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Surface Modification of Microfiltration Membrane with GO Nanosheets for Dyes Removal from Aqueous Solutions

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The presence of dyes in water cause problems in biological processes, because it reduces the light transmission. Hence, the development of efficient and low cost methods for dyes removal from aqueous solutions has received more attention. Thus, the aim of this study was to evaluate the modification of polyethersulfone microfiltration membranes (PES-MF), by a simple and novel method using grapheme oxide (GO) aiming the methylene blue (MB) removal. PES-MF (0.2 µm, 47 mm) and modified membrane (PES-MF/H_2SO_4+GO) were characterized by ATR-FTIR and water angle contact. The concentration of MB was analyzed using a Spectrophotometer UV-VIS. FTIR spectra and water contact angle measurements indicated the success of the PES-MF surface modification with GO. In filtration tests, the modified membrane presented much higher rejection rates, reaching a rejection rate of 92.1%. Therefore, the proposed modification suggest that GO nanosheets can be applied on modification of PES-MF membranes surface, to improve their efficiency.

1. Introduction

The problems associated with water pollution are becoming a huge challenge for sustainable development of world society. Specially on last years, the increase on the number of process industries has been followed by an alarming amount of wastewater containing many hazardous organic compounds, which are highly toxic (Qiu et al., 2015, Yao et al., 2014).

Synthetic dyes are one of the most typical class of organic polluents. Nowadays, there are more than 100.000 dyes commercially available, with an annual production of $7x10^5$ ton. Hence, a huge amount of wastewater contaminated by dyes is generate on the entire world. It is estimated that more than 15% of all dyes produced are released on the environment during their synthesis or dyeing process (Yao et al., 2016).

The treatment of effluents contaminated by dyes is a challenge, once that most of the commercial dyes are complex aromatic structures, recalcitrant and resistant to degradation, even when exposed to conventional and advanced treatment processes (Qiu et al., 2015). Thus, the development of efficient methods for the treatment of wastewater of textile industries has received more attention, and is being considered as an environment protection and public health problem (Chiu et al., 2009).

Various techniques are being investigated in order to remove dyes from effluents, as for example the adsorption, coagulation/flocculation and chemical or biologic degradation. Authors pointed that each one of these techniques present specific advantages and disadvantages. For instance, the adsorption process usually proves to be highly efficient, being considered as a flexible process. The coagulation/flocculation are also presented as efficient processes. However, the high production of secondary products in both of these processes avoids them from being applied on an industrial scale, considering the need to carry out a subsequent treatment of the toxic sludge, which would make the process expensive (Yagub et al., 2014, Liang et al., 2014). Another technique that is been widely used in water treatment is the membrane separation processes (MSP) (Dai et al., 2016, Chiu et al., 2009, Karim et al., 2014, Shao et al., 2013).

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Among the advantages of the application of membrane separation processes in water treatment we can cite the absence of chemical products, regeneration capacity of valuable components, low energetic cost and the simplicity of the process (Mierzwa et al., 2008). The main disadvantage is the reduction of flux through the membrane during filtration, caused by processes like *fouling*. As a result, both the academic and industrial sectors have focused their efforts on investigating solutions to these problems, in order to make membranes more resistant to problems related to *fouling* and thus to obtain improvements with respect to dye removal. Recent studies point out that one promising solution is the application of nanotechnology in water separation membranes (Goh et al., 2015).

Due to its unique transport properties, allied with its flexibility and the one atomic thickness two-dimensional structure, recently, graphene oxide nanosheets (GO) are being applied as a potential material in the surface modification of membranes (Hegab and Zou, 2015, Mahmoud et al., 2015). Thus, the aim of this study was to evaluate the modification of polyethersulfone microfiltration membranes (PES-MF), by a simple and novel method using GO nanosheets, aiming the removal of methylene blue dye removal.

