Development of a stable cation modified graphene oxide membrane for water treatment

Wenzheng Yu1, Tong (Yet) Yu2 and Nigel Graham1,2

1 Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom
2 Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

E-mail: w.yu@imperial.ac.uk and n.graham@imperial.ac.uk

Keywords: graphene oxide, membrane separation, membrane stability, cation adsorption, biopolymer treatment

Abstract

Membranes prepared from layers of graphene oxide (GO) offer substantial advantages over conventional materials for water treatment (e.g. greater flux), but the stability of GO membranes in water has not been achieved until now. In this study the behavior of GO membranes prepared with different quantities and species of cations has been investigated to establish the feasibility of their application in water treatment. A range of cation-modified GO membranes were prepared and exposed to aqueous solutions containing specific chemical constituents. In pure water, unmodified and Na-modified GO membranes were highly unstable, while GO membranes modified with multivalent cations were stable provided there were sufficient quantities of cations present; their relative capability to achieve GO stability was as follows: Al3+ > Ca2+ > Mg2+ > Na+. It is believed that the mechanism of cross-linking, and membrane stability, is via metal-carboxylate chelates and cation-graphite surface interactions (cation-π interaction), and that the latter appears to increase with increasing cation valency. The instability of cation (Ca or Al)-modified GO membranes by NaCl solutions during permeation occurred as Na+ exchanged with the incorporated multivalent cations, but a high content of Al3+ in the GO membrane impeded Al3+/Na+ exchange and thus retained membrane stability. In solutions containing biopolymers representative of surface waters or seawater (protein and polysaccharide solutions), Ca-GO membranes (even with high Ca2+ content) were not stable, while Al-GO membranes were stable if the Al3+ content was sufficiently high; Al-formed membranes also had a greater flux than Ca-GO membranes.

1. Introduction

The inaccessibility to adequate clean water is one of the most serious problems affecting large numbers of people worldwide (Shannon et al 2008). Effective and economical methods to purify water are required and continue to be the subject of extensive research and development (Shannon et al 2008, Pendergast and Hoek 2011). Among the range of appropriate technologies, membrane separation has many advantages (Han et al 2013) as the chemical and energy requirements may be less than conventional processes and treated water of high quality can be obtained (Pendergast and Hoek 2011).

Membranes act as selective barriers and play an integral role in water treatment for a range of contaminants (Dikin et al 2007, Koenig et al 2012). Pressure-driven membrane processes remain the most widely applied technologies (e.g. ultrafiltration, nano-filtration), and there continues to be a need for new, improved materials to enhance membrane performance (Pendergast and Hoek 2011). Nowadays, the most common materials applied in water treatment are inorganic (ceramic) and organic polymeric membranes. In general, polymeric membranes are simpler and easier to prepare, and more flexible, but their limitations include relatively poor chemical resistance, a limited lifetime, and serious membrane fouling (Han et al 2013, Zeng et al 2016). In contrast, although ceramic membranes enjoy a distinct advantage in strength, thermal stability, solvent resistance, and longer lifetime, they are more complex and expensive to fabricate, and more brittle (Karan et al 2012, Han et al 2013). Therefore, ideal filtration membranes
should be made by a simple process, and possess the advantages of both kinds of membranes (Han et al 2013).

Graphite is inexpensive and available abundantly from both natural and synthetic sources (Eda and Chhowalla 2010). Graphene is a single atomic layer of graphite (Bunch et al 2008, Geim 2009, Han et al 2013), consisting of a flat monolayer of sp2 hybridized carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice nanostructure (Geim and Novoselov 2007, Li et al 2008, Eda and Chhowalla 2010). Graphene has a number of important beneficial properties, including high chemical and thermal stability (Geim and Novoselov 2007), great flexibility and mechanical strength (Lee et al 2008), and impermeability to all standard gases and liquids (Bunch et al 2008, Leenaerts et al 2008). Given these important qualities, graphene is a potential membrane material for water treatment (Nair et al 2012, Huang et al 2013).

However, recent research has shown that graphene sheets tend to form agglomerates or re-stack to form graphite under van der Waals interactions, which represent significant obstacles to water treatment applications (Li et al 2008). In order to overcome this problem, some materials made from graphene readily disperse and form solutions of individual sheets in water, such as graphene oxide (GO). Sheets of GO have almost all the beneficial properties of graphene and in addition, they have widely spread oxygen functional groups on basal planes and edges (Park et al 2008, Eda and Chhowalla, 2010, Yeh et al 2015). By employing a facile flow-directed filtration-assisted assembly method, the GO sheets can form a highly ordered free-standing carbon-based membrane material with 2D nano-channels between two graphene sheets (Dikin et al 2007, Li et al 2008, Han et al 2013). GO nano-sheets are easily stackable because of their single-atom thickness. Initial results with assembled GO membranes show them to have distinct and beneficial characteristics including a degree of hydrophilicity and mechanical strength, tunable electrical properties (Eda and Chhowalla 2010), a combination of stiffness and macroscopic flexibility due to the unique interlocking-tile structure of the GO crystallites (Dikin et al 2007, Nair et al 2012), and a slightly enhanced antibacterial ability arising from the cytotoxic mechanisms of physical piercing and oxidative stress (Zeng et al 2016). A recent study has introduced a new way to produce large-area GO membranes in very short time periods, by using a shear alignment of the discotic nematic phase of GO liquid crystals (Akbari et al 2016). It has been suggested that GO membranes, with all their favorable properties, are ideal for contaminant filtration, sieving and separation in water treatment (Nair et al 2012, Huang et al 2013, Wang et al 2016). Graphene oxide has been studied either as a pure/skeleton membrane material or as an additive in, and a functional coating on, matrix membranes for water purification because of its unique physico-chemico-mechanical properties (Fathizadeh et al 2017). Fabrication of the GO membrane on a highly porous support may provide many new opportunities for high performance nanofiltration applications (Wang et al 2016). GO functionalization of thin-film composite membranes could mitigate the problem of biofouling (Han et al 2016, Perreault et al 2016).

