Development of a reduced nanoporous graphene oxide membrane synthesized from *Oryza sativa* husk using the Tour method for the reduction of salt ions

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Article Info	Abstract
	Membrane desalination is limited by issues of high costs and energy consumption. Moreover, high-quality membranes require high carbon content sources such as biowastes, among others. One example of biowastes commonly found in the Philippines are *Oryza sativa* (rice) husks. Thus, this study aimed to determine the feasibility of developing a reduced nanoporous graphene oxide (rNPGO) membrane synthesized from *Oryza sativa* husks using the Tour method for membrane desalination. To assess the membrane, a salt solution (1% w/v) was prepared and subjected to membrane desalination. After three readings, the recorded mean salt rejection rate of the membrane was 6.55%. The results indicate a significant difference between the salinity content before and after desalination. Therefore, rNPGO synthesized from *O. sativa* husks using the Tour method can be used for the reduction of salt ions.

Introduction. - Membrane desalination is a process that removes salt ions from saltwater with the use of membranes [1,2,3]. Recent developments in the field of membrane desalination have led it to become one of the primary solutions to address saltwater intrusion [1,3]. Saltwater intrusion is a form of groundwater contamination wherein saltwater intrudes into freshwater sources, making it unsuitable for human consumption. By removing the salt ions in the water, membrane desalination provides the possibility of expanding the water supply by supplementing it with water from oceans and brackish waters [4].

However, the current leading technologies for membrane desalination are limited in part due to high costs and energy consumption [2]. One of the causes of the elevated operating costs is the presence of membrane fouling, which is the degradation of the membrane due to the deposition of permeate molecules on the surface [5]. This leads to the deterioration of permeate flux, frequent chemical cleaning, and replacement of the membrane, contributing to a shorter membrane lifespan [6,7].

In a study conducted by Wang et al. [7], graphene-based membranes can withstand membrane fouling. Graphene is an ultra-thin carbon film that contains a honeycomb lattice structure which gives it a large surface area and excellent conductivity [8]. Additionally, graphene-based membranes can withstand membrane fouling due to their hydrophilic nature as well as their strong adsorption capacity and large surface area [9].

Moreover, the introduction of nanopores to graphene-based membranes causes an increase in permeate flux while maintaining a relatively high salt rejection rate [4,10,11]. Additionally, graphene-based nanoporous membranes are commonly utilized in membrane desalination because of their attractive properties to salt ions [11], and effective nanopore filtration [12]. The attractive properties of graphene-based nanoporous membranes to salt ions derive from the Gibbs-Donnan effect wherein negatively charged membranes such as graphene-based nanoporous membranes attract positively charged molecules such as sodium ions. Furthermore, due to the size difference between nanopores and salt ions, salt ions are unable to pass through nanopores that are under a certain size [13].

Since nanoporous graphene oxide (NPGO) membranes are chemically unstable due to the presence of oxygen-containing functional groups, they must be stabilized through thermal reduction. Thermal reduction is a controlled approach to removing the oxygen-containing functional groups

in the NPGO membranes, which increases membrane permeability, uniformity, and stability [13].

When synthesizing a graphene oxide (GO) membrane, the quality of the resulting membrane is dependent on the quality of the graphite used in its synthesis. Hence, in order to obtain high-quality membranes, high carbon content sources are necessary. One example of sources with high carbon content are biomasses such as rice husks, among others [7,14,15]. In the study conducted by Supriyanto et al. [16], promising results were obtained for the synthesis of GO from graphite that had been obtained from *O. sativa* (rice) husk.

The two main methods used for the synthesis of GO are the Tour method and Hummer's method. However, in the study of Habte and Ayele [17], the Tour method was shown to have a clear advantage in the synthesis of GO in comparison to the Hummer's method. This is because the oxidation degree of the synthesized GO was found to be better when the Tour method is used. The higher oxidation degree implies that the attractive filtration property of the membrane was stronger and therefore increased the salt rejection rate of the membrane. Additionally, the presence of health risks and hazards when synthesizing the GO was reduced when the Tour method is utilized because it minimizes the fumes released during the process in contrast with Hummer's Method.

