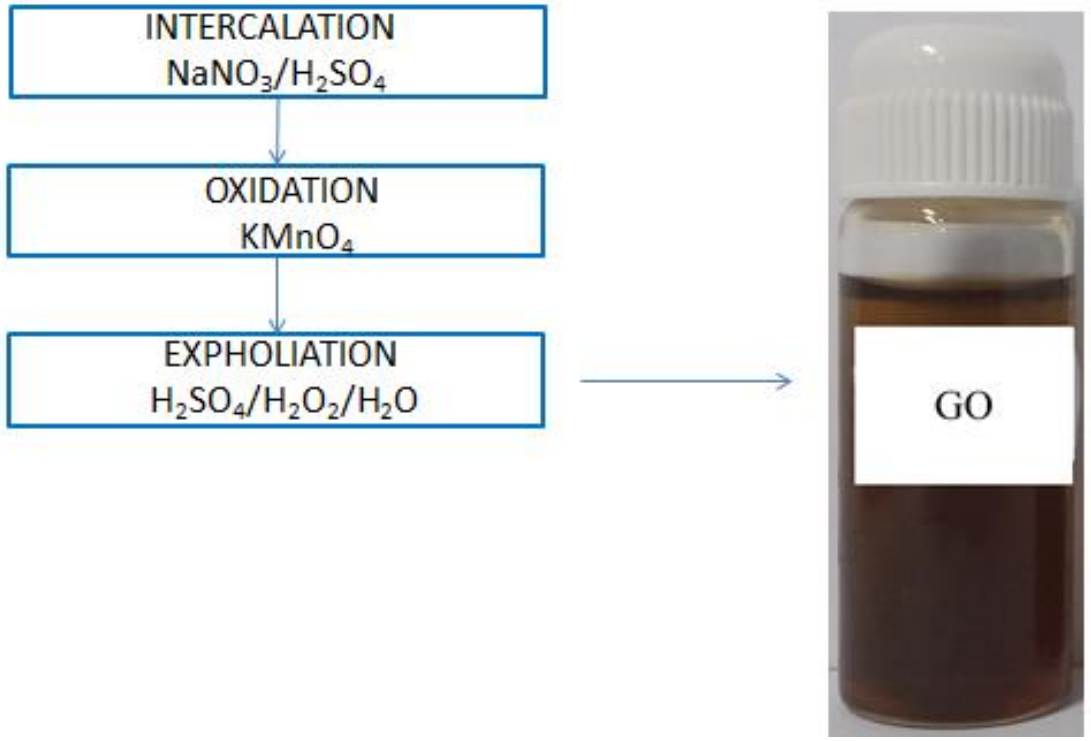



**Figure 2** – GO preparation.

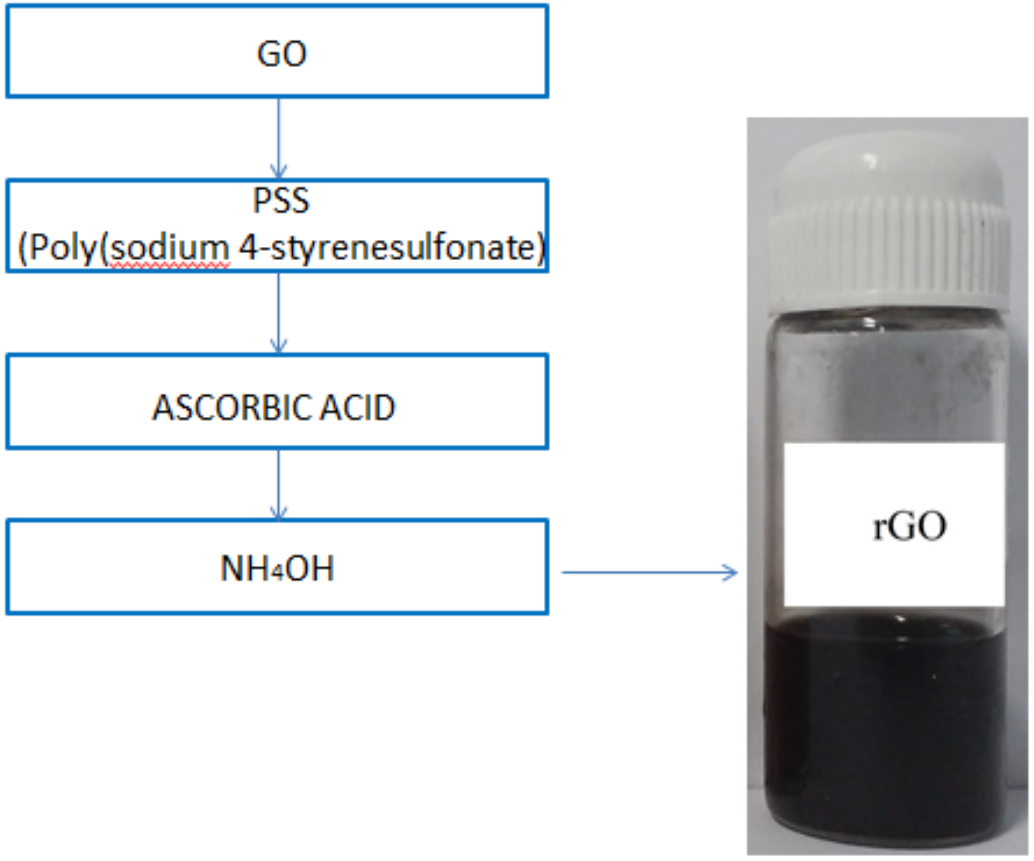



**Figure 3**– rGO preparation.

# Materials and Methods

- Preparation of rGO filtration membranes

  - Cellulose acetate (CA) membranes, with 0.2 μm of pore size and 25 mm of diameter, were used as substrates to deposit graphene.

  - rGO dispersions were elected to produce filtration membranes (FM) because of his hydrophobic character.

  - Filtration membranes were produced in a home-made spray coating deposition equipment (Figure 4), with parameters presented in Table 1.

**Table 1** – Deposition parameters.

| Sample | rGO concentration (mg/ml) | Ni pressure (psi) | Temperature (°C) | Deposition/ Drying time (s) | Number of layers |
|---|---|---|---|---|---|
| 40-ly rGO FM | 1,0 | 20 | 90 °C | 1/30 | 40 |
| 60-ly rGO FM | 1,0 | 20 | 90 °C | 1/30 | 60 |
| 80-ly rGO FM | 1,0 | 20 | 90 °C | 1/30 | 80 |
| 100-ly rGO FM | 1,0 | 20 | 90 °C | 1/30 | 100 |

