

Double Layer Graphene Oxide Loaded With Propylammonium Nitrate for Selective Adsorption of Inorganic Salts

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Abstract - Due to freshwater scarcity, desalination process gains more importance. Developing a green and environmentally friendly solution for extraction of the salts from the seawater becomes a major challenge nowadays. Among all desalination processes, membrane desalination is widely used. About 80 % of total desalination plants are based on reverse osmosis (RO) worldwide. However, RO desalination is considered to be costly owing to the short lifetime of the membranes and high replacement costs. Membrane fouling is one of the main causes of this limitation. Membrane inorganic fouling can be easily affected by calcium and magnesium inorganic salts. Hence, it is important to develop an efficient adsorbent used in RO pre-treatment processes to address the problem of inorganic fouling. The great advantages offered by nanomaterials and green solvents allow the creation of new functional materials for inorganic salt adsorption. Ionic liquids (ILs) comprising of an organic cation and an organic or inorganic anion, exhibit superior characteristics and are used widely for different applications, including separation and extraction processes of salts and of several heavy metals in the seawater. However, ILs which have good solubility of inorganic salts are mostly hydrophilic. Therefore, cross-contamination of the pre-treatment water during the extraction process can occur. However, if ILs are supported on carbon nanostructures (CNS), as graphene oxide (GO) or other types of CNS, this can be avoided. As a result, this will reduce the operational costs of the plants by decreasing the amount of inorganic fouling in the membranes. Experimental findings showed that GO modified with IL can successfully adsorb CaCl₂, MgCl₂ and NaCl salts. Physical functionalization has been confirmed using thermal gravimetric analysis (TGA) and Raman Spectroscopy analysis. Moreover, leaching of IL from GO has been studied using Total Organic Carbon (TOC).

Keywords: graphene oxide, ionic liquids, desalination, inorganic salts, pre-treatment

1. Introduction

Novel carbon nanostructures (CNS) can be used in wide range of applications due to its superior properties. The progress in nanotechnology and material science opened the way to CNS based novel functional materials. Especially CNS found to be interesting in the scientific world due to their superior properties, accessible structure, present high external surface area, and its mechanical properties [1]. The scientists use CNS based material in the different applications and depending on the structure of carbon atoms, CNS can be subdivided into different types, where graphene is particularly interesting due to its versatility [2]. Graphene consists of sp^2 hybridized carbon sheet with a bond length of 0.142 nm [3]. When graphene reacts with oxygen atoms it forms more valuable graphene oxide, where different oxygen groups can react with diverse atoms and molecules due to its functionalization [4]. By incorporating suitable functionalities on the surface graphene oxide, it is possible to create more efficient adsorbent material [5, 6]. However, the layers of graphene sheets tend to aggregate due to π - π stacking, which can significantly decrease their specific surface area, hence decrease the surface area available for adsorption. Therefore, it is necessary to modify GO by inserting a spacer material between the graphene sheets to mitigate

its aggregation [7]. ILs are widely used for different applications, including separation and extraction processes [8], as they are capable of multiple types of interactions, as π - π , n- π , and hydrogen bonding [9] Moreover, using ionic liquids is gaining particular emphasis because of their high thermal and chemical stability, low volatility, very high ability to dissolve a wide range of compounds and more importantly their environmental-friendly behaviour [10, 11]. Due to positively or negatively charged groups, IL can be used to modify the graphene oxide surface in order to enhance adsorption capacity because of improved ion-exchange, electrostatic, and π - π interactions [12]. The covalent functionalization of graphene is mostly performed by acylation, esterification, isocyanate formation, nucleophilic ring opening, amide formation, and diazotization and cycloaddition reactions [13]. Whereas, non-covalent functionalization mostly involves electrostatic forces, hydrogen bonding, π - π interactions, van der Waals interaction and donor-acceptor interactions. [14].