While in many previous studies GO membranes have shown extraordinary stability, they have also been reported occasionally to re-disperse in water (Yeh et al 2015). Un-bonded GO layers can be easily damaged (even by a gentle finger touch) or become detached from the membrane support by water rinsing (Hu and Mi 2013), which indicates possible problems regarding the stability of GO membranes. Pure GO membranes will readily disintegrate in water, because GO sheets will become negatively charged on hydration, and the electrostatic repulsion between GO sheets will overcome the van der Waals attraction and hydrogen bonding, causing the GO sheets to separate from each other (Yeh et al 2015). Some researchers have used a layer by layer method to make stable GO membranes for water treatment using cross-linking organic polymers (Hu and Mi 2013). Alternatively, intercalating monolayer titania (TO) nano-sheets into graphene oxide (GO) laminates has been reported to exhibit excellent water desalination performances (Sun et al 2015). Also, Cu(NO3)2 and ethanol amine have been used to form stable nano-strand-channelled GO ultrafiltration membranes, comprising a network of nano-channels after the ethanol amine was washed away by NH4 (Huang et al 2013). Very recently, it has been shown that GO nanosheets could be modified/connected by solvent green (8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt) through the strong π–π stacking interactions (Shen et al 2017) or by ethylenediamine (Han et al 2016).

An alternative approach for preparing a stable GO membrane is by introducing small amounts of multivalent cations, such as Al3+, which can crosslink the GO sheets and thereby stabilize the membrane (Yeh et al 2015). Evidence has also been found that a small amount of divalent cations can enhance mechanical stiffness and fracture strength (Park et al 2008). However, all these previous studies have not considered the stability of GO membranes in the context of the filtration of surface waters. Thus, in this paper we have considered in detail the influence of cations on GO membrane stability in respect of its application in water treatment. The properties of GO membranes prepared with small amounts of multivalent cations have been evaluated, and their stability in treating solutions containing common surface water contaminants, namely NaCl, a polysaccharide (sodium alginate) and protein (bovine serum albumin) have been determined. The testing of the GO membrane for the filtration of surface water was undertaken over several days to ensure its suitability in practice. Finally, the quantity of cations applied in the membrane...
preparation has been investigated and found to be critical to the membrane stability and performance.

2. Results

2.1. Characteristics of GO membranes

The effect of different cations, at different nominal quantities, on the zeta potential of GO sheets (2 mg GO) is shown in figure 1(a). In the absence of cations, the zeta potential of GO sheets was found to be strongly negative (around −40 mV), because of the de-protonation of carboxyl groups on the edges/layers of the GO sheets (Park et al. 2008, Chua and Pumera 2013). Modification by the addition of low quantities of Na⁺ resulted in an increase of zeta potential and the charge was constant (~32 mV) at 0.2 mmol Na⁺ or greater. For Ca²⁺ and Mg²⁺, the results were very similar for the two divalent cations, with a sharp increase in zeta potential from ~40 mV to ~19 mV at low cation quantities (~0.05 mmol), and a gradual increase in zeta potential to ~15 mV with cation quantity at 1 mmol Ca²⁺/Mg²⁺. For GO membranes modified by Al³⁺, very low cation quantities resulted in a steep rise in zeta potential and charge reversal occurred at about 0.4 mmol Al³⁺. At higher quantities of Al³⁺, the zeta potential reached a plateau value of around +10 mV. From these results, it can be seen that the zeta potential values for the different cations were in the order of their valence and charge neutralizing ability, viz: Al³⁺ > Ca²⁺ > Mg²⁺ > Na⁺.

The x-ray photoelectron spectroscopy (XPS) data (figure 1(b)) showed that about 47.1% of carbon in the GO membrane was not oxidized, 42.1% had C−O bonds (representing hydroxyl and epoxide groups), and 10.8% had COOH bonds. Therefore, there are sufficient oxidized chemical bonds on the GO membrane to react with cations, and this led to an increasing zeta potential of the GO membranes with increasing quantities of bound cations. As only about half of the C atoms in the GO flakes, comprising the membranes, are oxidized, it is likely that pristine regions account for a significant proportion of the membrane, and graphite surfaces with π electron-rich structures have a strong adsorption capability for cations (Shi et al. 2013, Williams et al. 2017).

XRD (x-ray powder diffraction) was used to characterize the interlayer spacing between GO sheets in the modified GO membrane with 0.01 mmol cations (figure 1(c)). According to Bragg’s Law, the incident x-rays are scattered from lattice planes (GO sheets) of the GO membrane can be calculated from the following formula (Myers 1997):

\[ n \lambda = 2d \sin \theta \]

where \( n \) is a positive integer and \( \lambda \) is the wavelength of incident wave.