Therefore, the study aimed to explore the feasibility of developing a reduced nanoporous graphene oxide membrane (rNPGO) synthesized from rice husk using the Tour method to reduce salt ions. It specifically aimed to:

(i) synthesize graphite from *O. sativa* husk;

(ii) synthesize graphene oxide from graphite using the Tour method;

(iii) etch nanopores in the graphene oxide powder;

(iv) prepare and reduce the NPGO membrane; and

(v) assess the salinity level of the water samples pre and post-desalination using the rNPGO membrane.

Methods. - *Oryza sativa* husks were gathered from the Department of Agriculture - Western Visayas Agricultural Research Center and synthesized into graphite. The graphite was then synthesized into graphene oxide using the Tour method. Subsequently, nanopores were etched into the graphene oxide. After the preparation of the membrane, a salt solution was prepared and measured based on its salinity content. It was then filtered using the membrane and the salinity content of the permeate was measured.

Synthesis of Graphite. The synthesis of graphite was needed to make a graphene oxide membrane. The graphite powder for this research was derived from *O. sativa* husks. The rice husks (500 g) were washed with distilled water and subjected to oven-drying for 24 hours in different batches at 50°C. The material produced was then ground and screened using a sieve mesh size 60 (0.250 mm). A hundred grams of the rice husk residue was placed in a furnace at 1000 °C for 2 hours, under 1 atm. To obtain graphite, silica was removed from the furnaced rice husk using 4 M sodium hydroxide (NaOH) that was pre-diluted in a volumetric flask. This was done by dissolving 10 g of the furnaced rice husk in 30 mL of 4 M NaOH in a flask which was then heated and stirred for 3 hours. The solution was then vacuum-filtered and oven-dried for 3 hours at 50 °C. The resulting graphite underwent a confirmatory test using the Fourier-Transform Infrared Radiation - Attenuated Total Reflectance (FTIR-ATR) to confirm if the synthesized material is indeed graphite by comparing it with the FTIR-ATR spectroscopy results of related literature.

Synthesis of Graphene Oxide using the Tour Method. Ninety milliliters (90 mL) of concentrated 98% sulfuric acid (H_2SO_4) was mixed in a glass beaker with 10 mL of concentrated 85% phosphoric acid (H_3PO_4). The mixture was poured into a beaker with a mixture of 0.5 g of graphite powder and 4.5 g of potassium permanganate ($KMnO_4$), heated at 50 °C using a water bath, and stirred for 12 hours. The mixture was then cooled at room temperature and 250 mL distilled water was added. Ten milliliters (10 mL) of 30% hydrogen peroxide (H_2O_2) was added to reduce the manganese ions present. The resulting solution was filtered using a 45 microns filter paper. The produced graphite oxide filter cake was washed using a 5% hydrochloric acid (HCl) (aq) in a centrifuge at 4000 rpm for 4 hours. The GO was then manually stirred with distilled water at 60 °C for 12 hours in a water bath [17]. The solution was vacuum-filtered and oven-dried to produce GO powder which was tested using the FTIR-ATR to confirm if the synthesized material is indeed GO.

Etching of GO. Thirty milligrams (30 mg) of GO powder was redispersed into 90 mL of 30% hydrogen peroxide and placed in an ultrasonic bath treatment for 20 minutes to ensure a good dispersion. After 20 minutes, the solution was heated up to 70 °C in a water bath and was refluxed in a reflux set-up for 10 hours. The mixture was purified in a permeable plastic bag with deionized water for 3 days to obtain a stable NPGO solution. The NPGO was diluted to 50 mg/L using deionized water for membrane preparation.

Preparation of NPGO membrane. An NPGO membrane was prepared using vacuum filtration. The NPGO solution was filtered by using a filter paper with a pore size of 45 microns to remove the moisture. The filtered NPGO sheet was poured from the Buchner flask to the beaker, vacuum-filtered, and dried in an oven at 60 °C for 12 hours. Then, it was thermally reduced in an oven at 150 °C at 1 atm for 1.5 hours to maximize salt rejection to synthesize an rNPGO membrane. The surface and cross-sectional morphology of the rNPGO membrane was characterized using Scanning Electron Microscopy (SEM). The membrane was captured and the pores in

the resulting image were measured using the 2D image of the result from the SEM Imaging.

Assessment of salinity content. To measure and evaluate the efficiency of the rNPGO membrane, an assessment of the salinity level of water samples was conducted. A salt solution was prepared using one gram of analytical reagent grade sodium chloride (NaCl) to make a 1% NaCl solution. Prior to testing the membrane, a control made of a blank filter paper was utilized. The salt solution was poured on top of the filter paper until the funnel was full. The permeate was then placed in a 250 mL beaker for salinity content testing. A conductivity meter, pre-calibrated by dipping it in a container filled with distilled water, was used by dipping it in the solution until the value stabilized after three minutes. For the final testing, the same method was then utilized for the rNPGO membrane.