2. Material and Methods

2.1 Materials

Graphene oxide nanosheets (GO) were prepared from graphite powder (Sigma Aldrich, <20 μm). Potassium peroxodisulfate ($K_2S_2O_8$, ≥99.5%, Sigma-Aldrich), phosphorous pentoxide (P_2O_5, ≥99.5%, Sigma-Aldrich), potassium permanganate ($KMnO_4$, ≥99.0%, Sigma-Aldrich), sulphuric acid (H_2SO_4 ≥98%, Sigma-Aldrich), hydrochloric acid (HCl 37%, Merck) and hydrogen peroxide (H_2O_2, 30wt% in H_2O, Sigma Aldrich) were used in the synthesis of GO. The commercial PSf microfiltration membranes (47 mm of diameter, average pore size of 0.2 μm and thickness of 165 μm) used as the support for the GO layer were purchased of Hexis Científica. For the filtration tests, methylene blue dye (MB, Merck) was used. All reagents were used as received.

2.2 Preparation of graphene oxide nanosheets

GO nanosheets were prepared using the modified Hummer's method adapted by Yamaguchi (2016). In a round bottom flask, 5 g of graphite powder, 2.5 g of $K_2S_2O_8$, 2.5 g of P_2O_5, and 18 mL of H_2SO_4 were added. This mixture was kept in a reflux and constant stirring system by 80 ºC, for 5 h. After this period, the heat was turned off and the mixture was diluted with 1 L of deionized water. The solid obtained (pre-oxidized graphite) was filtered, rinsed with deionized water to remove the excess of acid, and dried in an oven for 12 h in a constant temperature of 60 ºC. Subsequently, 1 g of the pre-oxidized graphite was diluted in 23 mL of H_2SO_4, under stirring in ice bath. To this mixture, 3 g of $KMnO_4$ were added slowly, the mixture was kept for 5 min still under stirring, and then the ice bath was removed. The temperature was adjusted to 35 ºC and the mixture was left for reaction for 2 h. Next, 46 mL of water were slowly added, keeping the temperature of the mixture under 50 ºC. The mixture was kept under stirring for more 2 h and then 140 mL of deionized water and 2,5 mL of H_2O_2 were added to end the reaction. A purification step was performed by washing the mixture with 250 mL of HCl. To separate the graphite oxide obtained, the mixture was centrifugated, washed with deionized water and dried in an oven at 60 ºC for 12h. Finally, the GO nanosheets were obtained by exfoliation in a bath sonication for 150 min.

2.3 Surface modification of PES microfiltration membranes

The membranes with were modified in a glass filtration system (Milipore glass filter, 47mm). First, to ensure a positively charged membrane surface and benefit the assembly of GO molecules, a H_2SO_4 solution (0.5 N) was used to prepare the surface of the membrane (Shah et al., 2005). The membranes were placed in the system and the H_2SO_4 solution was permeated through the membrane for 3h. After that, the membrane was rinsed with deionized water (DW) until the water pH reached 7. For the assembly of the GO nanosheets, a GO dispersion with a known concentration (0.5 mg/mL) was poured into the tank and permeated through the membrane for 3h. For both cases (the permeation of the H_2SO_4 e GO through the membrane), the system was applied using only gravity to promote the driven force.

2.4 Characterization

A UV-VIS scanning spectrophotometer (UV-1800, Shimadzu, Japan) with a 1 cm cuvette was used to measure the absorbance of GO solutions. The measurements were made at a wavelength range between 200 and 800 nm. The surface chemistry and chemical composition of the commercial (PES-MF) and modified membranes (PES-MF/H_2SO_4+GO) were analysed using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR, IRAffinity-1S FTIR HATR 10) in a wavenumber range of 400 - 4000 cm^{-1}. The surface hidrophilicity/hydrophobicity of the membranes was evaluated by water contact angle (WCA) in a goniometer system (OCA 15 PLUS DataPhysics). Before the characterization tests, the membranes were dried overnight at room temperature. Each one of the analysis made were repeated at least 5 times in different places of the surface of the membranes, to reduce error. To the WCA measurements, a microsyringe with a stainless steel needle dropped a 0,3μL drop of distilled water on the surface of the membrane. The images of the static angle were recorded and the data was saved on the software of the equipment. The results of the measurements were achieved by an average between the five analysis made.