As the result of development of sea water desalination technologies there is increasing demand in creating new functional materials for salt extraction. Although ILs are widely used for different applications, including separation and extraction processes [8], ILs which have good solubility with inorganic salts present in the sea water, specifically MgCl_2 and CaCl_2 are hydrophilic [15]. Therefore, cross contamination of the water during the extraction process cannot be avoided [16, 17]. However, if ILs are supported on proper structural materials, as graphene, graphene oxide (GO) or other type of Carbon Nanostructures (CNS), this problem can be evaded. The main idea of current research work is to use GO functionalized IL, namely Propylammonium Nitrate for adsorption of sea salts as pre-treatment step for desalination process. The idea behind is to reduce the concentration of these inorganic salts, namely CaCl_2 , MgCl_2 and NaCl , causing the inorganic fouling in membranes [18]. By addressing the problem of fouling in the membrane the overall load on desalination plants can be decreased and RO membrane performance and lifetime can be increased.

2. Experimental

2.1. Chemicals and Materials

Double-layer Graphene oxide with the following specifications: lateral dimensions < 4 micro meters, defect ratio > 1 av. I_D/I_G and surface area of $7 \text{ m}^2/\text{g}$ was provided from Versarien. Ionic Liquid namely - Propylammonium Nitrate (PAN) with purity >97% was purchased from IoLiTec-Ionic Liquids Technologies (Germany). NaOH solution was prepared from NaOH purchased from Sigma Aldrich with Deionized (DI) Water. MgCl_2 , CaCl_2 and NaCl were purchased from Acros Chemicals and solutions are prepared by dilution with DI water.

2.2. Modification of Double-Layer Graphene Oxide (GO) by Ionic Liquid (IL)

Solution of 200 mg of GO was sonicated in 40 ml of DI water (5 mg per 1 ml) for 1 hour in water bath. 0.5 M of NaOH solution was added dropwise till pH has reached 11. The mixture was sonicated in water bath for 3 hours. After 2 ml of IL-Propylammonium Nitrate (PAN) has been added to the solution (2 ml of IL per 40 ml of DI/GO) and sonicated at 50°C for 6 hours. Lastly the solution was filtered using filter paper. For drying the sample has been pre-frozen at -80°C overnight in the freezer, after it has been dried in the Freeze Drier (FD) under low pressure and low temperature for 24 hours.

2.3. Characterization

The surface morphology of the modified CNS was investigated using High Resolution Scanning Electron Microscopy (HRSEM) (Nova NanoSEM, FEI, The Netherlands). Raman Spectroscopy analysis was performed using Raman-AFM combination Alpha300 RA (WITec, Germany) at 532 nm laser wavelength. Thermogravimetry Analysis (TGA) of the materials was done using Netzsch STA 449 F3 Jupiter TGA, Germany with a heating rate of $10^\circ\text{C}/\text{min}$. Leaching has been tested using Total Carbon Content (TOC) analyser TOC-LCSH/CSN (Shimadzu, Japan). All the adsorption studies involved the use of Inductively coupled plasma - Optical emission spectrometry (ICP-OES Model 5100 SVDV, Agilent, USA) after calibration with the proper standards.

2.4. Experimental procedure for MgCl_2 , CaCl_2 and NaCl adsorption

25 mg of adsorbent was placed in 50 ml of $\text{MgCl}_2/\text{CaCl}_2/\text{NaCl}$ solution with different concentrations (200 ppm and 1000 ppm) in a 50 ml flask. Using a mechanical shaker, the solution would be shaken for 24 hours at 300 rpm at 20°C . Afterwards, the solution was filtered using a filter syringe and was analysed for the concentration of salt using ICP-OES.

2.5. Experimental procedure for quantification of IL leaching

15 mg of adsorbent has been placed in 30 ml of DI water in 50 ml flask. Using mechanical shaker, the solution has been shaken for 7 hours at 300 rpm at room temperature. The residue solution has been analysed for its TOC. Leaching of the IL has been calculated using (1).

$$\text{Leaching (\%)} = \frac{\Delta\text{TOC} \cdot V_s}{m_{IL}} * 100 * C_{IL} \quad (1)$$

where ΔTOC (mg L^{-1}) is the measured concentration of TOC in the sample after the leaching minus measured TOC which is already present in the solution. $V_s(L)$ is the volume of the feed solution and $m_{IL}(mg)$ is the mass of IL used. C_{IL} is the carbon content of IL. Calculated value represents the percentage of IL leached from double-layer GO matrix [19].