The salt rejection of the membrane was analyzed using the salinity content of both the feed and the permeate. After all the data were plotted, data analysis was using the formula for salt rejection.

$$R_{salt\%} = \left(1 - \frac{c_p}{c_f}\right) * 100\%$$

Where:
$R_{salt\%}$ = percent of salt rejection
C_p = concentration of the permeate
C_f = concentration of the feed

Data Analysis. The results were analyzed using t-test for dependent samples using RStudio (version 1.3.1093.0, free license) to observe any significant difference between the salinity content before and after desalination. The salt rejection was analyzed among the three replicates. This was to ensure that the efficiency of the membrane was not reduced by washing it with deionized water.

Safety Procedures. During the conduct of the data gathering process, the wearing of the proper personal protective equipment such as gloves, masks, and goggles was observed. The methods were conducted alongside the supervision of experts. A wash bottle was utilized in cleaning the glassware and the contaminants in the conductivity meter to ensure accurate readings. Furthermore, the safety data sheet of each chemical and equipment was strictly followed. Additionally, when performing methods with the use of chemicals, a fume hood was utilized to avoid the inhalation of fumes. Lastly, for the disposal of chemicals, each chemical was disposed of according to the safety data sheet and in accordance with the disposal protocol of the laboratory.

Results and Discussion. - This study aimed to explore the feasibility of developing an rNPGO membrane synthesized from *O. sativa* husk using the Tour method to reduce salt ions. This was done through membrane assessment by analyzing its pore size, membrane thickness, and salt rejection rate.

The graphite powder synthesized from rice husk was analyzed using the FTIR-ATR analysis with three replicates. The mean result of the FTIR-ATR analysis of the graphite powder, colored in red, was compared

with the FTIR-ATR results of the graphite powder in the study of Wenxuan et al. [18], colored in black (Figure 1). Since a graphite library was unavailable in the FTIR-ATR used, the graphs were superimposed and the peaks were compared. The peaks of both graphs are similar, which peaks at around 624.38/cm, 790.75/cm, and 1066.50/cm.
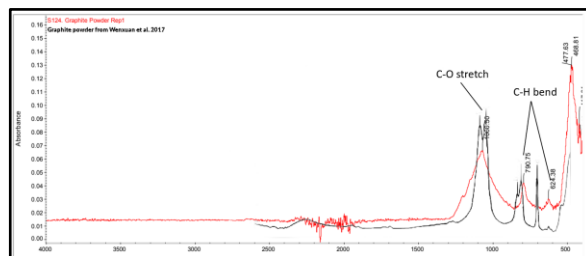

Figure 1. The image comparison of FTIR-ATR spectra of graphite produced and graphite from Wenxuan et al. [18].

The graphene oxide powder synthesized using the Tour method was analyzed using the FTIR-ATR analysis with three replicates. The mean result of the FTIR-ATR analysis of the graphene oxide powder, colored in red, was compared to the FTIR-ATR results of the graphene oxide powder in the study of Çiplak et al. [19] colored in blue (Figure 2). The peaks of both graphs which peaks at around 791.67/cm and 1070.04/cm are similar.
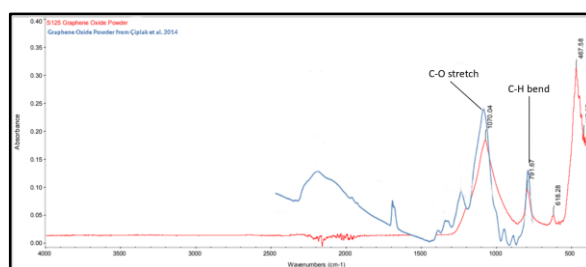

Figure 2. The image comparison of FTIR-ATR spectra of graphene oxide produced and graphene oxide from Çiplak et al. [19].

Using an SEM, the rNPGO was analyzed for its pore size and thickness. The nanopore sizes were measured from three different locations and different magnifications respectively on the rNPGO membrane. This was done so that the pores are visible with the use of the instrument. The statistical mean pore sizes of the three replicates are 555.4 nm, 615.1 nm, 837.9 nm respectively. Moreover, the pores have varying sizes that range from 286.0 nm to as large as 1920.0 nm (Table 1).