The XRD intensity peaks of the GO membranes were found to be 11.85°, 11.50°, 11.50°, and 11.03° for Na⁺, Mg²⁺, Ca²⁺ and Al³⁺, respectively, at an applied quantity of 0.01 mmol. Therefore, the relative interlayer spacings of the lamellar structures of the GO membranes were in the order \( \text{Na}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Al}^{3+} \); these were estimated to be 0.85 nm, 0.89 nm, 0.89 nm, and 0.91 nm, respectively, using Bragg’s Law. The XRD patterns of the cation-modified GO membrane showed an increased layer-to-layer distance (d-spacing) compared to that of the unmodified GO membrane, which is also confirmed by previous research. As there was little difference in the spectra of unmodified and 0.01 mmol Na⁺ modified GO membranes (not shown in figure 1(c)), only membranes with greater quantities (10 mmol) of Al³⁺, Ca²⁺ and Mg²⁺ were further analyzed. The results (figure 1(d)) confirmed that there was little difference in the structure of Ca²⁺ and Mg²⁺ modified GO membranes, with the intensity peak of both membranes at approximately 10.41° (\( d = 0.95 \) nm; cf. ionic radius of Mg²⁺ and Ca²⁺ is 0.078 nm and 0.108 nm respectively), while for Al³⁺, the peak was at 9.15° (\( d = 1.07 \) nm; cf. ionic radius of Al³⁺ is 0.114 nm). The results confirm that the interlayer spacing between GO layers in the modified membrane increases with both the amount of the adsorbed cation and its valence. It is noted that a previous study (Lerf et al. 2006) showed that the distance between sheets in a pure GO membrane increased as the presence of water (humidity) increased, but the addition of Al³⁺ imparted stability to the interplanar distance, with the degree of stability increasing with the quantity of Al³⁺.

Further analysis by Fourier Transform Infrared spectroscopy (FTIR) was used to characterize the variation of chemical bonds on the membrane surface and between the GO layers (figure 1(e)). The FTIR spectrum of the unmodified (pure) GO membrane indicates the presence of unoxidized sp² C−C bonds in the carbon lattice (1608 cm⁻¹), oxygen-containing functional groups of C−O vibrations (1045 cm⁻¹), and C=O stretching vibration (1718 cm⁻¹). In comparison, those for cation modified GO membranes exhibited decreased C−O stretch intensities, as well as increased carboxy C−O stretch intensities whose peak positions were also shifted to larger wavenumbers (1066 cm⁻¹); the peak at 1591 cm⁻¹ is believed to be significantly related to carboxylate chelates to the metal or cross-linking between GO layers by π electron-rich structures. The adsorption of cations by π electron-rich structures on graphite surfaces decreases the intensity of π electron-rich structures (C= C bonds). Therefore, it is believed that the mechanism of cross-linking, and membrane stability, is via metal-carboxylate chelates and cation-graphite surface interactions (π electron-rich adsorption), and the latter appears to increase with increasing cation valency.

2.2. SEM images of GO membrane

The unmodified GO membrane was compared with the GO membrane modified with 10 mmol Al³⁺ by scanning electron microscopy (SEM) to further
identify differences in their properties (figure 2). Comparing the top view SEM images of the GO membranes (figures 2(a) and (c)), there appeared to be many more folds on the unmodified GO membrane than on the Al\textsuperscript{3+}-modified GO membrane. As there was little connection between two layers at the folds, it is suggested there were more cross-linking points between the GO layers for the cation-GO because of the presence of Al\textsuperscript{3+}. Cross-sectional SEM images (figures 2(b) and (d)) did not show any apparent difference in the lamellar ordering of GO layer for the two membranes, except that the distance between two GO layers was less with the presence of Al\textsuperscript{3+}; however, the comparative interplanar distances are not representative of the membranes prepared in water owing to the SEM analytical procedure (i.e. N\textsubscript{2} drying under high pressure (Lerf et al 2006). Therefore, in general, the GO layers with their 2D structure are believed to have different degrees of cross-linking owing to the presence of different types and quantities of cation associated with the GO sheets.

2.3. Stability of GO membranes in DI water

The GO surface is functionalized with various oxygen-containing groups, predominantly hydroxyl and epoxide moieties (figure 1(b)), on both its basal planes and edges (Cai et al 2008). At least four kinds of interactive forces exist: electrostatic attraction, electrostatic repulsion, hydrogen bonding, and hydrophobic interaction (Wu et al 2015). It is well known that a GO membrane can be strengthened by crosslinking with divalent metal ions (Park et al 2008).
Being a trivalent cation, \(\text{Al}^{3+}\), or its hydrated form, is highly effective at flocculating negatively charged colloids (Yu et al 2016) and consequently is also effective at crosslinking the GO layers. This implies that the variation in reported interplanar distance of GO layers obtained with different species and quantities of ions can be attributed to different degrees of crosslinking. Thus, while GO membranes with different species and concentrations of ions may have very similar microstructures, they can have drastically different mechanical properties and stability in water (Ye et al 2015).

The stability of the various modified GO membranes in DI water was evaluated by visual inspection and marked differences were found. When \(\text{Na}^+\) was used as the cross-linking ion for the GO membrane, the GO-\(\text{Na}^+\) membrane completely re-dispersed after 30 min for all applied levels of \(\text{Na}^+\) (figure 3(a)). Comparing figures 3(a) and 1(a), it is evident that the strong negative charge (around \(-32\) mV) of the GO nano-layers, even at high applied levels of \(\text{Na}^+\), caused the layers/sheets within the membrane to be electrostatically repulsive, and thus, the membrane to gradually disintegrate. In contrast, the GO membranes prepared in the presence of \(\text{Mg}^{2+}\), \(\text{Ca}^{2+}\) and \(\text{Al}^{3+}\) had greater degrees of stability. For \(\text{Mg}^{2+}\), the GO membrane with 0.02 mmol \(\text{Mg}^{2+}\) was unstable in water after 30 min, but with a higher quantity of 0.05 mmol \(\text{Mg}^{2+}\) the modified GO membrane was stable over 4 h (figure 3(b)). For \(\text{Ca}^{2+}\), 0.01 mmol \(\text{Ca}^{2+}\) enabled the GO membrane to be stable for 30 min, but not over 4 h; stability over 4 h could be achieved at the higher \(\text{Ca}^{2+}\) level of 0.02 mmol (figure 3(c)). GO membranes modified with \(\text{Al}\) were stable over 4 h for 0.01 mmol \(\text{Al}^{3+}\) and higher \(\text{Al}^{3+}\) quantities (figure 3(d)).