**Figure 4** – Home-made spray coating.

# Materials and Methods

- Characterization

  - **rGO dispersion:**

**Raman spectroscopy** – NT-MDT NTEGRA spectrometer, with 473 nm of laser wavelength and 100 s of radiation time;

**SEM** – QUANTA FEG FEI, voltage of 2 kV, spot size 4.5 to 5.0 and working distance from 4.7 to 8.3 mm.

  - **Filtration membranes:**

**XDR** – X'Pert MRD PANalytical, cobalt source, 40 KV and 40 mA of voltage and current;

**Raman spectroscopy** - NT-MDT NTEGRA spectrometer, with 473 nm of laser wavelength and 100 s of radiation time;

**SEM** – QUANTA FEG FEI, voltage of 5 kV, spot size 3 to 5 and working distance from 11.2 to 14.0 mm.

- Dye removal

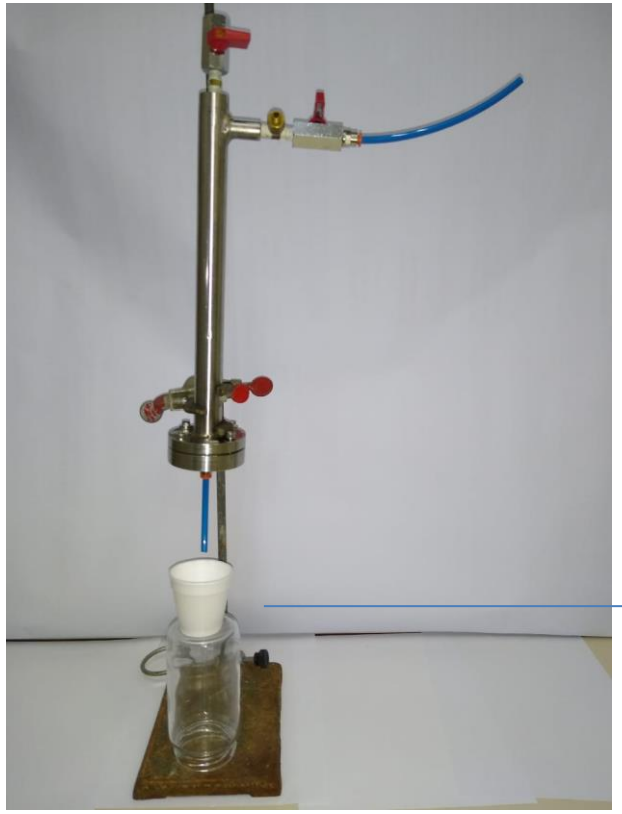



**Figure 5** – Permeation cell.

# Results and Discussion

- rGO dispersion characterization

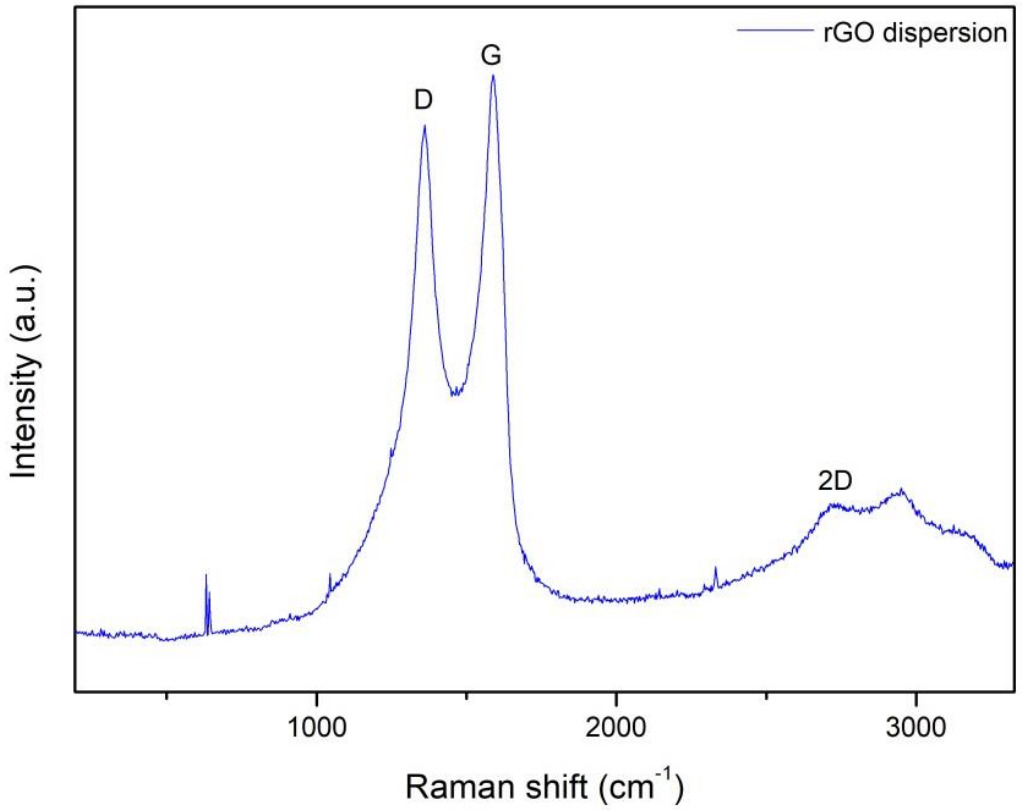



**Figure 6** – Raman spectra of rGO dispersion.

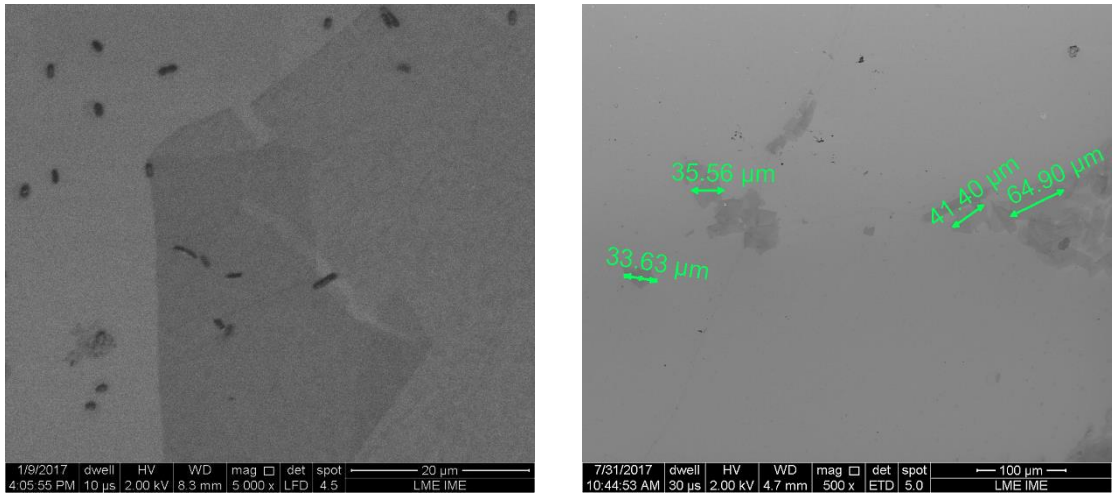



