Carbon 129 (2018) 415–419

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Application of graphene oxide membranes for removal of natural organic matter from water

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ARTICLE INFO

Article history:

ABSTRACT

Changes in the complexity of natural organic matter (NOM) have impacted the performance of direct filtration plants of water industries, resulting in reduced treatment capacity, and can lead to increased disinfection by-products. Hence, the need to identify new materials in future can be converted into more effective technologies and processes. We report a laboratory scale innovative use of graphene oxide membranes to remove NOMs from water that had been treated and still contained 5 mg/L DOC. Our study shows that graphene oxide based membranes can reject ~100% of NOM while maintaining high water flux of 65 L m^{-2} h^{-1} bar^{-1} at atmospheric pressure. Our results indicate that it is possible to develop a graphene oxide-based water filtration technology.

1. Introduction

Natural organic matter (NOM) is ubiquitous in raw water that reaches water treatment plants [1]. Many water authorities have reported an increase in periods where coagulant and filter media are less effective for the removal of natural organic matter (NOM) and finely dispersed solids (turbidity) [1–7]. Changes in the complexity of natural organic matter (NOM) in Sydney's catchments have impacted the performance of direct filtration plants, resulting in reduced treatment capacity. The Nepean Water Filtration plant in Western Sydney has reduced its capacity by around 40% after some heavy rain events that increase NOMs in the raw water [8,9]. The length of time with reduced water produced is unpredictable and can last many weeks. Failure to successfully control the NOM issue could result in highly expensive to the treatment processes at Sydney's Water filtration plants in the next decade [10]. Hence the need to identify new alternatives can potentially be converted into technologies to be retrofitted to existing water filtration plants.

Graphene oxide is a new material that is being widely researched to establish potential industrial applications [11–16]. Graphene oxide is a compound of carbon, oxygen, and hydrogen in a variable ratio that mainly depends on the synthesis procedure [17–19]. It can be prepared from graphite by introducing oxygenated functionalities using oxidizing agents [20,21]. These functionalities expand the layer separation between two stacked layers and make the material hydrophilic [22,23]. Although pristine graphene, a monoatomic layer of carbon atoms is completely impermeable to any gases or solutions, graphene oxide exhibits highly selective permeability to water molecules and has thus shown potential for applications in filtration material [17,24–28]. The advantage of graphene oxide-based membranes is that it can be prepared as laminates from stacks of graphene oxide monoflake using a very simple and cost-effective method [29]. In the laminated form, graphene oxide layers are stacked together (which is also known as graphene oxide paper [29]) with an interlayer distance of ~0.86 nm which is the path for mass transport of ions using it as a filtration membrane [17,30–32]. Based on the reported graphene oxide membrane characteristics, it appears that graphene oxide can offer 100% rejection for any species of a size equivalent to NOMs.

This paper describes laboratory scale studies to determine whether graphene oxide can be used to tackle the removal of NOMs in water. Hence, the objectives of this paper are two-fold, namely to establish whether graphene oxide (GO) membranes can reject NOMs and to quantify water fluxes and whether the GO membranes get blocked during laboratory scale testing.

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https://doi.org/10.1016/j.carbon.2017.12.032
0008-6223/

2. Experimental

2.1. Graphene oxide synthesis

Graphene oxide dispersions were prepared from graphite oxide which was synthesized using Hummer's method in which natural graphite was oxidized using appropriate quantity of sulfuric acid, potassium permanganate and sodium nitrate under controlled temperature [20]. The reaction mixture after treating with hydrogen peroxide was washed several times with de-ionized water to obtain graphite oxide paste. Later, the graphite oxide was exfoliated using ultra-sonication in water followed by centrifugation to obtain monolayer flakes of graphene oxide in water. Just to make it clear that the sonication exfoliates the individual layer of graphene oxide from the original graphite oxide in a similar way as graphene layers are exfoliated from natural graphite, and subsequent centrifugation can separate out monolayer graphene oxides from multilayers. The schematic below (Fig. 1) shows the various steps of graphene oxide synthesis.

2.2. GO membrane preparation

Graphene oxide suspension prepared as above can be easily transformed in the form of membranes using by either spraying the dispersion onto a porous template or by vacuum filtration of GO dispersion in the porous template. In the present work, we adopted the vacuum filtration method to make thin membranes of graphene oxide on the PVDF templates with a pore size of 0.22 μm. Vacuum filtration of the GO dispersion produced a uniform film of graphene oxide on the template. Using this method, membranes with required thickness were produced by changing the volume of GO dispersion.