In order to determine more clearly the stability of the modified GO membranes formed from the interaction of the different cations and their quantities, the stability ratio of each GO membrane was determined by image analysis (Scion Images software), defined as the ratio of unchanged membrane area to the total membrane area, using the images shown in figures 3(a)–(d) and other un-shown figures. The results illustrated in figure 3(e) indicate clearly that a GO membrane with incorporated \(\text{Na}^+\) is not stable in water for all the \(\text{Na}^+\) quantities considered. Incorporating \(\text{Mg}^{2+}\) into the GO membrane achieves partial stability with quantities between 0.01 and 0.02 mmol, and complete stability with \(\text{Mg}^{2+} \geq 0.05\) mmol (for 2 mg GO). For \(\text{Ca}^{2+}\) and \(\text{Al}^{3+}\), complete stability corresponded to the corresponding cation quantities of 0.02 mmol and 0.01 mmol. The adsorption and stability effects of higher valent cations are known to be significantly stronger than those of lower valent cations (Shi et al 2013, Williams et al 2017). The reason why \(\text{Mg}^{2+}\) is not as good as \(\text{Ca}^{2+}\) for stability is believed to be related to their respective atomic properties. \(\text{Ca}^{2+}\) is a bigger atom, and has a lower ionization potential and thus a greater complexation (and cross-linking) ability, thereby giving a greater stability to the GO membrane.

**Figure 2.** SEM images of GO membranes (2 mg): unmodified GO, top view (a) and cross-section (b); modified with 10 mmol \(\text{Al}^{3+}\), top view (c) and cross-section (d) (sampled when membrane was prepared and then air-dried for 3 d).
Thus, in summary, the results have demonstrated the capability of multivalent cations, in sufficient quantities, to produce a stable, ultra-thin GO membrane in water, with the cation effectiveness as follows: $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ = \text{none}$.

2.4. The stability of modified GO membranes in NaCl solution
The stability of Al-GO and Ca-GO membranes with different quantities of $\text{Al}^{3+}$ or $\text{Ca}^{2+}$ in 1 M NaCl solution was explored (figure 4). It was found that all Al-GO membranes prepared with Al quantities in the range of 0.01 mmol $\text{Al}^{3+}$ to 10 mmol $\text{Al}^{3+}$ were stable in 1 M NaCl solution (figure 4(a)). Similar results were found for the Ca-GO membranes (figure 4(b)), but for $\text{Ca}^{2+}$ quantities $\geq 0.1$ mmol (GO membrane prepared with 0.01 mmol $\text{Ca}^{2+}$ was not shown as it was not stable in DI water—figure 3). The results are in contrast to a recent study which reported that the interlayer cation ($\text{Al}^{3+}$) in GO membranes could be exchanged with hydrogen ions (from hydrochloric acid) or other monovalent cations such as $\text{Na}^+$ and $\text{Li}^+$, after which the membrane readily disintegrated in water (Yeh et al 2015). In order to consider the mechanism further, the permeation (filtration) of NaCl solution by Al-GO membranes with different $\text{Al}^{3+}$ contents was undertaken, and described in the next section.
2.5. Effect of NaCl permeation on the stability of Al-GO membranes

To investigate the possibility of membrane instability during permeation by cation exchange with the influent solution (NaCl), further experiments were undertaken. Two Al-GO membranes (2 mg GO) with 0.01 mmol Al$^{3+}$ or 10 mmol Al$^{3+}$ were used to filter 300 ml of 0.1 mol l$^{-1}$ NaCl solution (corresponding theoretically to enough Na$^+$ to exchange all of the Al$^{3+}$ in the GO membrane, if the exchange occurred), and were subsequently soaked in DI water (figure 5). After 2 h in DI water the stability of the membranes was observed and recorded. The results showed that the GO membrane with 0.01 mmol Al$^{3+}$ was stable for a short while after permeation of the NaCl solution, but after prolonged standing in water the membrane clearly disintegrated into a powder (figure 5(a)). These results are consistent with previous research, where it was found that a Al-modified GO, when separated from the membrane support, re-dispersed in NaCl solution (Yeh et al 2015). It is believed that the reason for the variation in stability of the modified GO membranes in NaCl solution is related to the relative difficulty of Na$^+$ ions to enter the inner GO membrane when it was immersed in the NaCl solution. In contrast, the 10 mmol Al$^{3+}$ modified GO remained stable over an extensive period (>10 d). The results indicate that the membrane stability is dependent on the quantity of incorporated Al$^{3+}$, and consequently the interlayer structure (see subsequent results that show an inverse relationship between membrane flux and Al$^{3+}$ quantity—section 2.7). Therefore, it is concluded that an Al-GO membrane is more likely to be stable when there is a high degree of Al$^{3+}$ ion incorporation within the GO membrane.