**Figure 7** – SEM micrographs.

**Raman spectroscopy**

- D band (1370 $cm^{-1}$) - associated to $sp^3$ hybridized carbon atoms, which corresponding to structural imperfections of graphene sheets and disorder, due to oxidation;
- G band (1590 $cm^{-1}$) - related to $sp^2$ hybridized carbon and tangential vibration, responsible for identifying graphene structure.

**SEM analysis**

- Lateral dimension of 45.9 ± 26.6 µm.

# Results and Discussion

- rGO filtration membranes characterization

**XRD**

- 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.

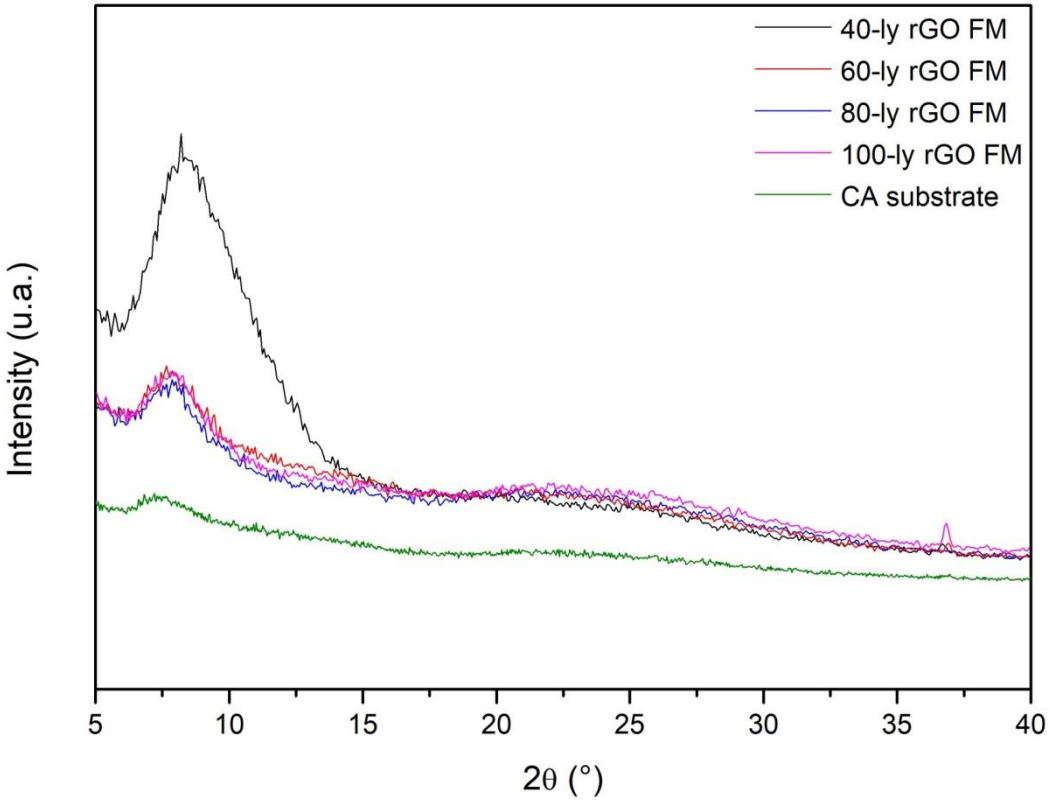



**Figure 8** – XRD patterns for CA substrate and rGO fm.

**Raman spectroscopy**

- Noticed elevations in the Raman shift correlated to the D (1368 $cm^{-1}$) and 2D (2737 $cm^{-1}$) bands and a evident presence of G band (1584 $cm^{-1}$), proving that the deposition method was efficient.