3. Results and Discussion

3.1. Surface Morphology

Surface morphology of Graphene Oxide can be observed in Fig.1 (a) and has been studied using HRSEM. From Fig. 1 (a) it can be noticed that double layer GO (mostly 2 layers with lateral diameter less than $4 \mu\text{m}$ based on manufacturer 2-D Tech, Versarien specifications) have layers stack together. However, after the modification of GO with IL it was observed from Fig. 1 (b) that graphene layers are less agglomerated and more free space is created between the double layer GO. Fig.2 depicts Graphene Size distribution from 100 counts, average lateral dimension was equal to average 4 micrometres.

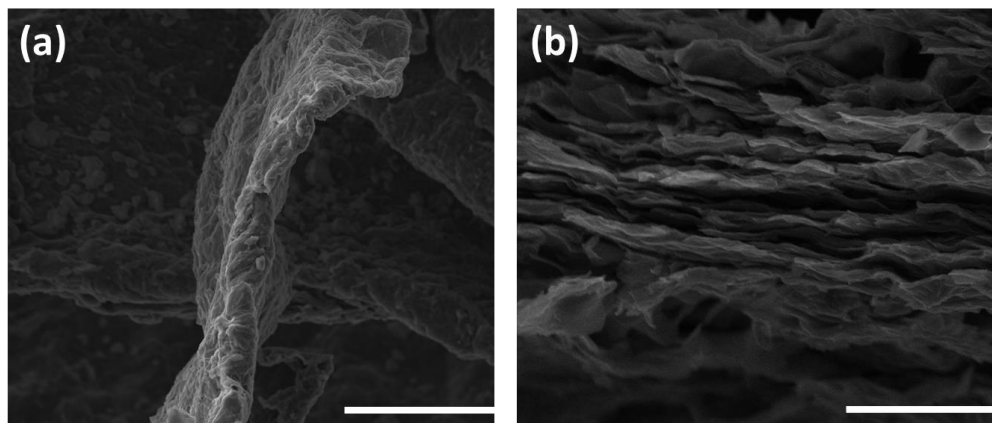


Figure 1. Scanning Electron Microscopy images of a) GO before modification with IL, Scale Bar = $10 \mu\text{m}$; b) GO after modification with IL, Scale Bar = $4 \mu\text{m}$

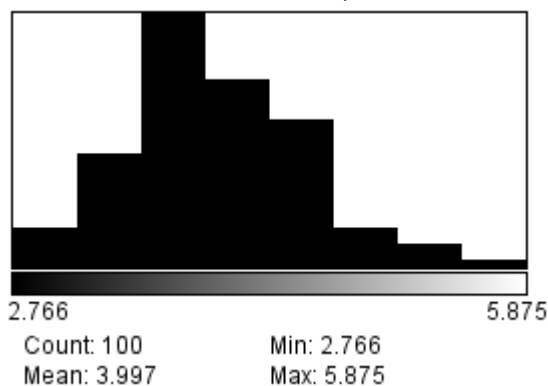


Figure 2 Graphene Size Distribution

3.2. Thermal Gravimetric Analysis

Thermal Gravimetric Analysis was done for GO, IL and modified GO with IL. From TGA analysis it has been identified that 10 wt. % of IL has been loaded on the GO, as can be seen in Fig. 3. In case of GO modified with IL the onset temperature of decomposition has been increased from 123°C till 180 °C as can be seen in Table 1. Decomposition temperature for IL-PAN was found to be 240°C which agrees with the literature [20].