Table 1. Statistical parameters of rNPGO membrane pore sizes based on the 3 locations with 3 magnifications (8500x, 5000x, 3000x).

Parameters	Replicate at 8500x (nm)	Replicate at 5000x (nm)	Replicate at 3000x (nm)
Statistical Mean	555.4	615.1	837.9
Standard Deviation	323.9	372.7	413.6
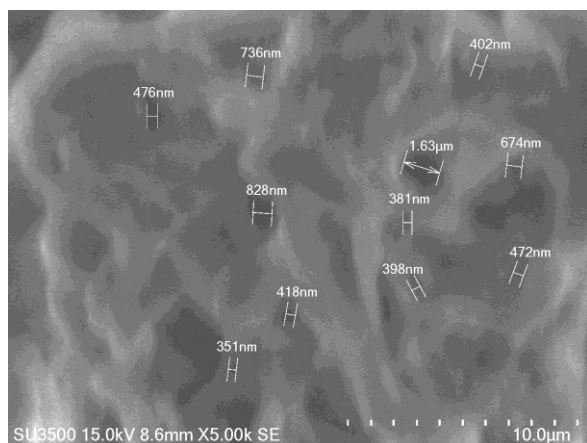
Figure 3. The SEM Image of the rNPGO membrane at 5000x magnification with the pore measurements.

The thicknesses of the rNPGO membrane were measured from three different locations and different magnifications respectively. This was done so that the rNPGO membrane was visible enough to measure its thickness with the use of the instrument. The mean thickness, as well as the standard deviation from the three replicates, varies as shown (Table 2). The statistical means of the three replicates are 37.33 µm, 33.19 µm, and 45.43 µm, respectively. Additionally, the thickness of the membrane varies from a range of 27.0 µm to 53.6 µm.

Table 2. The statistical parameters of nanoporous graphene oxide membrane thickness based on the 3 locations with 3 magnifications (420x, 370x, 250x).

Parameters	Replicate at 420x (µm)	Replicate at 370x (µm)	Replicate at 250x (µm)
Statistical Mean	37.73	33.19	45.43
Standard Deviation	3.66	4.98	4.75

The mean salinity content of the prepared salt solution was measured using a conductivity meter (PS-2230 Advanced Water Quality Sensor). The salinity content of both pre-desalination and post-desalination were further analyzed using the Salt Rejection Rate formula. Additionally, the statistical mean and standard deviation were calculated (Table 3).

Table 3. The statistical parameters of pre-desalination and post-desalination salinity content of the water samples.

Replicates	Pre-Desal-ination Salinity Content (%)	Post-Desal-ination Salinity Content (%)	Salt Rejection Rate (%)
1	1.04479815	0.96423745	7.710647267
2	1.04164610	0.98627760	5.315480949
3	1.03442845	0.96588000	6.626698057
Statistical mean	1.04029090	0.97213168	6.551938501
Standard deviation	0.00434051	0.01002512	0.979288738

The FTIR-ATR spectra results showed that the graphite powder produced is similar to the graphite produced in the study of Wenxuan et al. [18], thus, it is feasible to synthesize graphite powder from *O. sativa* husks. The graphs of the FTIR-ATR spectra can be presented in two ways, wavelength vs. transmittance and wavelength vs absorbance. In the study of Wenxuan et al. [18], they utilized wavelength vs transmittance which in turn caused the graph to be reflected based on Beer-Lambert's Law as stated in the study of Mayerhöfer et al. [20].

To determine the feasibility of synthesizing graphite powder from *O. sativa* husk, the reflected graph was compared to the study of Wenxuan et al. [18] based on its fingerprint region. With this, it reflected the result of the study of Supriyanto et al. [16] wherein they also utilized *O. sativa* husk to synthesize graphite.

The FTIR-ATR spectra results showed that the graphene oxide powder produced is similar to the graphite produced in the study of Çiplak et al. [19]. Thus, it is feasible to synthesize graphene oxide powder from graphite using the Tour method. In the study of Çiplak et al. [19], they also utilized the wavelength vs transmittance which in turn caused the graph to be reflected based on Beer-Lambert's Law as stated in the study of Mayerhöfer et al. [20]. To determine the feasibility of synthesizing graphene oxide powder from *O. sativa* husk, the reflected graph was compared to the study of Çiplak et al. [19] based on its functional groups. The graph of the graphene oxide produced has two visible peaks within the fingerprint region of the spectra. By comparing the graphs in this region, it could help indicate if the product is similar to another.