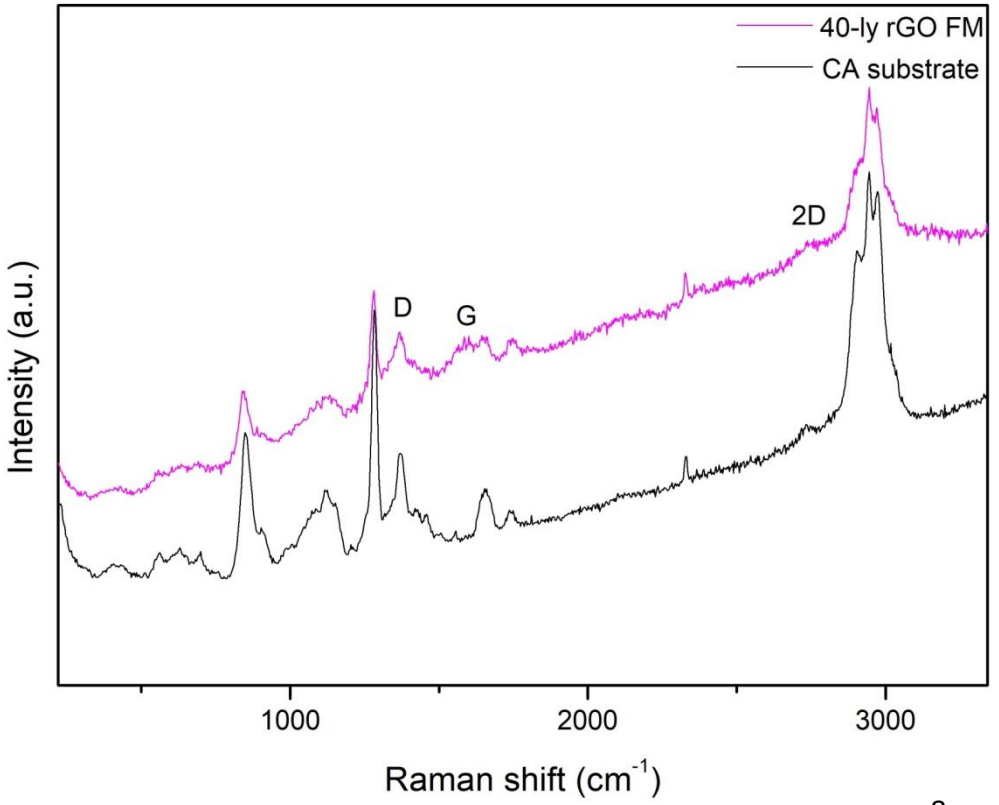
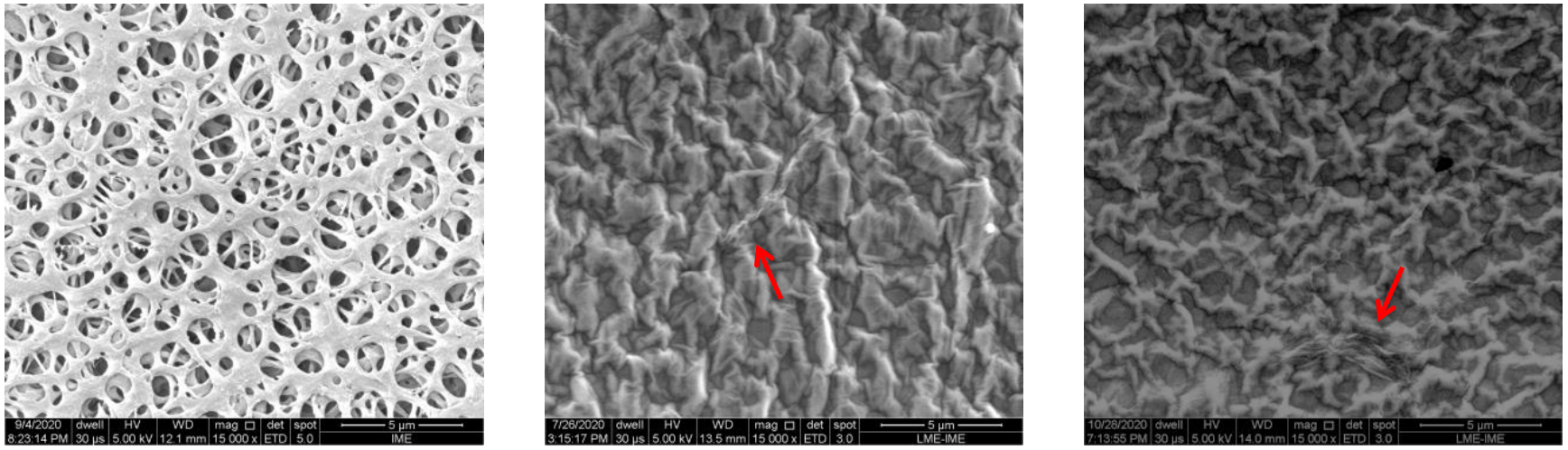



**Figure 9** – Raman spectra of CA substrate and rGO fm.

# Results and Discussion

- rGO filtration membranes characterization




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

**Figure 10** – 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.

**SEM analysis**

- it is possible to note the uniform surface with pores from the commercial CA substrate, whereas in as-prepared rGO filtration membranes samples, the micrographs acquire a rough aspect, characteristic from an accumulation of graphene, making even feasible to see some flakes.

