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A methodology for synthesis of reduced graphene oxide membranes for desalination of produced water

B Arenas¹, N Gutiérrez¹, R Cabanzo¹, E Mejía¹
¹ Laboratorio de Espectroscopía Atómica y Molecular (LEAM), Universidad Industrial de Santander, Bucaramanga, Colombia

E-mail: brayan.arenas@correo.uis.edu.co, rcabanzo@uis.edu.co

Abstract. We present a simple methodology for desalination of produced water generated on crude oil fields, using reduced graphene oxide based membranes. This work was developed in three steps: 1) Synthesis of graphene oxide through Modified Hummers method, 2) A novel method for membrane fabrication through a layer-by-layer thermal-chemical reduction of graphene oxide on a hydrophilic paper and 3) Vacuum filtration of produced water of a Colombian crude oil field. The rGO was characterized by Fourier transform infrared spectroscopy – attened total reflection, scanning electron microscopy and X-ray diffraction. The efficiencies of adsorption of \( Na^+ \) and \( Mg^{2+} \) cations on produced water were evaluated by determining the percentages of removal for each cation through Atomic Absorption Spectroscopy. Conductivity test was made on produced water in crude oil field to determine the useful life of membranes synthetized. These results confirm that rGO membranes are very efficient for water purification.

1. Introduction

In crude oil extraction activities, a large amount of water is obtained, and that is called produced water. This produced water contains different types of salts, impurities and pollutants [1], which can affect the ecosystems where the deposit is located if it is irrigated irresponsibly and without additional processing. Due to this, different investigations have been carried out to try to purify the produced water and reduce the environmental impacts caused by its improper handling. Among these, the processes of desalination by membranes created from different materials and synthesis techniques stand out. In the last decade, several studies have been made to solve this problem [2]. Among these, graphene oxide based membranes have been a good candidate for water desalination process.

Graphene is the 2-D allotropic form of carbon. It has excellent mechanical and chemical properties, from which is possible create a lot of materials for different applications. Due graphene is a thin layer totally waterproof, this makes it an excellent candidate for separation processes. One method for obtaining a material similar to graphene is the reduced graphene oxide [3]. A typical method for obtaining graphene oxide is by modified Hummers method [4], which is a promising chemical process for produce graphene oxide to large scale. However, graphene oxide doesn’t have the properties and features of graphene, because it’s oxygenated functional groups which decorate each layer above and below the crystallographic carbon plane. Therefore, it is necessary to reduce the graphene oxide to eliminate oxygenated functional groups and partially restore the properties of graphene [5]. This process generates imperfections and holes over basal plane of graphene, allowing the pass of specific molecules. Thus, several studies have been made for manufacturing graphene oxide membranes. A typical method
is by vacuum filtration. However, with this way we fabricate membranes with low uniformity and rejection, in addition to it’s not a viable method for large-scale manufacturing [6].

In the present study, we use a methodology for synthesis of reduced graphene oxide membranes by layer-by-layer reduction of graphene oxide using polyurethane paper as support, for desalination of production water, and we analyzed the results over two cations: Na\(^+\) and Mg\(^{2+}\), which are in high concentrations in these waters.

2. Materials and methods

2.1. Materials
Graphite spectroscopic powder SP1 grade was purchased from Union Carbide Corp. New York, USA. Prior to GO synthesis, graphite was passed through 400 mesh screen (particle size < 37µm). Sulfuric acid 98% (Panreac AppliChem GmbH, Darmstadt, Germany), hydrogen peroxide 30% (Panreac AppliChem GmbH, Darmstadt, Germany), potassium permanganate (Merck KGaA, Darmstadt, Germany), sodium borohydride 98% (Merck KGaA, Darmstadt, Germany) and calcium chloride (Duksan Pure Chemicals, Korea) were used directly. Removal test were applied to salts of sodium chloride (Merck KGaA, Darmstadt, Germany) and magnesium chloride (J. T. Baker, México).

2.2. Synthesis of graphene oxide
Graphene oxide was prepared through the modified Hummers method [6]. Briefly, 2g of graphite powder grade SP-1(Union Carbide Corporation) were added an Erlenmeyer and followed for slowly addition of 100mL of sulfuric acid 95 – 97%. The mixture was subjected to constant stirring at 1000rpm and 60°C. Then, 9g of potassium permanganate were added slowly in rates of 0.5 g min\(^{-1}\), keeping the temperature at 60°C. This conditions were maintained during 24 hours. After of this, hydrogen peroxide 30% was added drop by drop for stop the oxidation. Then, we added 500mL of distillate water and it let to decant during 24 hours at 27°C. Finally, we eliminate residual acids in graphene oxide by washing and centrifugation up to obtain a pH of 5 and a concentration of 4.4 mg mL\(^{-1}\) of graphene oxide.

2.3. Reduced graphene oxide membranes fabrication
The second step of this work was the fabrication of reduced graphene oxide based membranes. A polyurethane paper support (supplied by Filtros Partmo S.A) was completely immersed in the graphene oxide solutions subjected to ultrasound sonication (Sonics Vibra Cell) for 10 minutes and then thermally reduced in an oven (memmert UN 55) at 100°C for 10 minutes. The formation of graphene oxide based membrane was done layer-by-layer by fifteen times repetition of the immersion and reduction processes. After, a coagulation bath with a 1% solution of calcium chloride was prepared and the previously treated polyurethane paper was placed in this solution for 10 minutes. Then, a reducing bath with 1% sodium borohydride 98% was prepared and the paper was immersed in this solution for 10 minutes. Finally, the obtained graphene oxide based membranes were washed in a 5% acetone solution for 15 minutes and dried at room temperature. Figure 1 shows the graphene oxide membrane.