A further experiment was conducted to examine the potential displacement of Al$^{3+}$ ions by Na$^+$ as indicated by changes in solution conductivity. In this experiment 300 ml DI water was filtered through the Al-GO membrane (10 mmol Al$^{3+}$), followed by 300 ml...
0.1 mol l\(^{-1}\) NaCl solution. The results are summarized in figure 5(b) and show that the conductivity of the DI water was unchanging, except for the first DI water sample at 60 ml, which was relatively greater than the four subsequent samples (120, 180, 240, and 290 ml), suggesting that some residual, unbound Al\(^{3+}\) was present from the membrane preparation. Notwithstanding the slightly higher conductivity at 60 ml, there was little evidence of a sustained destabilization and loss of the cross-linked Al\(^{3+}\) within the membrane. For the subsequent filtration of NaCl solution, the samples again showed a relatively unchanging conductivity although there was a slight decrease of the conductivity at 60 ml. Overall, these results are consistent with the absence of any significant Na\(^+\)/Al\(^{3+}\) exchange with the 10 mmol Al-GO membrane during NaCl permeation.

2.6. Effect of polysaccharide and protein on the stability of GO membrane

All previous studies with GO membranes have involved their evaluation in DI water only or salt solutions. However, it is possible that the stability of GO membranes may be susceptible to other components of surface waters/sea waters, not only salts but biopolymers, such as polysaccharides and proteins. Therefore, in this study further tests were undertaken with modified GO membranes in the presence of a representative polysaccharide, sodium alginate (NaAlg), and a representative protein, bovine serum albumin (BSA). In these tests GO membranes, modified with quantities of Al\(^{3+}\) and Ca\(^{2+}\), were immersed in NaAlg solution of different concentrations in a range that is realistic of, and significantly greater than, surface waters (figure 6 and figure S1 (stacks.iop.org/TDM/4/045006/mmedia)). The GO membrane formed with 0.01 mmol Al\(^{3+}\) was stable in 10 mg l\(^{-1}\) NaAlg solution, but was unstable in 50 mg l\(^{-1}\) or higher NaAlg concentrations. Since the GO membrane with 0.01 mmol Al\(^{3+}\) was shown previously to be stable in NaCl solution, it is unlikely that the instability with NaAlg was caused by Al\(^{3+}\) replacement by Na\(^+\) through ionic exchange, but through the interaction with the alginate. A similar effect has been reported previously where the removal of Al\(^{3+}\) was accelerated by soaking the GO films in a solution of the metal-chelating agent, ethylenediaminetetraacetic acid (Yeh et al 2015).

For GO membranes formed with greater quantities of Al, for example 10 mmol Al\(^{3+}\), the modified GO membrane was stable for all alginate concentrations tested and there was no disintegration of the GO membrane, even after 7 d (figure 6(b)). In contrast, the GO membrane formed with the highest Ca\(^{2+}\) quantity, 10 mmol Ca\(^{2+}\), was unstable in 10 mg l\(^{-1}\) alginate solution after 7 d, and at the higher alginate concentrations of 50 mg l\(^{-1}\) and above, the GO membrane was
not stable after 3 d, and disintegrated fully after 7 d (figure 6(c)). Therefore, the results show that Ca-modified GO membranes are not stable in alginate solution while Al-modified GO membranes with a sufficiently high Al\(^{3+}\) content appear to be stable.

For the stability tests with the protein solution, there was no Na\(^+\) associated with the BSA solution, so potential cation exchange was not a relevant factor in these tests. GO membranes modified with different amounts of Al\(^{3+}\) and Ca\(^{2+}\), both separately and mixed in a 1:1 mole ratio, were immersed in 1 g l\(^{-1}\) BSA solution (figure 7) or filtrated with 10 mg l\(^{-1}\) BSA (figure S2). For all the GO membranes formed with Al\(^{3+}\) (between 0.01 mmol and 10 mmol), there was no sign of instability or disintegration of the membrane over 14 d in BSA solution. In contrast, Ca-modified GO membranes prepared with \(\geq 0.1\) mmol Ca\(^{2+}\) were stable in BSA solution up to 1 d only. All Ca-modified GO membranes were unstable after 7 d (especially with 0.1 mmol Ca\(^{2+}\)) and disintegrated in the BSA solution after 14 d. For GO membranes formed with a Al\(^{3+}\) and Ca\(^{2+}\) mixture (molar ratio = 1:1) (Al + Ca-GO), the stability of the GO membrane was very similar to the GO membrane with only Al\(^{3+}\), and all the Al + Ca-GO membranes were still stable after 14 d in BSA solution.

The BSA filtration results further confirmed that high contents of Al\(^{3+}\) or Ca\(^{2+}\) in the GO membranes would increase their stability, and for the same molar content the stability was greater for the Al\(^{3+}\), compared to Ca\(^{2+}\). In summary, the results confirmed that the presence of sufficiently high quantities of Al\(^{3+}\) within the GO membrane made it stable when exposed to BSA and alginate solutions, which suggested that it would be suitable for use in drinking water treatment, assuming that it is equally resilient to the presence of other proteins and polysaccharides found typically in real source waters.

2.7. Influence of cations on membrane flux

The variation of GO membrane flux with the type and quantity of cations was evaluated using GO membranes modified with Al\(^{3+}\), Ca\(^{2+}\) and Ca\(^{2+}\) + Al\(^{3+}\) and formed on a PVDF ultrafiltration supporting membrane; the results are summarised in figure 8. At the lowest cation level (0.1 mmol), the Al-GO membrane had a water permeability of 66 ± 6 l m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), and the Ca-GO membrane had a lower permeability of 44 ± 8 l m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). For the GO membrane prepared with mixed Al and Ca cations (1:1 molar ratio), the flux was between that of the Al-GO and the Ca-GO, but closer to the former. In comparison to a conventional nanofiltration membrane (pore size near 1.55 nm), which had a permeability of around 6 l m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) found by previous research (Zhu et al 2016), the permeabilities of the modified GO membranes were nearly an order of magnitude greater. The results also showed that the flux of the modified GO membranes decreased systematically with the quantity of cations used in the membrane preparation (from 0.1 mmol to 10 mmol) (figure 8(a)). This trend could be explained by an increase in the connection points between GO layers through cross-linking of the cations, thereby causing greater resistance to flow.