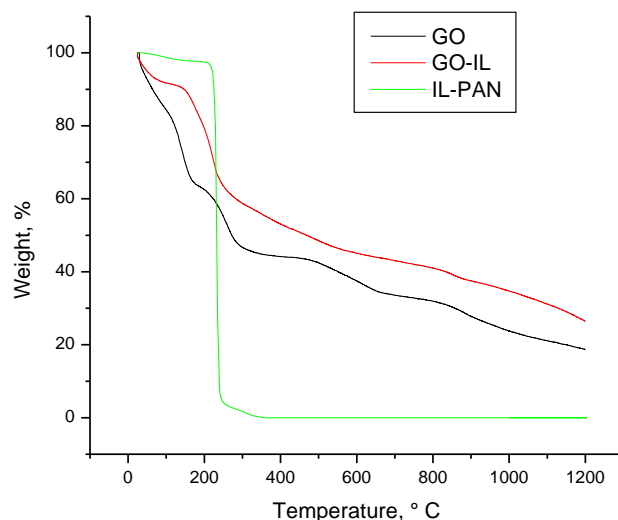


Figure 3. TGA Analysis of GO with and without IL-PAN functionalization

Table 1: TGA Analysis: Onset Temperature, Mass Loss %

Name	Onset Temperature, °C	Mass Loss, %
Double-Layer GO	123	9,35
Double-Layer GO-IL	180	19,65
IL-PAN	240	90,01

3.3. Raman Spectroscopy Analysis

Raman Spectroscopy Analysis results can be observed in Fig. 4. Generally, the G band is related to sp_2 -bonded carbon atoms in the hexagonal lattice of the graphene structure. However, the D band reflects the presence of defects or disorders caused by sp_3 hybridized carbon in the lattice, while G' is caused by second-order, zone boundary phonons that are related to the assembly of the multilayers [21]. The intensity ratio of I_D/I_G provides an indication of degree of oxidation and/or functionalization [22]. Results of I_D/I_G ratio can be seen in Table 2 and it increases for GO modified with IL from 1.03 to 1.08. This can indicate the increase in degree functional groups. Functionalization can add different functional groups on graphene oxide surface which result in increase of I_D/I_G value.

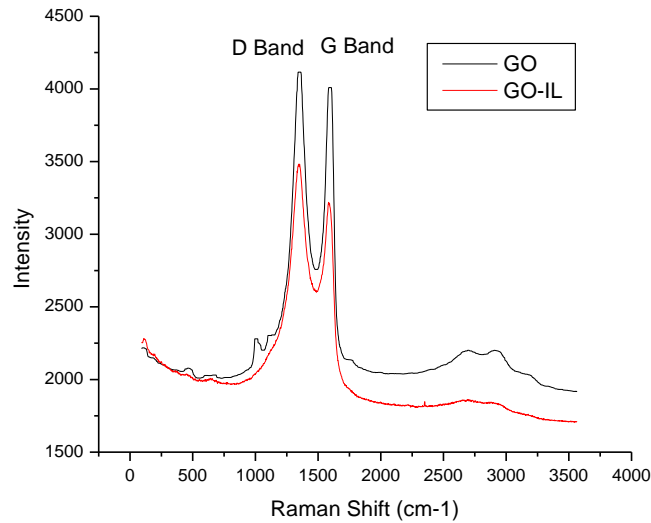


Figure 4. Raman Spectroscopy Analysis of GO and GO modified with IL

Table 2: Raman Spectroscopy Analysis data, I_D/I_G values for both GO and GO modified IL

Material	$\frac{I_D}{I_G}$
Origin GO	1.03
Functionalized with PAN	1.08

3.4. Leaching of IL from GO matrix analysis

Leaching percentage has been identified following the methodology and procedure of Pirkwieser et al [19]. From the TOC analysis it has been identified that GO modified with IL has low degree of leaching after 7 hours of continuous shaking and was equal to 6 %, as can be seen in Table 3. The cross contamination of the feed water is undesirable and less degrees of leaching are expected after adding another washing step with DI water in the methodology of preparation of double-layerGO-IL adsorbent.