2.5 Filtration experiments

The permeation and MB removal performance of the proposed membranes were investigated using a *dead-end* filtration system (Milipore glass filter, 47mm), working with only gravity to promote the driven force. The system has a feed tank of 300 mL of capacity, to store the solution to be filtrated. In this work, the tests were carried out at 0.02 bar, which corresponds to 200 millimetres of water column. The PES-MF and PES-MF/H_2SO_4+GO membranes, with an effective surface area of 0.962 x 10^{-3} mm², were fixed at the centre of the filtration module. Then, a 7.5 mg/L MB solution was filtrated and the permeate was collected perpendicularly to the membrane area. The permeate flux was determined by using the following equation:

$$J = \frac{Q}{APt} \quad (1)$$

Where *Q* is the volume of permeate (L), *A* is the effective surface area of membrane (m²), P is the filtration pressure (bar), and *t* is the running time (h). The rejection rate for MB (*R*, %) was determined through the following equation:

$$R=1-\frac{C_p}{C_f} \quad (2)$$

where, C_p and C_f are the solute concentrations in permeate and feed, respectively. The concentration of MB was analysed using a UV-VIS scanning spectrophotometer (UV-1800, Shimadzu, Japan) at a wavelength of 663 nm.

3. Results and discussion

3.1 Characterization

3.1.1 FTIR

As can be seen in Figure 1, ATR-FTIR spectra of PES-MF/H_2SO_4+GO showed the presence of hydroxyl groups (—OH stretching in the range 3320 – 3420 cm^{-1}), carboxyl groups (C═O stretching at 1727 cm^{-1}), epoxy groups (C—O—C stretching at 1231 cm^{-1}) and alkoxy groups (C—O stretching at 1050 cm^{-1}). Also, ATR-FTIR spectra of the modified membrane presented a peak in 1626 cm^{-1} that can be attributed to the C═C vibration of aromatic group of graphene, which indicates the success of the PES-MF surface modification with GO. The results find are in agreement with previous studies. These results are in agreement with those found by other authors (Liu et al., 2014, Xia et al., 2015, Liang et al., 2015)

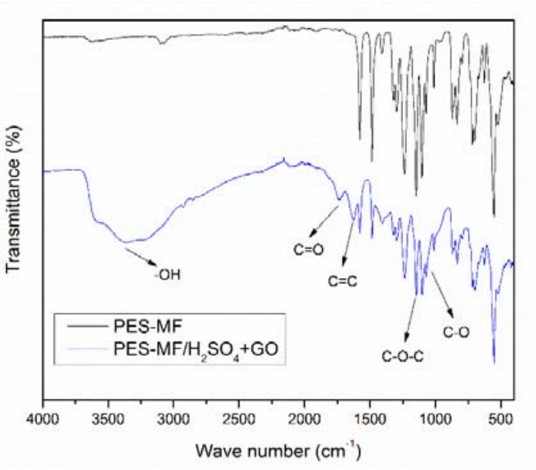

Figure 1 - ATR-FTIR spectra of PES-MF and PES-MF/H_2SO_4+GO membranes.

3.1.2 Water contact angle

The water contact angle measurements showed that the incorporation of GO on the surface of membranes enhanced the hidrophilicity of the membrane, as can be seen in the Table 1.

Table 1: Water contact angle for commercial and modified membranes.

Membrane	Water contact angle
PES – MF	66,4° ± 2,0
PES – MF/H_2SO_4 + GO	40,8° ± 2,1

While the water contact angle of the unmodified membrane was on the average of 66.4°, the GO modified membrane showed values near to 40°. This can be explained by the fact that GO is abundant in functional groups, as could be seen in FTIR analysis. These functional groups i.e. epoxide, carboxyl, and hydroxyl groups, are responsible for hydrophilic properties and, consequently, the membrane modified with GO presented a lowest water contact angle (Hegab and Zou, 2015).