The flux through the GO membrane was found to increase linearly with applied pressure (figure 8(b)), indicating quasi-laminar flow behaviour. The modified Hagen-Poiseuille equation for slit-shaped pores gives an approximate explanation of fluid flow through these multilayered structures (Huang et al 2013). Also, the flux of the Al-GO membrane was greater than the Ca-GO membrane at the same cation concentration, which may be related to the larger d-spacing of Al-GO membrane (d = 1.07 nm), compared to the Ca-GO membrane (d = 0.98 nm) (section 2.1).

As a preliminary indication of the performance of the Al-modified GO membrane for treating a representative surface water, the flux variation and permeate molecular weight (MW) distribution were investigated using samples of River Thames near London. As can be seen in figure 9(a), the flux decreased by approximately 40% during 2.2 h of filtration time for the GO membrane with 0.1 mmol Al\(^{3+}\), but it was evident that with increasing Al content the extent of flux decline decreased, and was approximately 30% (at 2.2 h) for an Al\(^{3+}\) content of 10 mmol. The treatment performance of the Al-modified GO membranes was investigated by comparing the MW distribution of UV-adsorbing organic matter of the River Thames samples before and after membrane filtration to reveal which fractions of the organic matter were retained by the GO membrane. It is evident from figure 9(b) that the GO membrane achieved a major reduction in the MW of the organic matter across all size fractions. The results also suggested that the removal of organic matter increased slightly with the Al\(^{3+}\) content of the GO membrane, especially for the organic fractions larger than 1000 Dalton. Thus, as well as inducing membrane stability, the incorporation of higher levels of Al\(^{3+}\) in the formation of the GO membrane induces a lower sensitivity to flux decrease (fouling), and a slightly superior treatment performance.

3. Discussion

Graphene oxide can be readily dispersed in water and manipulated to form membranes comprising hydrophilic layers that have a great number of oxygen functional groups on their basal planes and edges (Dikin et al 2007), and this enables GO to be exfoliated and functionalized (Park et al 2008, Eda and Chhowalla 2010, Yeh et al 2015). However, the negative surface potential of unmodified GO is sufficiently high that electrostatic repulsion between GO layers is able to overcome van der Waals attraction and hydrogen bonding, thereby preventing adhesion between layers (Yeh et al 2015). In this study we have investigated the benefits of cation addition as a means of reducing the negative surface charges, since oxygen functional
groups on the basal planes, and carboxylate groups on the edges, have been shown to bond to multivalent cations, such as Mg$^{2+}$ and Ca$^{2+}$ (Park et al 2008). In addition, surface potentials can be reduced by the adsorption of cations to pristine graphite surfaces with π electron-rich structures. By addition of such cations, the adhesion between GO layers is possible, and a membrane can be prepared from multiple GO layers.

Figure 7. Variation of Al-GO, Ca-GO and Al + Ca-GO membrane stability with cation quantity in 1 g l$^{-1}$ BSA solution (2 mg GO): (a) GO membrane with 0.01 mmol–10 mmol Al$^{3+}$; (b) 0.1 mmol–10 mmol Ca$^{2+}$; (c) 0.01 mmol–10 mmol Al$^{3+}$ and Ca$^+$ (molar ratio = 1:1).
However, once formed and in operation, the integrity of the membrane will depend on the resilience of the cation-GO linkages, and this may be strongly influenced by the composition of the influent water during treatment.

In this study the results have shown that the monovalent cation, Na\(^+\), is unable to stabilize GO layers, but the multivalent cations (Mg\(^{2+}\), Ca\(^{2+}\) and Al\(^{3+}\)) can produce a stable membrane provided there is a sufficient quantity of cation incorporated. When immersed in NaCl solution both Al-modified and Ca-modified GO membranes were not destabilized, probably because Na\(^+\) ions did not diffuse significantly into the GO membrane where they could replace the Al\(^{3+}\) or Ca\(^{2+}\) ions. However, with permeation/filtration of NaCl solution some replacement of the Al\(^{3+}\) ions by Na\(^+\) within an Al-modified GO membrane was observed, for a low level of incorporated Al, causing the membrane to be unstable. This effect was dependent on the quantity of Al present in the membrane, as at a higher level of Al the modified GO membrane appeared to be more stable. The stability of cation-modified GO membranes in the presence of alginate and BSA, as representative biopolymers, was also found to be dependent on the level of cation present within the membrane. It is suggested that the reason for the membrane instability is complexation between the alginate, or BSA, and the GO-bound cation, leading to the cation release. For the Al-GO membrane the instability was found to be dependent on the amount of incorporated Al and the concentration of the alginate, but the Al-GO membrane was stable in the presence of BSA under the test conditions. In contrast, the Ca-GO membrane was clearly not stable in the NaAlg and BSA solutions, which suggests its unsuitability for the treatment of typical surface waters. However, by combining Al\(^{3+}\) with Ca\(^{2+}\) into the GO membrane the stability of the modified GO was enhanced; this further indicated the important role of Al\(^{3+}\) in providing stability to the GO membrane. The stability of the Al-GO membrane

**Figure 8.** Variation of membrane flux for GO (2 mg) membranes prepared with different cation quantities (a), and the variation of flux with applied pressure (10 mmol cations) (b).
was also demonstrated by the tests with a real surface water (River Thames) containing a range of organic components, including biopolymers (MW > 40 kDa), and the membrane performed well in terms of maintenance of flux and contaminant retention, particularly where the membrane had a high Al content (figure 9).