2.4. Characterization of reduced graphene oxide based membranes
Membranes were characterized by FTIR-ATR (iS50 Thermo Scientific), DRX (D8-ADVANCED BRUKER) and SEM (Quanta FEG 650). Atomic absorption spectroscopy was used to determine the removal rates of the Na\(^+\) and Mg\(^{2+}\) cations present in the production water. Conductivity measurements were made on the produced water to determine the saturation point of the membranes.
2.5. **Desalination method**

The desalination was carried out by vacuum filtration. A piece of membrane of 44 mm of diameter was placed in a system for separation by vacuum filtration. 20 mL of produced water from a Colombian crude oil field were used for the experiment.

3. **Results and discussion**

FTIR spectroscopy was used in order to analyse the variations in the absorption bands of graphene oxide and the reduced graphene oxide membranes manufactured. The graphene oxide samples were lyophilized before performing the spectral analysis. For the graphene oxide it was not necessary to carry out any previous treatment.

Figure 2 shows FTIR-ATR spectra of polyurethane paper, reduced graphene oxide-based membrane and graphene oxide. FTIR-ATR spectra of the polyurethane paper and reduced graphene oxide based membrane are very similar. This means that these bands are mostly attributed to the polyurethane paper used as a support. FTIR-ATR spectrum of graphene oxide only present bands corresponding to vibrational modes of $\text{C} = \text{C}$ and $\text{C} = \text{O}$ groups [7]. The interference of the signals produced by the polyurethane paper indicate that the reduced graphene oxide is not deposited as a thin film, but is impregnated on the pores and structure of the support. This statement is supported by the results of the other characterization techniques.

The scanning electron microscopy (SEM) was used to analyse the morphology of the membranes. A section of membrane was cut and deposited on sample holders. Figure 3 show the micrographs obtained.

The SEM micrographs show homogeneous membranes without fissures or cracks on surface each layer. It can also be observed several overlapped sheets of reduced graphene oxide, similar to those found in other reports [8].
Figure 3. Morphology of reduced graphene oxide-based membranes, (a) 2000x, (b) 10000x and (c) 40000x. Images show the uniformity and multi-layer graphene oxide sheets in the membranes and crystals of calcium (b) after coagulation process.

DRX patterns of reduced graphene oxide-based membranes and polyurethane paper were obtained (Figure 4). Samples were mounted directly on a polymethyl methacrylate sample holder for clays by the frontal filling technique.

Figure 4 display DRX pattern of rGO based membrane on polyurethane paper and polyurethane paper. All the peaks are observed in both systems, except one peak at 8 degrees, corresponding to rGO. The observation of peaks corresponding to polyurethane paper in rGO based membrane is evidence that this membrane is very thin. [9].

The concentrations of the salts present in the production water and the percentage of removal, were obtained and calculated from the calibration curves using the Atomic absorption spectroscopy technique. We performed calibration curves corresponding to sodium and magnesium ions respectively, from standard solutions of NaCl and MgCl₂, for concentrations of 1000 ppm each. The pH of the standard solutions was adjusted to a value of 2 using nitric acid (HNO₃). For the produced water, it was necessary to perform a $\frac{1}{100}$ dilution after filtration, because of the concentrations of ions of Sodium and Magnesium were out of the detection range of the equipment. The results obtained are showed in the Table 1.

| Ion   | Initial concentration (ppm) | Final Concentration (ppm) | Removal (%) |
|-------|-----------------------------|---------------------------|-------------|
| Na⁺   | 30996                       | 22508                     | 27.38       |
| Mg²⁺  | 149453                      | 10225                     | 47.44       |
In the literature it is found that the estimated diameter of the hydrated ions are: $Na^+ = 7.1\,\text{Å}$ and $Mg^{2+} = 9.4\,\text{Å}$ [10], and the results obtained indicate a higher percentage of removal for magnesium than for sodium, so it can be said that the approximate pore size of the GO membranes is less than 9Å.

In the oxidation process of the graphite, carbon atoms are gasified from each graphene sheet, which generates defects or gaps, which make graphene oxide sheets more selective. Additionally, the oxidation of graphite involves adding a greater number of oxygenated functional groups on each sheet of graphene, which despite applying the respective reduction, fails to eliminate all of these groups (Figure 2), making the material obtained have areas partially oxidized that adsorb the cations present in the water through electrostatic interaction and ion exchange [11]. Figure 5 shows the produced water before and after the vacuum filtration.

![Figure 5. Produced water before (left) and after (right) the filtration.](image)

The useful life of the reduced graphene oxide membranes was evaluated, making measurements of water conductivity of production after multiple filtrations. A volume of 20$\,\text{mL}$ of produced water was taken. It was filtered by a single membrane. The results obtained are in Table 2.

These results show that the use life of the membranes is around 140$\,\text{mL}$ of produced water, confirming the high efficiency of reduced graphene oxide membranes synthetized by this method [12].

| Cycle | $\sigma (\text{mS/cm})$ |
|-------|----------------------|
| 0     | 17.36                |
| 1     | 11.22                |
| 2     | 10.43                |
| 3     | 9.86                 |
| 4     | 9.01                 |
| 5     | 8.74                 |
| 6     | 8.25                 |
| 7     | 8.19                 |
| 8     | 8.15                 |
| 9     | 8.12                 |

4. Conclusions
We developed a novel and simple methodology for fabrication of reduced graphene oxide based membranes with high efficiency and promise large scale production. This process allows manufacturing membranes of any size for different scales of operation, better than the typical and limited vacuum filtration method. It is recommended to use more precise techniques (eg TEM and AFM) that give accurate information about the nominal pore size of the membranes and their stability as a function of time.
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