2.3. GO membrane characterization

Physical characterization of membranes prepared using above method was carried out extensively to ensure the characteristics before using as a membrane for filtration. For that purpose, initially scanning electron microscope (SEM) was used to confirm the surface morphology and laminated structure of graphene oxide membranes. X-Ray Diffraction (XRD) was used to assess changes in the crystallographic structure as well as to determine the interlayer spacing between laminates in the membrane.

The physical integrity of the flat membranes prepared was determined with a leak test [25]. It is essentially a container with an aperture covered by a GO membrane and filled with a desired solvent such as ethanol or water, which is kept on a computerized weighing scale. The custom-made setup and membrane performance are described in detail in section 3. For ensuring the membrane effectiveness, prior to the NOMs rejection test, other relatively larger (in hydrated radius > 0.45 nm) species such as $[Fe(CN)_6]^{3-}$, glycerol, and sucrose were tested on GO membranes via U-tube type experiments. Membranes after testing for species were taken out, rinsed in water, dried and again tested for ethanol vapor leak test (described in Fig. 3). For all these U-tube permeation experiments the permeate samples have been taken in regular intervals from 3 h to 120 h.

2.4. NOMs rejection test and water flux measurements

Samples of filtered water from the Sydney Water's Nepean Water Filtration Plant were used throughout this study. The filtered water was the product of the standard water treatment process at the plant, namely coagulation with $FeCl_3$ and a cationic poly-DADMAC followed by filtration in deep bed filters. The dissolved organic carbon of the filtered water was 5 mg/L and the turbidity <0.2 NTU.

We have used two methods (shown in Fig. 2) to insure error free NOMs removal and water flux measurements. In the first experiment, the NOMs containing water was fed on one side, and pure de-ionized water was on the permeate side of the U-tube (Fig. 2a). Chemical analyses such as ion chromatography (IC), inductively coupled plasma optical emission spectrometry (ICP-OES), dissolved organic carbon (DOC) of samples of both sides (of the u-tube shown in Fig. 2) were carried out for quantitative analysis of permeate. More specifically, a highly sensitive liquid chromatography-organic carbon detection (LC-OCD) test was extensively conducted to analyze the presence of NOMs in the feed and permeate solutions taken from the U-tube at regular intervals during the filtration experiment.

In the second experiment, a pressure controlled filtration method was used to accurately determine the water flux. The applied pressure P during filtration was controlled at $0.5 \leq P \leq 1.0$ bar while storing the permeate in a container kept on the weight scale. GO membranes of an average effective area of ~3.0 cm^2 were used for the filtration experiments.

3. Results and discussion

3.1. Membrane characterization results

In this section, properties of the membranes (with thickness values of 1, 2, 4, 6, 8 μm) produced by vacuum filtration method are discussed. SEM images in Fig. 3 show the surface morphology and cross-section of GO membrane/laminates. Fig. 3a shows the surface morphology of the membrane with wrinkle like regions indicating the folding of GO laminate whereas Fig. 3b illustrates the layer-by-layer laminated structure of our GO membrane. The spacing between two layers in the GO laminated structure was determined using X-Ray diffraction (Fig. 3c). The sharp peak at a 2θ value of 10.7° is equal to the d-spacing value of 8.25 Å for the membranes which is typical for GO membranes.

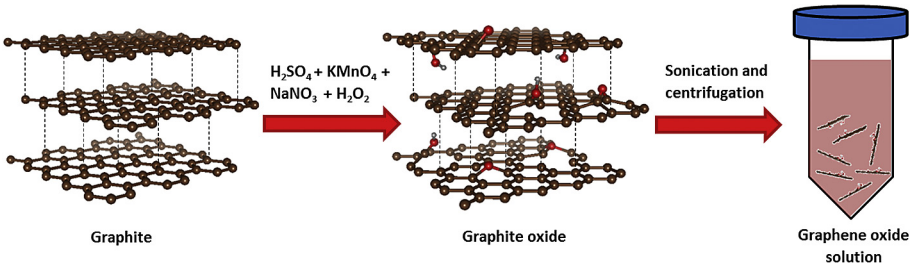

Fig. 1. Schematic representation of graphene oxide synthesis.