4. Experimental section

4.1. Preparation of GO membranes
GO was synthesized from purified natural graphite (Fisher Scientific, UK) by the Hummers method (Hummers and Offeman, 1958). Aqueous dispersions of GO at a concentration of 2 g l\(^{-1}\) were prepared with the aid of ultrasound (KC3 Ultrasonic Cleaning Bath (38 kHz, 85 W), KERRY, GUTSON, United Kingdom) in 50 ml batches. Unmodified GO membranes were made by filtration of the GO solution through a cellulose acetate (CA) membrane filter (47 mm in diameter, 0.2 \(\mu\)m pore size, Whatman, Middlesex, UK) or PVDF ultrafiltration membrane (Ande membrane separation technology & engineering (Beijing) Co., Ltd, China) with a nominal molecular weight cutoff of 100 kDa (76 mm in diameter), equivalent to a GO mass of 2 mg. For the modified GO membranes, the GO solution was mixed with alternative salt solutions of the general form, MCl\(_n\) (where M represents the cations, Na, Mg, Ca and Al; and associated chloride \(n = 1–3\)), and then filtered as indicated above by either CA or PVDF membranes. The quantity and concentration of salt solution used in the preparation of the modified GO membranes was adjusted to correspond to different nominal cation amounts (as indicated in the results).

4.2. Chemical reagents and membrane stability
All salt solutions were prepared in DI water with reagent grade chemicals. For the AlCl\(_3\) solution the pH was adjusted to pH 3 (by addition of HCl) to prevent precipitation. Sodium alginate (NaAlg) and bovine serum albumin (BSA) were obtained as reagent grade chemicals (Sigma, USA), and fresh solutions at a total

**Figure 9.** Temporal variation of flux (a), and molecular weight distributions of raw and permeates (b), of Al-GO membranes formed with different quantities of Al\(^{3+}\) for samples of River Thames.
concentration of 10 g l\(^{-1}\) were prepared using DI water. The stock solution was stored in the dark at 4 °C and was brought to room temperature prior to use before working solutions were made, and the stock solution was used within 3 d.

To investigate the stability of the formed GO membranes, they were placed into the respective test solution (i.e. DI water, NaCl solution, alginate solution and BSA solution) for periods ranging from several hours to several days. Subsequently, each GO membrane was shaken in its respective water for 1 min, and then photographic images of the GO membrane were taken.

4.3. GO membrane flux and fouling

Dead-end flow experiments were undertaken using formed GO membranes in a stirred cell apparatus (Amicon 8400, Millipore) with a constant upstream pressure (1 bar–4 bar) under nitrogen gas. Immediately before the stirred cell test the DI water flux of the membrane was determined by passing DI water through the membrane until a stable permeate flux was reached. The flux of the GO membrane with different concentrations of Al\(^{3+}\) + Ca\(^{2+}\) under 4 bar N\(_2\) gas was investigated, as well as the flux with 10 mmol Al\(^{3+}\) + Ca\(^{2+}\) under different applied pressures of N\(_2\) gas.

The fouling characteristics of the GO membrane were studied by filtering samples of River Thames abstracted near London from March 2016 to August 2016. In each test the performance of the membrane was evaluated by recording the variation of normalized flux, \(J/J_0\), as a function of time, where \(J_0\) is the initial membrane flux.

4.4. Characterization

Samples of selected GO membrane were platinum-coated by a sputter and observed under high resolution field emission gun scanning electron microscope (FESEM, LEO Gemini 1525, Germany). Analysis of XRD patterns were collected by a Rigaku Dmax powder diffractometer with Cu K\(\alpha\) radiation (\(\lambda = 1.5418 \) Å) at 40 kV, and x-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) spectra were collected to identify the relative abundance of the different functional groups. The nature of the membranes was also analysed by fourier transform infrared spectroscopy (FTIR, Spectrum 400, PerkinElmer, USA) with Quest ATR Accessory (SPECAC Ltd, UK), and the zeta potential of GO sheets, with different concentrations of cations (Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\) and Al\(^{3+}\)), were measured by a Zeta Sizer instrument (Nano-ZS90, Malvern Instruments Ltd, UK).

Acknowledgments

This work was supported by the Engineering and Physical Sciences Research Council in United Kingdom (grant number EP/N010124/1).

Supporting information

Supporting information is available from the 2D Materials (online) or from the author.

References

Akbari A, Sheath P, Martin S T, Shinde D B, Shaibani M, Banerjee P C, Tkacz R, Bhattacharyya D and Majumder M 2016 Large-area graphene-based nanofiltration membranes by shear alignment of discotic nematic liquid crystals of graphene oxide Nat. Commun. 7 10891

Bunch J S, Verbridge S S, Alden JS, van der Zande A M, Parpia J M, Craighead H G and McEuen P L 2008 Impermeable atomic membranes from graphene sheets Nano Lett. 8 2458–62

Cai W W et al 2008 Synthesis and solid-state NMR structural characterization of (13)C-labeled graphite oxide Science 321 1815–7

Chua C K and Furnera M 2013 Covalent chemistry on graphene Chem. Soc. Rev. 42 3222–33

Dikin D A, Stankovich S, Zimney E J, Piner R D, Dommett G H B, Evmenenko G, Nguyen S T and Ruoff R S 2007 Preparation and characterization of graphene oxide paper Nature 448 457–60

Elda G and Chihmowalla M 2010 Chemically derived graphene oxide: towards large-area thin-film electronics and optoelectronics Adv. Mater. 22 2392–415

