

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

Andreza Lima <sup>1,\*</sup>, Anthony de Oliveira <sup>1</sup>, Luana Demosthenes <sup>1</sup>, Talita Sousa <sup>1</sup>, Artur Pereira <sup>1</sup>, Roberto de Carvalho <sup>2</sup> and Wagner Anacleto <sup>1</sup>

<sup>1</sup> Instituto Militar de Engenharia (IME), Seção de Engenharia de Materiais, Rio de Janeiro 22290-270, Brasil; 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.)

<sup>2</sup> Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio), Rio de Janeiro 22541-041, Brasil; rbcarvalho@puc-rio.br

\* Correspondence: andrezamenezeslima@gmail.com

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**Abstract:** Dye removal from manufacturing and textile industry wastewater is one of 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 spray coating method, and its capability to remove dyes from water was evaluated. Graphene oxide was prepared by 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  $\mu\text{m}$  of lateral dimension; X-ray diffraction, SEM and Raman analyses indicate that spray method was efficient in producing stable and uniform filtration membranes; 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

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## 1. Introduction

Dyes are widely used in various industrial segments, resulting in wastewater containing dyes one of the most common discards in textile, paper, cosmetics and others 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 carcinogens substances. Membrane separation technology is being widely studied for this application because is a simple, versatile, energy saving, cost-effectiveness and able to remove pollutants with different sizes [4,5].

Membrane-based separation and purification process can also be used to 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 of its good mechanical stability, oxygen-containing groups and surface area. In contrast, the 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 rGO dispersions to produce membranes also could be an alternative. The hydrophobic areas between layers of reduced material are responsible to generate low-friction flow of water, contributing to elimination of impurities. Furthermore, the  $\pi$ -conjugated rGO structure presents the advantage to attract 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 ( $\text{NaNO}_3$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and potassium permanganate ( $\text{KMnO}_4$ ), followed by exfoliation with washing/centrifugation steps. rGO was produced from GO dispersion, adding ascorbic acid as reducing agent, ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and polystyrene sulfonate (PSS), while heating at  $80^\circ\text{C}$  for 3 days, also followed by washing/centrifugation steps [11].

### 2.2. Preparation of rGO Filtration Membranes

Cellulose acetate (CA) membranes, with  $0.2\ \mu\text{m}$  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 its hydrophobic character, which can improve the water flux and the stability of the membrane [12]. rGO filtration membranes were produced in a home-made spray coating deposition equipment with a Steula BC 66-08 airbrush with nozzle of 0.8 mm, rGO dispersions with 1.0 mg/mL of concentration, 20 psi of nitrogen as carrier gas, substrate temperature of  $90^\circ\text{C}$ , 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  $500\times$  to  $5000\times$ , 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 a 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 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. 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 CARY 5000 spectrophotometer, from VARIAN. The analyses were obtained for wavelengths from 400 nm to 800 nm.

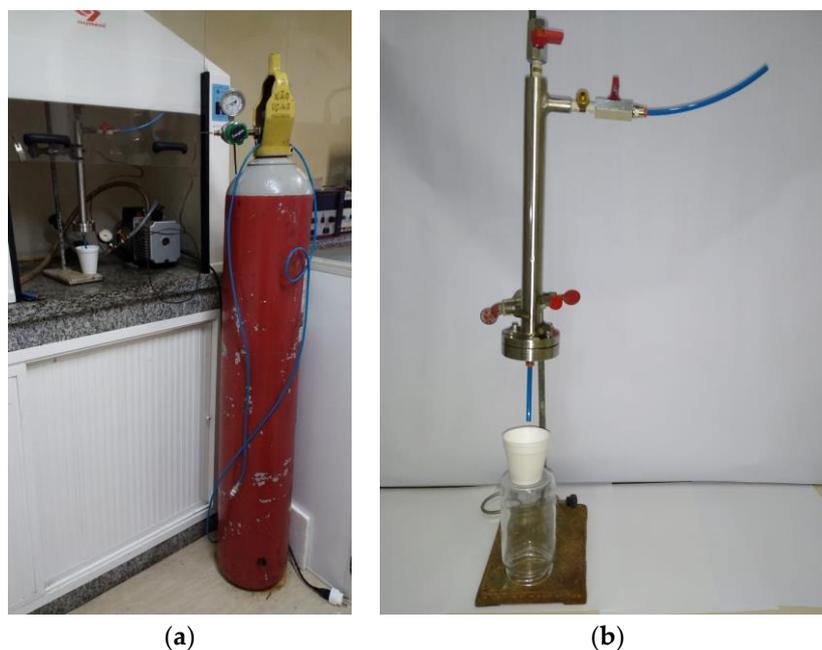


Figure 1. (a) Permeation system; (b) Permeation cell.

