# Gypsum scale formation on graphene oxide modified reverse osmosis membrane

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## ARTICLE INFO

## ABSTRACT

Graphene oxide (GO) coatings on membranes can improve antifouling performance against a variety of microorganisms and organics. However, the effects of GO coatings on mineral scaling were not investigated. Here gypsum scaling on bare (ESPA2) and GO-modified thin-film polyamide membranes (ESPA2-GO) followed by cleaning with deionized (DI) water were investigated with a bench-scale reverse osmosis setup. The flux decline caused by gypsum scaling on ESPA2-GO was slightly reduced than on ESPA2. This is because the ESPA2-GO membrane is more hydrophilic than ESPA2, indicating a higher energy barrier for heterogeneous nucleation and/or the deposition of gypsum on it. Moreover, the more negatively charged ESPA2-GO membrane lead to stronger electrostatic repulsive forces between the membrane and the negatively charged gypsum particles and thus further inhibiting gypsum deposition onto membranes. Interestingly, during the cleaning process, smaller flux recovery was observed for ESPA2-GO. This is because ESPA2-GO surfaces have higher densities of carboxyl (–COOH) groups, which form complexes with $Ca^{2+}$, building strong bonds between GO coatings and gypsum. This study provided unique insights on the physicochemical interactions among membrane, the scaling mineral, and aqueous species, which can help the rational design of coatings for better simultaneous anti-scaling and antifouling performances.

## 1. Introduction

Nowadays, the lack of clean water accessibility reaches approximately 2.7 billion individuals, and the global demand for clean water is expected to increase in the coming decades [1]. Under this global situation, water desalination and reuse are potential solutions to mitigate the challenge of global clean water supply. Reverse Osmosis (RO) has been considered as one of the most promising technologies to meet the worldwide increasing clean water demand [2,3]. Hence, over the past ten years, the number of RO plants all over the world has increased significantly [4]. These plants are able to treat different types of water such as seawater, groundwater, wastewater and surface water [4]. In the RO process, fresh water is forced through a semipermeable membrane by a high pressure, and this process can produce freshwater by wastewater reuse and seawater desalination [2,3]. Thin-film polyamide membrane has been considered the state-of-art material for desalination systems due to its high water permeability and salt rejection capability [5]. Currently, the major issues of RO operations are the scaling of minerals on membranes, as well as the fouling of organics and microorganisms on membranes [6–10]. Such scaling/fouling processes

can clog the membranes and reduce the overall performance and lifetime of the membranes [2,3,11–14]. Therefore, the simultaneous prevention of mineral scaling and organic- and bio-fouling on RO membranes are essential for efficient RO operations [15,16].

Recently, the unique properties of graphene oxide (GO), such as its high hydrophilicity, negative charge, and antimicrobial property, have attracted great interests for its application in water filtration [1–4,9,11–14,17–21]. Graphene oxide (GO) is a single-layer carbon sheet with a honeycomb lattice and functionalized with oxygen-rich groups in the form of carboxyl, hydroxyl, ether, and epoxy groups [13]. Since the discovery of GO by Geim and Novoselov, extensive research has been done in the applications of GO in both academic and industrial fields [11,22]. Lots of research have been done to take advantage of the unique properties of GO to reduce organic- and bio-fouling and increase the water permeability of the filtration systems [3,4,9,11–14,17–19]. Researchers have demonstrated that GO modified membrane surfaces can induce disruption of cell integrity as well as reduce the cell viability, thus reducing biofouling [1–4]. Other researchers have exhibited that GO-coatings on membranes can also reduce the fouling of organics, such as bovine serum albumin (BSA), biomolecules, proteins, and

alginate, due to increased surface hydrophilicity [9,13]. However, to our knowledge, the potential effects of GO coating on mineral scaling during RO operations have not been investigated.