# Results and Discussion

- Dye removal evaluation

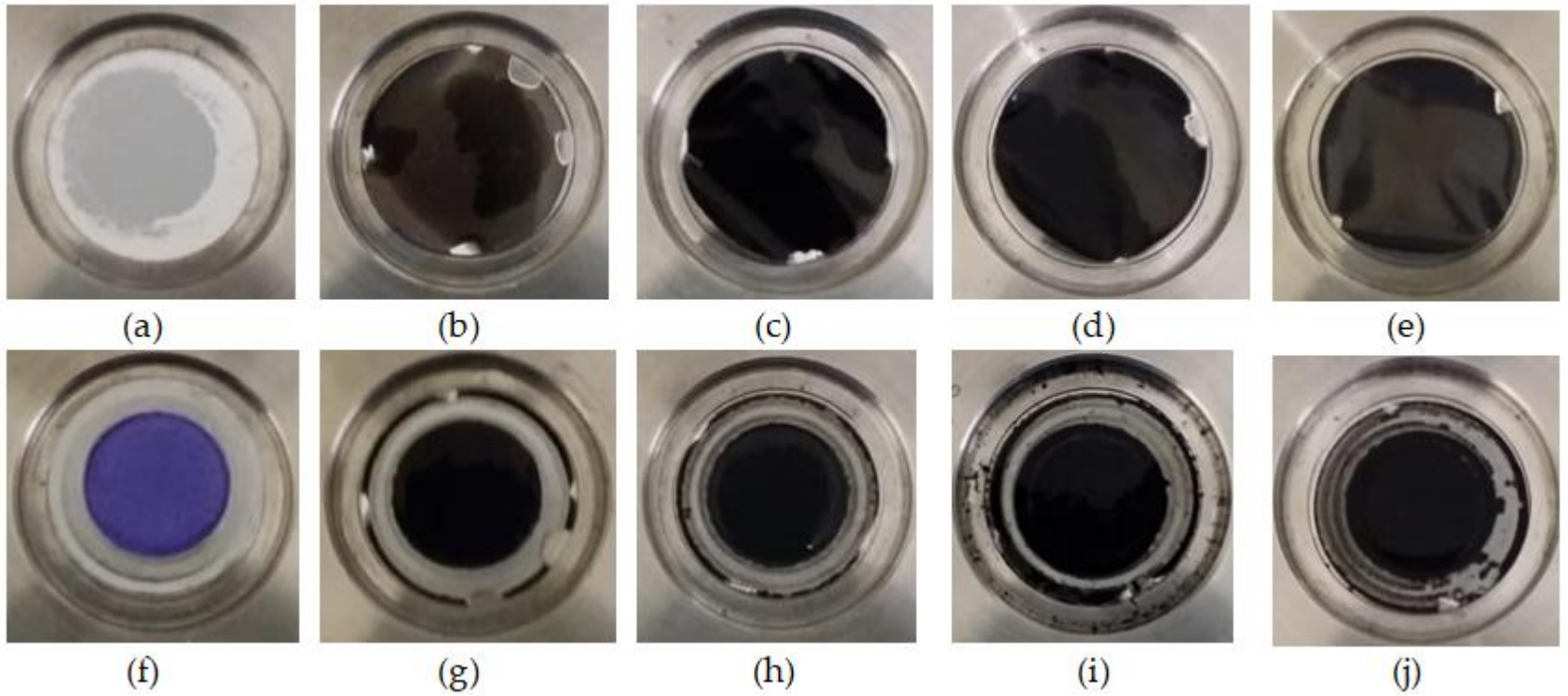



**Figure 11** – Filtration membranes: (a) CA substrate; (b) 40-ly rGO FM; (c) 60-ly rGO FM; (d) 80-ly rGO FM; (e) 100-ly rGO FM before permeation test; (f) CA substrate; (g) 40-ly rGO FM; (h) 60-ly rGO FM; (i) 80-ly rGO FM; (j) 100-ly rGO FM after permeation test.

- The area of interest of none rGO's filtration membrane suffered significant damage during tests, what means that the studied membranes are stable.