### 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 ( $1370\text{ cm}^{-1}$ ), which is associated to  $\text{sp}^3$  hybridized carbon atoms, corresponding to structural imperfections of graphene sheets and disorder, due to oxidation. It is also observed a strong G band ( $1590\text{ cm}^{-1}$ ), related to  $\text{sp}^2$  hybridized carbon and tangential vibration, responsible for identifying graphene structure [13,14]. In  $2705\text{ cm}^{-1}$ , a weak peak belongs to the 2D band is notice; this band is always observed in carbon materials and is related to the numbers of graphene layers of the rGO [15].

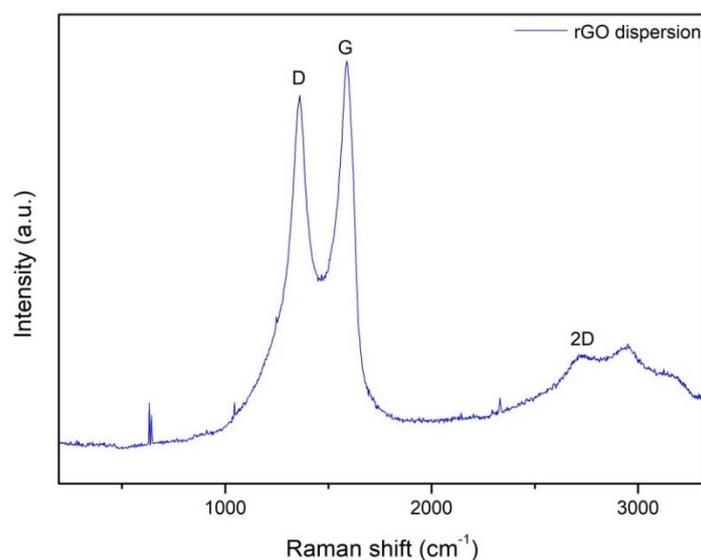


Figure 2. Raman spectra of rGO dispersion.

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  $45.9 \pm 26.6 \mu\text{m}$ ; this characteristic is very interesting since large GO and rGO sheet size can direct affect permeability, salt rejection and other properties. For example, large GO sheets are more successful in eliminate salt from water then medium and small sizes [16].

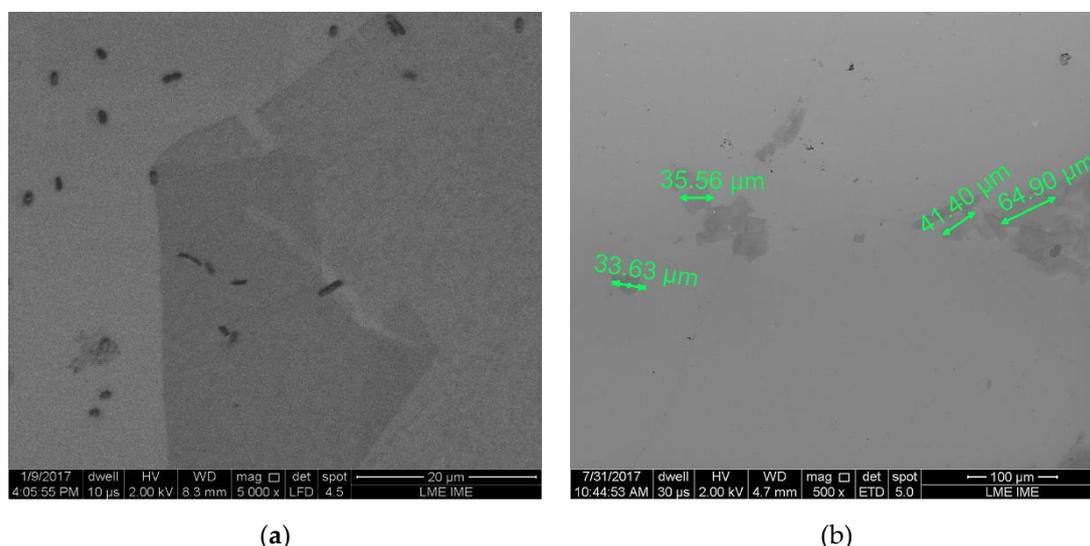


Figure 3. SEM micrographs for (a) rGO; (b) rGO with measurements.