The results obtained from the SEM showed that the graphene oxide membrane produced pore sizes ranging from as small as 286 nm to as large as 1920 nm. Although these are hundreds of nm in diameter, these could not be considered nanopores. This is probably because the nanopores could not be seen by the instrument used since the sample was not sputter-coated beforehand.

The rNPGO membrane was subjected to an SEM imaging analysis at 15 kV settings so that the membrane will not burn. The morphology was analyzed and the measured pores vary in size with a standard deviation of 323.9 nm, 372.7 nm, and 413.6 nm. The deviation between the pore sizes may also be due to the dispersion of the hydrogen peroxide with the graphene oxide powder in a plastic sheet instead of a cellulose dialysis bag as well as the placement of the bag during the stabilization phase [13]. To visualize the pore sizes smaller than 200 nm in size the membrane could have been sputter-coated with gold or analyzed using Atomic Force Microscopy.

Additionally, the results for the SEM imaging of the thickness of the membrane showed that a membrane was prepared onto the filter paper. The thickness of the membrane ranges from 27.0 μm to 53.6 μm which shows the uneven distribution of the membrane probably due to the process of uneven vacuum filtration of the NPGO solution. In addition, this assumption is also reflected by the standard deviation of the membrane thickness which are 3.66 μm, 4.98 μm, and 4.75 μm.

Furthermore, membrane desalination using rNPGO synthesized from *O. sativa* husk has resulted in a mean salt rejection rate of 6.55% and a significant difference between the pre-desalination and post-desalination salinity content. This was done through a t-test for dependent samples (α=0.05) and a p-value of 0.011. This shows that the rNPGO membrane developed and synthesized from *O. sativa* husks using the Tour method was capable of reducing salt ions.

The filtration of salt ions can potentially prove that the pore size of the graphene oxide can be considered as nanopores since it was able to reduce the salt ions in the water sample. This is because the attractive properties of graphene-based nanoporous membranes to salt ions are derived from the Gibbs-Donnan effect wherein negatively charged membranes such as graphene-based nanoporous membranes attract positively charged molecules such as salt ions. Furthermore, it can potentially prove that the pore size is nanoporous due to the size difference between nanopores and salt ions. Salt ions are unable to pass through nanopores that are under a certain size since salt ions have a size that is considered nanoparticles. This was reflected in the results when the NPGO membrane was tested for its salt rejection rate and permeate flux and compared with the results of a graphene oxide membrane [13].

Limitations. The FTIR-ATR results did not directly indicate that the sample is graphite due to the graphite library unavailability for the FTIR-ATR utilized. Additionally, the *O. sativa* husks did not undergo vacuum furnacing, one of the ideal methods for synthesizing graphite from biomass. Lastly, the removal of silica was not conducted using hydrofluoric acid (HF), which is better for removing silica than NaOH in terms of purity.

Conclusion. In this study, the feasibility of developing a rNPGO synthesized from *O. sativa* husk using the Tour method was explored. The FTIR-ATR results of both the graphite powder and graphene oxide powder indicated the feasibility of synthesizing graphene oxide powder using the Tour method from the graphite powder synthesized from rice husk. The membrane produced contained pores etched in the graphene oxide powder. Moreover, there is a significant difference in the salinity content of the pre-desalination and post-desalination water samples after undergoing desalination using the nanoporous graphene oxide membrane. Thus, a nanoporous graphene oxide membrane was developed and synthesized from *O. sativa* husk using the Tour method.

Recommendations. - The sample could be placed in a polyethersulfone filter and sputter-coated to better visualize the nanopores of the graphene oxide using an SEM. Atomic Force Microscopy could also be utilized for better magnification in the sample. Additionally, the salt load capacity of the membrane could be assessed by desalinating the sample multiple times. This study can be a step further towards the right direction for exploring new avenues for the use of biowastes such as *O. sativa* husk that is abundant in the Philippines. However, there is still a lot of room for improvement in the desalination aspect of a reduced nanoporous graphene oxide (rNPGO) membrane derived from *O. sativa* husk before it can be used as a solution to the saltwater intrusion in coastal areas in the Philippines.

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