Fathizadeh M, Xu W W L, Zhou F L, Yoon Y and Yu M 2017 Graphene oxide: a novel 2-dimensional material in membrane separation for water purification Adv. Mater. Interfaces 4 1600918

Geim A K 2009 Graphene: status and prospects Science 324 1530–4

Geim A K and Novoselov K S 2007 The rise of graphene Nat. Mater. 6 183–91

Han J L, Xia X, Tao Y, Yun H, Hou Y N, Zhao C W, Luo Q, Cheng H Y and Wang A J 2016 Shielding membrane surface carbonyl groups by covalent-binding graphene oxide to improve anti-fouling property and the simultaneous promotion of flux Water Res. 102 619–28

Han Y, Xu Z and Gao C 2013 Ultrathin graphene nanofiltration membrane for water purification Adv. Funct. Mater. 23 3693–700

Hu M and Mi B X 2013 Enabling graphene oxide nanosheets as water separation membranes Environ. Sci. Technol. 47 3715–23

Huang H B, Song Z G, Wei N, Shi L, Mao Y F, Ying Y L, Sun L W, Xu Z P and Peng X S 2013 Ultrafast viscous water flow through nanostranded-channelled graphene oxide membranes Nat. Commun. 4 2979

Hummers W S and Offeman R E 1958 Preparation of graphitic oxide J. Am. Chem. Soc. 80 1339–9

Karan S, Samitsu S, Peng X S, Kurashima K and Ichinose I 2012 Ultrafast viscous permeation of organic solvents through diamond-like carbon nanosheets Science 335 444–7

Koenig S P, Wang I D, Pellegrino J and Bunch J S 2012 Selective molecular sieving through porous graphene Nat. Nanotechnol. 7 728–32

Lee C, Wei X D, Kysar J W and Hone J 2008 Measurement of the elastic properties and intrinsic strength of monolayer graphene Science 321 385–8

Lemaerts O, Partoens B and Preters F M 2008 Graphene: a perfect nanoballoon Appl. Phys. Lett. 93 193107

Leif A, Buchsteiner A, Pieper J, Schottl S, Dekany I, Szoabo T and Boehm H P 2006 Hydration behavior and dynamics of water molecules in graphite oxide J. Phys. Chem. Solids 67 1106–10

Li D, Muller M B, Gilje S, Kaner R B and Wallace G G 2008 Processable aqueous dispersions of graphene nanosheets Nat. Nanotechnol. 3 101–5

Myers H P 1997 Introductory Solid State Physics (London: Taylor and Francis) pp 276–95
Nair R R, Wu H A, Jayaram P N, Grigorieva I V and Geim A K 2012 Unimpeded permeation of water through helium-leak-tight graphene-based membranes Science 335 442–4
Park S, Lee K S, Bozkulu G, Cai W, Nguyen S T and Ruoff R S 2008 Graphene oxide papers modified by divalent ions—enhancing mechanical properties via chemical cross-linking ACS Nano 2 572–8
Pendegast M M and Hoek E M V 2011 A review of water treatment membrane nanotechnologies Energy Environ. Sci. 4 1946–71
Perreault F, Jaramillo H, Xie M, Ude M, Nghiem L D and Elimelech M 2016 Biofouling mitigation in forward osmosis using graphene oxide functionalized thin-film composite membranes Environ. Sci. Technol. 50 5840–8
Shannon M A, Bohn P W, Elimelech M, Georgiadis J G, Marinas B J and Mayes A M 2008 Science and technology for water purification in the coming decades Nature 452 301–10
Shen H P, Wang N X, Ma K, Wang L, Chen G and Ji S L 2017 Tuning inter-layer spacing of graphene oxide laminates with solvent green to enhance its nanofiltration performance J. Membr. Sci. 527 43–50
Shi G S, Liu J, Wang C L, Song B, Tu Y S, Hu J and Fang H P 2013 Ion enrichment on the hydrophobic carbon-based surface in aqueous salt solutions due to cation–π interactions Sci. Rep. 3 3436
Sun P Z et al 2015 Highly efficient quasi-static water desalination using monolayer graphene oxide/titania hybrid laminates NPG Asia Mater. 7 e162
Wang J Q, Zhang P, Liang B, Liu Y X, Xu T, Wang I F, Cao B and Pan K 2016 Graphene oxide as an effective barrier on a porous nanofibrous membrane for water treatment ACS Appl. Mater. Interfaces 8 6211–8
Williams C D, Dis, Trisai A and Carbone P 2017 Effective polarization in pairwise potentials at the graphene-electrolyte interface J. Phys. Chem. Lett. 8 703–8
Wu L, Zeng L and Jiang X E 2015 Revealing the nature of interaction between graphene oxide and lipid membrane by surface-enhanced infrared absorption spectroscopy J. Am. Chem. Soc. 137 10052–5
Yeh C N, Raidongia K, Shao J J, Yang Q H and Huang J X 2015 On the origin of the stability of graphene oxide membranes in water Nat. Chem. 7 166–70
Yu W Z, Gregory J and Graham N 2016 Regrowth of broken hydroxide flocs: effect of added fluoride Environ. Sci. Technol. 50 1828–33
Zeng Z P, Yu D S, He Z M, Liu J, Xiao F X, Zhang Y, Wang R, Bhattacharyya D and Tan T T Y 2016 Graphene oxide quantum dots covalently functionalized PVDF membrane with significantly-enhanced bactericidal and antibiofouling performances Sci. Rep. 6 20142
Zhu J, Zheng J, Liu C and Zhang S 2016 Ionic complexing induced fabrication of highly permeable and selective polyacrylic acid complexed poly (arylene ether sulfone) nanofiltration membranes for water purification J. Membr. Sci. 520 130–8