### 3.2. rGO Filtration Membranes Characterization

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

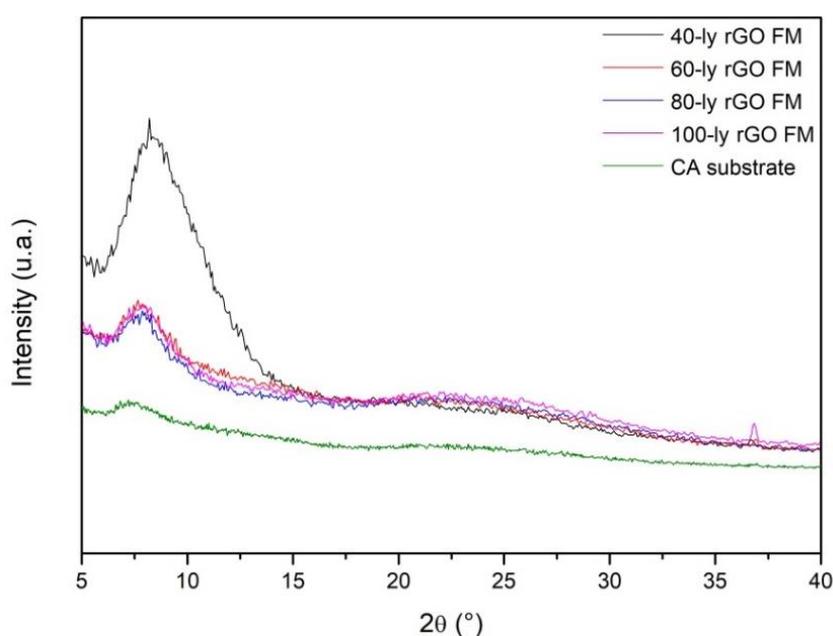


Figure 4. XRD patterns for CA substrate and rGO filtration membranes (FM) with different number of layers (ly).

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, elevations in the Raman shift correlated to the D ( $1368\text{ cm}^{-1}$ ) and 2D ( $2737\text{ cm}^{-1}$ ) bands in filtration membrane spectra are not clear, but is evident the presence of G band ( $1584\text{ cm}^{-1}$ ), proving that the deposition method was efficient [19,20].

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

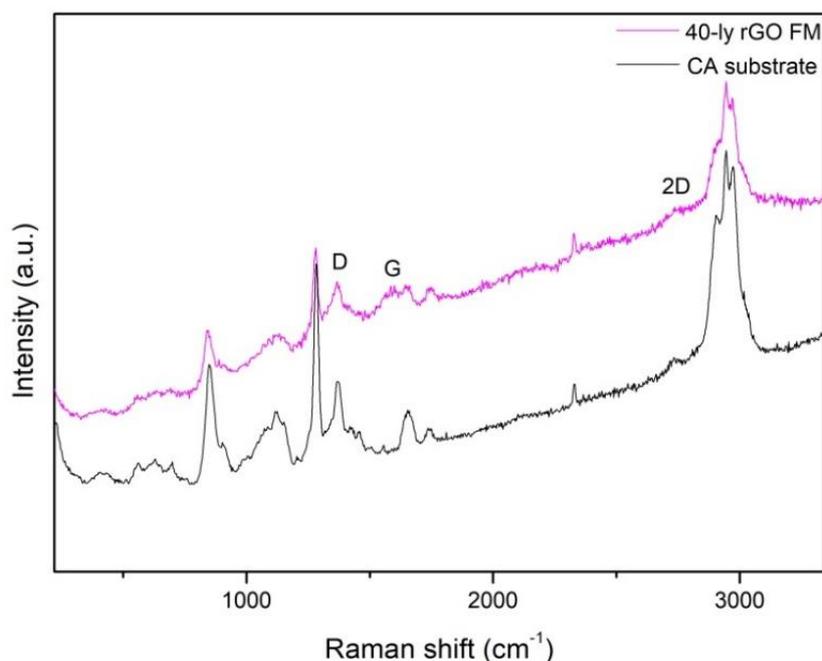
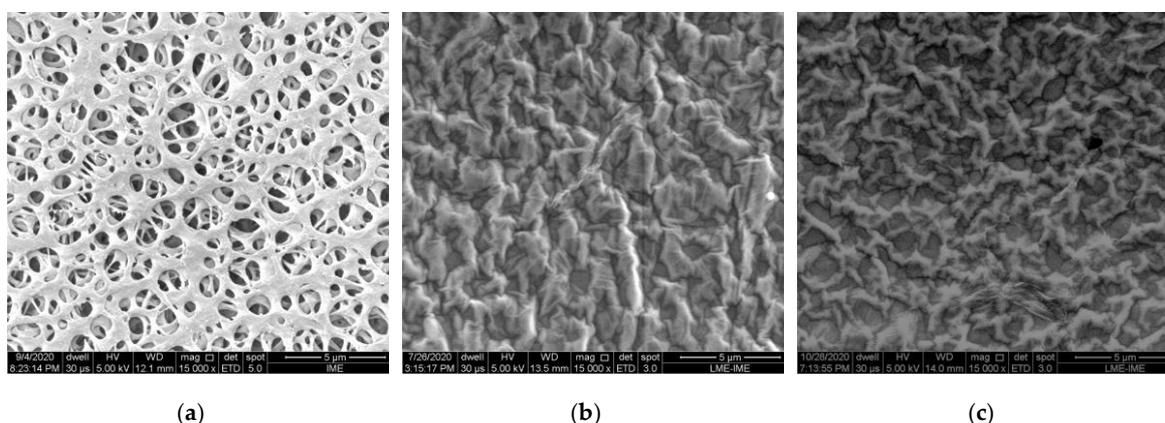