3.2 Filtration experiments

Figure 2 and Figure 3 shows the MB rejection rate and the permeate fluxes for the commercial and modified membranes, respectively.

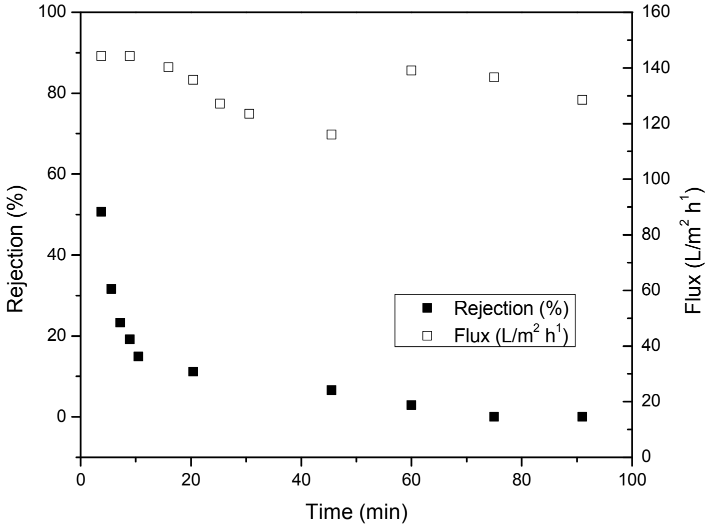

Figure 2 - MB rejection (%) and permeate flux for PES-MF membrane.

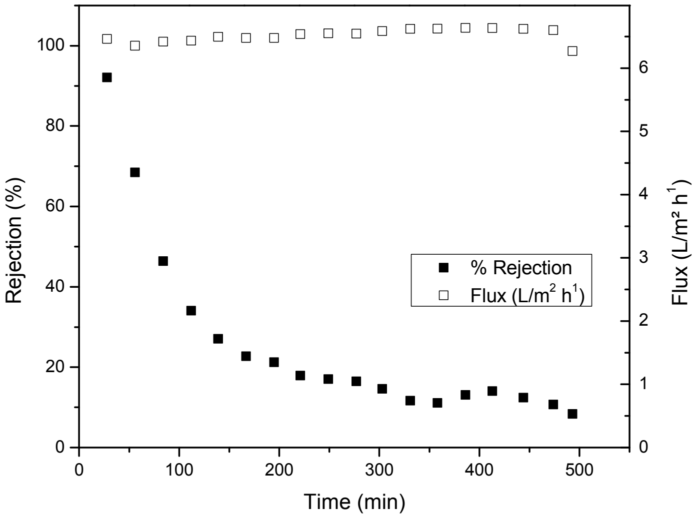

Figure 3 - MB rejection (%) and permeate flux for PES-MF/H_2SO_4+GO membrane.

As can be seen in Figures 2 and 3, the modified membrane presented much higher rejection rates to MB than the unmodified membrane, reaching a rejection rate of 92.1%, compared to a value of only 50.1% to the unmodified membrane. On other hand, the permeate flux value for the unmodified membrane was higher than the one found to the modified membrane. This may be due to the fact that the modification with GO nanosheets can reduce the diameter of the pores of the membrane by blocking the internal pore connection and hinder the permeate transport (Yang et al., 2017). Thus, the modification of the membrane with GO nanosheets proved to be a benefit for the removal of MB. Similar results were found by other authors that also studied the modification of commercial membranes with GO nanosheets (Hu and Mi, 2014, Park et al., 2015).

4. Conclusions

In this study, commercial polyethersulfone microfiltration membranes were modified with GO nanosheets, aiming the improvement of its performance. ATR-FTIR and water contact angle analysis showed that the modification was successfully achieved. The filtration experiments showed that the modified membrane presented higher rejection rates for methylene blue, than the commercial PES membrane. Therefore, the proposed modification on this work suggest that graphene oxide nanosheets can be applied on modification of PES-MF membranes surface, to improve their efficiency. In addition, studies will be conducted aiming to evaluate the parameter influence of the pH and initial concentration of GO on the surface modification of PES membranes.

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