In the process of desalination, mineral scaling can occur through either the deposition of homogeneous precipitates formed in bulk solution or the heterogeneous nucleation of minerals on membrane surfaces. When mineral scales form on the membrane surface, it could greatly lower the permeability of membranes, thus adding operational cost. In RO operations, typical mineral scales are calcium carbonate, calcium sulfate, silicate, and barium sulfate [3,11,13,17]. Carbonate scaling can be controlled by adjusting the pH of the water [3,11,13,17]. In most inland water sources, barium concentrations are typically very low ($\leq 0.5$ mg/L) as opposed to $Ca^{2+}$ that are generally high, and $BaSO_4$ precipitates in RO system would be less than 2% of the mass of $CaSO_4$ [11,13]. Therefore, $CaSO_4$ was chosen as the model mineral scale here [13,18].

In this study, gypsum ($CaSO_4 \cdot 2H_2O$) scaling on bare and GO-modified thin-film polyamide (PA) membranes were investigated in a laboratory-scale crossflow RO setup under different solution conditions, and the interactions among membrane surfaces, gypsum particles, and aqueous ions were explored to understand the controlling mechanisms of scaling.

## 2. Materials and methods

### 2.1. Grafting GO onto ESPA2 membrane surfaces

The graphene oxide nanosheets (GO) were synthesized as described in previous studies [23–25]. In brief, 2.0 g of graphite ($< 20$ μm, Sigma Aldrich, Mo) was added into a 1000 mL round bottom flask and then was oxidized by adding 92 mL concentrated $H_2SO_4$, 2.0 g $NaNO_3$ and 12.0 g $KMnO_4$ (Sigma Aldrich, Mo) at 35 °C for 16 h (overnight). After 16 h, 160 mL of DI water was added and the temperature was further raised to 90 °C. After 30 min, another 400 mL of DI water was added, then 40 mL of 30% $H_2O_2$ (Sigma Aldrich, Mo) was added to the mixture slowly. The mixture was centrifuged for several times until the supernatant pH became neutral. The brown precipitate was resuspended in 2 L of DI water then sonicated for 8 h. The sonicated suspension was settled overnight, then decanted and dried in a freeze drier for future use. All chemicals used in this study were ACS grade.

Commercial polyamide reverse osmosis membranes (ESPA2) were purchased from Hydranautics Inc. (Oceanside, CA). In previous studies of GO effects on organic- and bio-fouling, GO was either grafted on membrane surfaces or incorporated as nanocomposites during membrane synthesis [11–14,26]. As the interaction between foulants and membranes mainly occurred on membrane surfaces, surface modification has been considered as an effective method which requires smaller amounts of nanomaterials for modification; and hence reduces the cost and associated environmental concerns [14,27]. Here, GO was grafted on the ESPA2 polyamide membranes following Perreault et al.'s procedures [14]. Briefly, the ESPA2 polyamide membranes were first exposed to a solution of 4 mM 1-ethyl-3-[3(dimethylamino)propyl] carbodiimide hydrochloride (EDC, > 98%, Sigma Aldrich, Mo), 10 mM N-hydroxysuccinimide (NHS, 98%, Sigma Aldrich, Mo), 0.5 M NaCl in 10 mM MES monohydrate buffer (> 99%, BioXtra, Sigma Aldrich, Mo) with pH = 5.0 for 1 h to convert the carboxyl groups on membrane surface into amine-reactive esters. Then, the membranes were cleaned with DI water and exposed to a solution of 10 mM ethylenediamine (ED, BioXtra, Sigma Aldrich, Mo) and 0.15 mM NaCl in 10 mM HEPES pH = 7.5 buffer (> 99.5%, Sigma Aldrich, MO) for 30 min to form amide bonds with amine-reactive esters. After washing with DI water, the membranes were exposed to a GO solution previously reacted with 2 mM EDC, 5 mM NHS in 10 mM MES buffer at pH = 6.