# Results and Discussion

- Dye removal evaluation

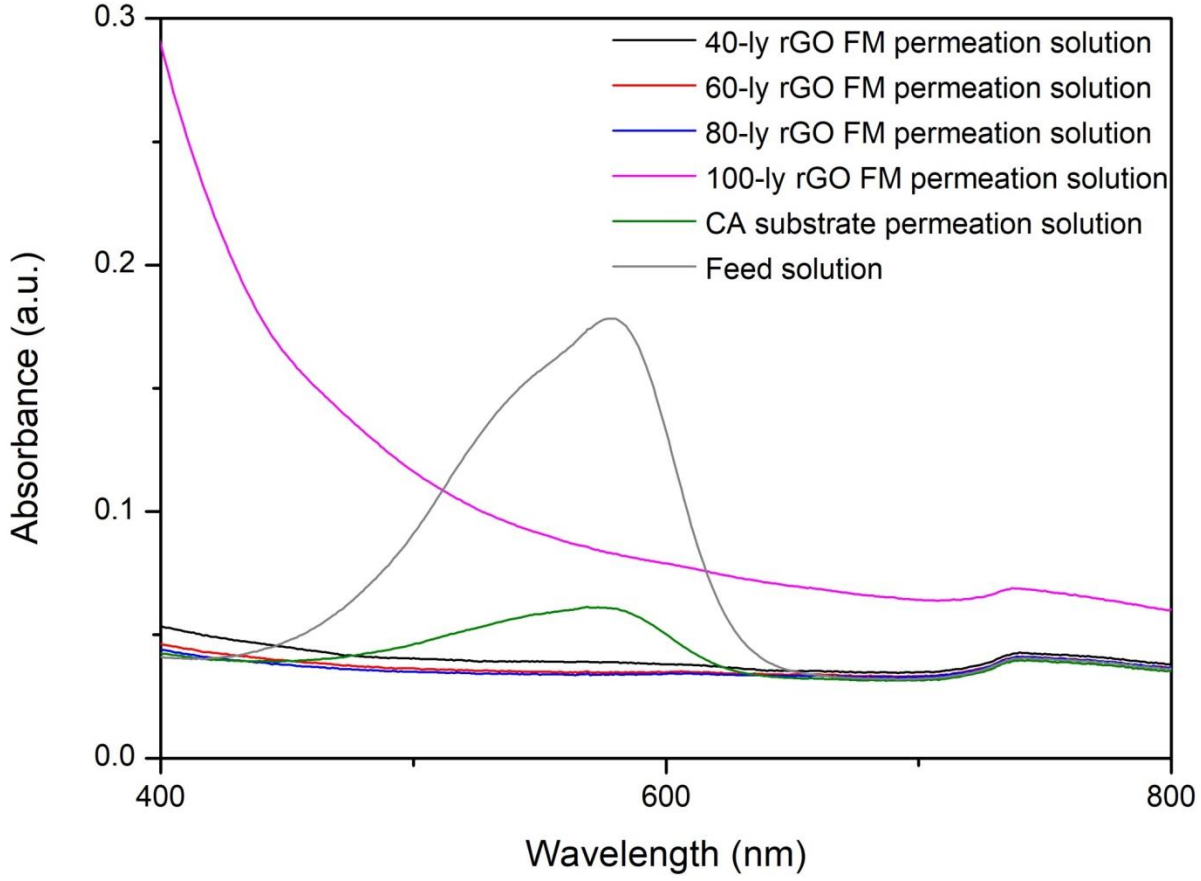



**Figure 12** – UV-vis absorption spectra for feed and permeation solutions.

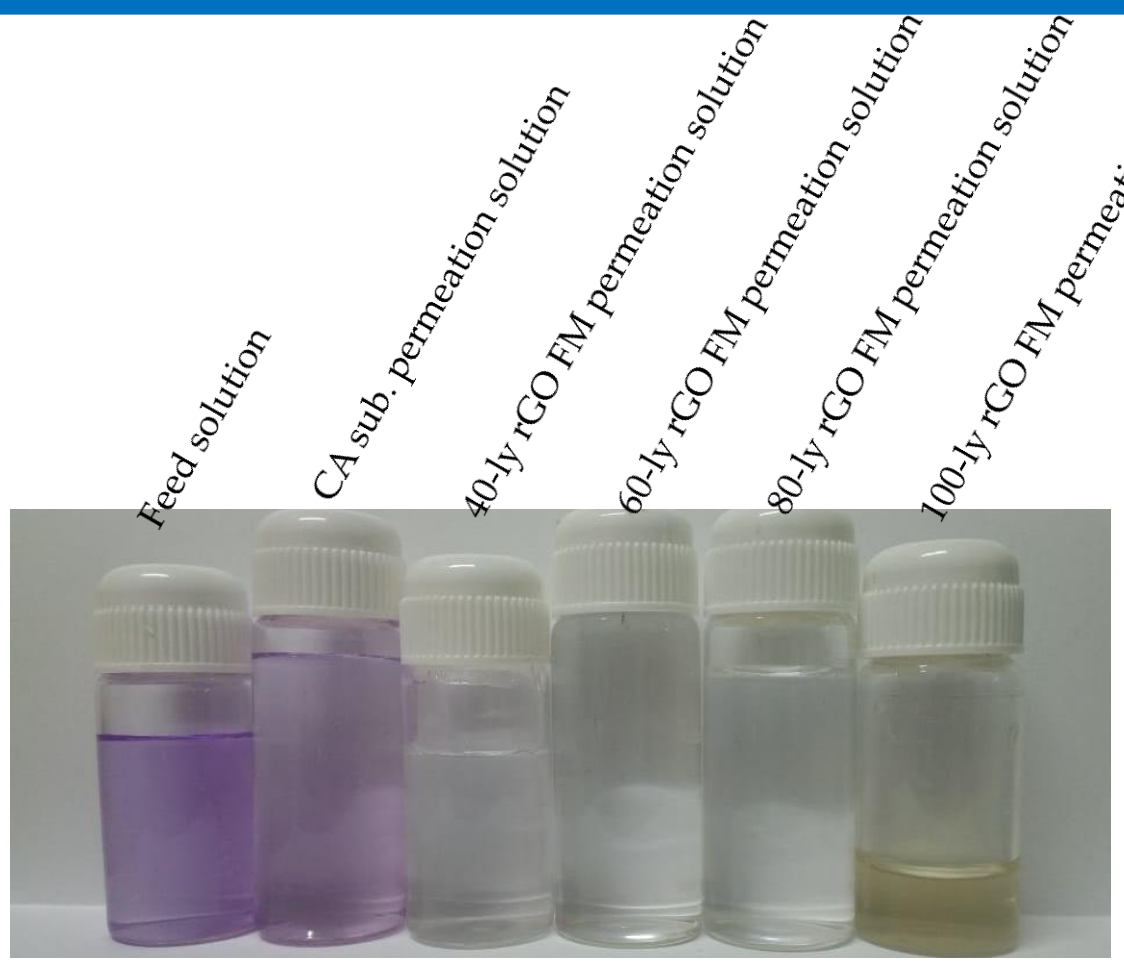



**Figure 13** – Solutions.

- The rGO film deposited above the substrate, successfully eliminated dye from feed solution in the samples with 40, 60 and 80 layers.

# Conclusions

- the rGO dispersion was successfully produced and has lateral size and properties suitable for an application as filtration membranes;

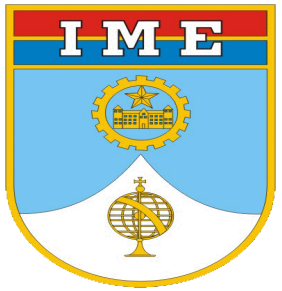
- the spray coating method produced uniform and stable rGO membranes;

- the permeation test indicates that rGO filtration membranes can be used to eliminate dyes from manufacturing and textile industry wastewater as a simples, low-cost and scalable method.

# 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.
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.
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. *Chinese Chem. Lett.* **2020**, *XX*, XXX-XXX.
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.
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.
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. Manage.* **2019**, *240*, 494-503.
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*. **2021**, *263*, 127892-127902.
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.
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.
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. *Revista Matéria*. **2017**, *22*, e-11918. 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.
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.
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.
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.
15. Xu, H.; Ma, L.; Jin, Z. Nitrogen-doped graphene: Synthesis, characterizations and energy applications. *J. Energy Chem.* **2018**, *27*, 146-160.
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.
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. Membra. Sci.* **2020**, *595*, 117547-117558.
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.
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.
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.
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.
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.

# Acknowledments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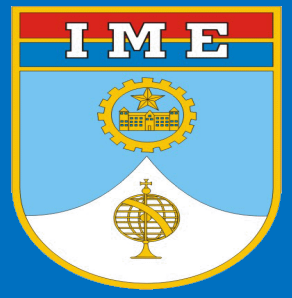


# Thank you!