Figure 5. Raman spectra of CA substrate and 40-ly rGO FM.

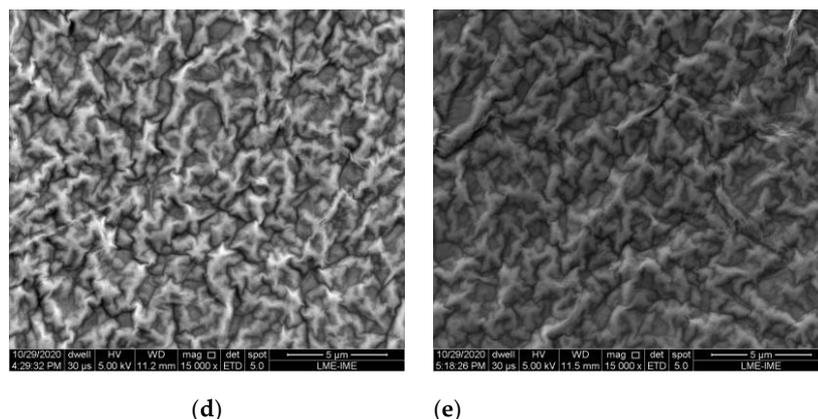
SEM micrographs (Figure 6) indicate that the spray coating method was efficient in deposit graphene flakes on substrate surface. In Figure 6a it is possible to note the uniform surface with pores from the commercial CA substrate, whereas in as-prepared rGO filtration membranes samples the micrographs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



(a)

(b)

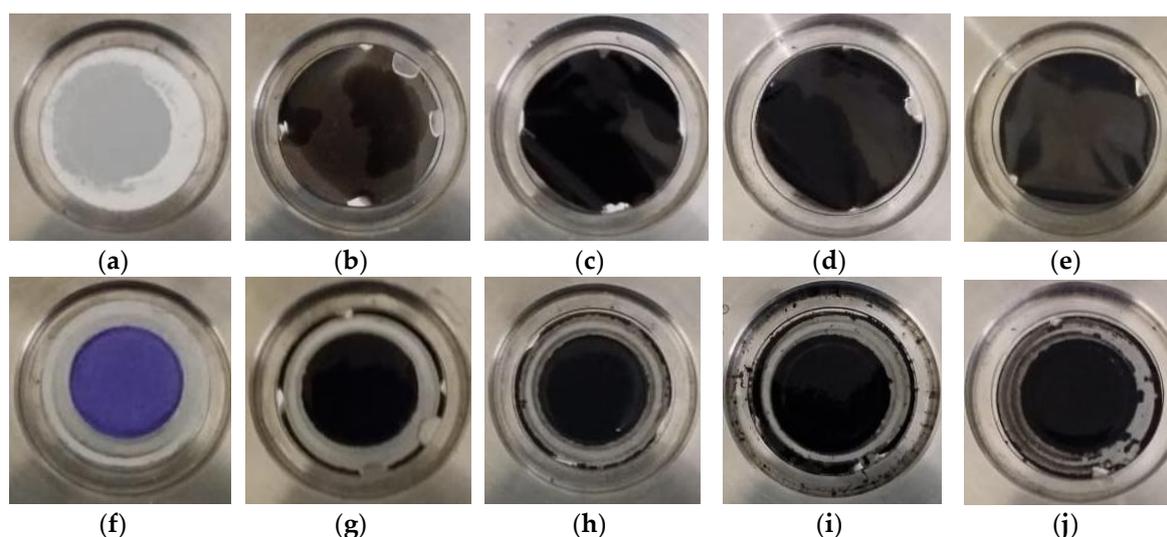
(c)