### 2.2. Surface Characterization of ESPA2 and ESPA2-GO Membranes

The surface morphologies of ESPA2 membranes before and after GO grafting (ESPA2-GO) were characterized using scanning electron microscopy (SEM, JSM-6010LA, JEOL) and atomic force microscopy (AFM, Veeco Instrument, Inc.). The surface roughness of the membranes was analyzed with Nanoscope Analysis 1.5 software. Surface hydrophobicity of the membranes were characterized through water contact angle measurements with a contact angle goniometer (FTA135, First Ten Angstroms Inc, Portsmouth, VA). Surface zeta potentials of the membranes were measured using a dynamic light scattering with a surface zeta potential cell kit (DLS, Zetasizer Nano, Malvern Industry Ltd). The membrane was adhered to a holder with the polyamide active layer facing up and the holder was then placed between two electrodes of the zeta potential cell. Then the zeta potential cell was inserted in a cuvette with 1.2 mL standard tracer solution of polystyrene latex particles (DTS1235, Malven Instruments). Then electrophoretic mobility of tracer particles were measured at distances of 125, 250, 500, 750, and 3000 μm from the membrane surface, and the surface zeta potential of the membrane was calculated. Details of AFM, water contact angle and surface zeta potential measurements can be found in our previous publications [28–32].

The chemical bonds on membrane surfaces were measured by Raman spectroscopy (IHR320, Horiba) using a 532-nm laser excitation. As GO contains substantial amount of carboxyl group (–COOH), to determine the density of carboxyl (–COOH) group on ESPA2 and ESPA2-GO surfaces, the toluidine blue O (TBO) colorimetric method was adopted [29,33]. Briefly, ESPA2 and ESPA2-GO membranes were glued on glass slides, and only the reactive polyamide membrane surfaces with or without GO coatings were exposed to the solution of 0.5 mM TBO (pH = 5.7) at 30 °C for 24 h. Then, the membranes were rinsed with DI water to remove the excessive TBO which did not form complexes with the carboxyl groups. Finally, the membranes were placed in 7 mL 50% acetic acid to desorb TBO from the surface of the membranes for 24 h and the concentrations of desorbed TBO were determined using ultraviolet-visible spectrometry (UV-is, DR600, Hach) [34]. Assuming that 1 mol TBO will form a complex with 1 mol –COOH, densities of –COOH on bare and GO-coated membranes were calculated.

### 2.3. Gypsum Scaling and Membrane Cleaning Experiments

Sodium sulfate anhydrous ($Na_2SO_4$, Fisher-Scientific, PA) and calcium chloride dehydrate ($CaCl_2$, Fisher-Scientific, PA) were used for gypsum scaling experiments, and the compositions of the solutions are shown in Table 1. The solutions' pH, ionic strength and saturation indices (SI = log $\{Ca^{2+}\}\{SO_4^{2-}\}/K_{sp}$, $\{Ca^{2+}\}$ and $\{SO_4^{2-}\}$ are the activities of calcium and sulfate ions and $K_{sp}$ is the solubility constant) with respect to gypsum were calculated using Geochemist's Workbench (GWB, 11.0. 6, Aqueous Solution LLC) using thermo.tdat database (Table 1). Due to the concentration polarization effect, the saturation indices on membrane surface will be higher than that in the bulk solution. The classical film model was used to estimate the concentration polarization ($C_p$) and calculate the local SI on membrane surface [35,36]:

$$C_p = \frac{C_m}{C_p} = (1 - R_o) + R_o \exp\left(\frac{J}{k}\right) \tag{1}$$

where $C_m$ is the local solute concentration near membrane surface, $C_b$ is the solute concentrations in the bulk solution. $R_o$ is the salt rejection. $J$ is the permeate flux (L/m²/h). $K$ is the mass transfer coefficient and can be estimated based on the Lévêque solution [35,37] using the axially averaged Sherwood number $Sh = 1.47(L/H)^{2/3} (uH/\nu)^{1/3}(\nu/D)^{1/3}$, where $L$ is the channel length (9.2 cm), $H$ is the channel height (4.6 cm), $u$ is the average cross-flow velocity in the cell frame (15.8 cm/s), $\nu$ is the