**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.

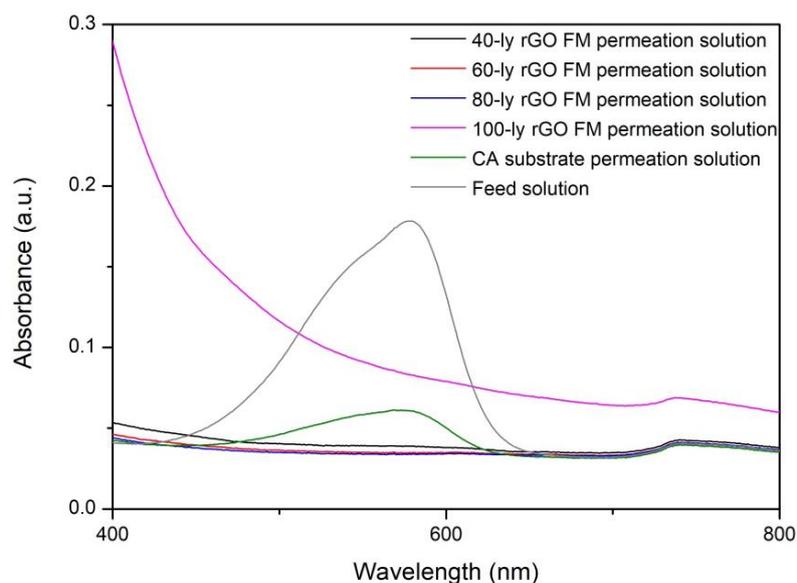
### 3.3. Dye Removal Evaluation

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



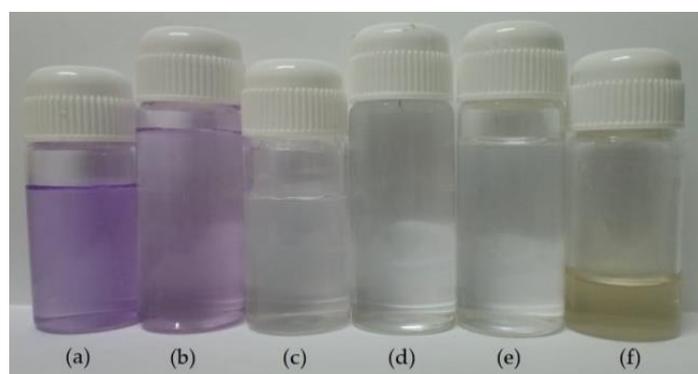
**Figure 7.** Filtration membranes: (a) CA substrate; (b) 40-ly rGO FM; (c) 60-ly rGO fm; (d) 80-ly rGO FM ; (e) 100-ly rGO FM before permeation test; (f) CA substrate; (g) 40-ly rGO FM; (h) 60-ly rGO FM; (i) 80-ly rGO FM; (j) 100-ly rGO FM after permeation test.

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 CA substrate has the capability to filtrate some part of dye, but not a significant amount. The rGO film deposited over CA substrate successfully eliminated dye from feed solution in the samples with 40, 60 and 80 layers.



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

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 to the permeated water, even if the appearance of membrane (Figure 7j) do not show a significant failure in rGO film surface. This can be confirmed by analyzing Figure 9, which shows the comparison among samples and emphasize 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 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 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.

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W.A.; visualization, W.A.; supervision, W.A. and R.C.; project administration, A.L.; funding acquisition, W.A. All authors have read and agreed to the published version of the manuscript.

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

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