Table 3: Leaching and TOC Analysis data

TOC results	
GO-IL 7 hours	10.14 mg/L
Leaching degree	
GO-IL 7 hours	6 %

3.4. Adsorption of $MgCl_2$ and $CaCl_2$ and NaCl salts

Adsorption capacities are shown in Fig. 5 and Table 4 with different initial concentrations of $CaCl_2$, $MgCl_2$ and NaCl using GO before and after modification with IL-PAN. The adsorption capacity described as q_e – adsorption coefficient and represents the mass of adsorbed salt (in mg) per mass of the adsorbent (in grams). 200 ppm and 1000 ppm of salts concentrations have been used to study the effect of higher concentrations on the adsorption coefficient q_e (mg - salt/g - adsorbent).

The adsorption capacity increased for almost all the salts and for both concentrations as can be seen from Table 4. For lower concentration of $CaCl_2$ the adsorption capacity increased over three times from 37 mg/g to 109 mg/g. Likewise, for lower concentration of $MgCl_2$ GO modified with IL gave three times higher adsorption coefficient. However, for lower concentration of NaCl the adsorption capacity did not increase. On the contrary, for higher concentration of NaCl the adsorption capability of GO-IL increased by 30 % compared to GO alone. Similarly, the adsorption coefficient for $CaCl_2$ and $MgCl_2$ at higher concentrations was higher for GO functionalized with IL compared to GO.

IL functionalized GO has an enhanced adsorption capacity due to less agglomerated structure created by functionalization with IL. Moreover, the positively and negatively charged groups of IL have ability to attract $CaCl_2$, Mg_2

and NaCl salt ions due to electrostatic forces. Additionally, high solubilities of PAN with these inorganic salts increases the affinity of such ions to be attracted to the surface of GO, where it can be further adsorbed. This resulted in greater adsorption capabilities of GO functionalized with IL-PAN compared to GO without the functionalization.

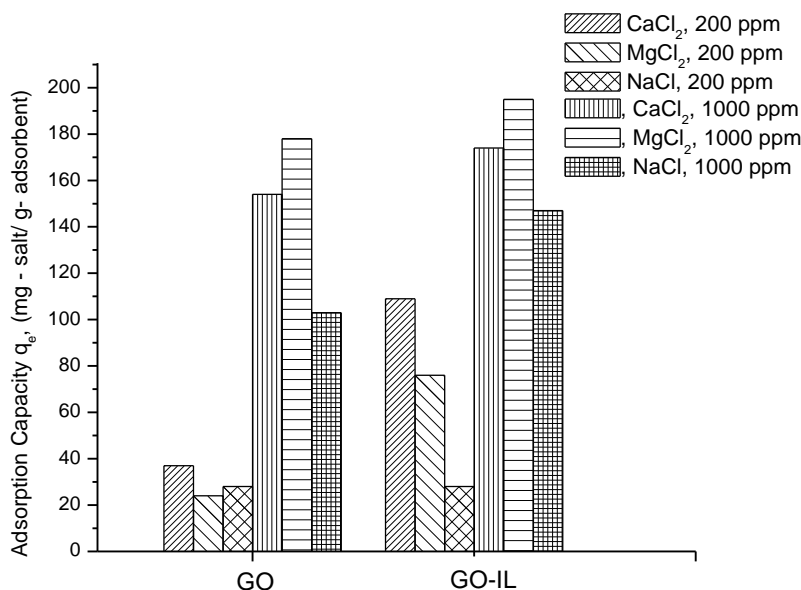


Fig. 5. Adsorption of CaCl₂, MgCl₂ and NaCl salts on GO and GO modified with IL

Table 4. Adsorption Capacities for GO and GO modified IL for CaCl₂, MCl₂ and NaCl salts

Salt Concentrations	Adsorption capacity, q_e , (mg-salt/g-adsorbent)	
	GO	GO-IL
CaCl ₂ , 200 ppm	37	109
MgCl ₂ , 200 ppm	24	76
NaCl, 200 ppm	28	28
CaCl ₂ , 1000 ppm	154	174
MgCl ₂ , 1000 ppm	178	195
NaCl, 1000 ppm	103	147

4. Conclusion

TGA and Raman Spectroscopy results have shown that Propylammonium Nitrate (PAN) has been successfully attached on double-layer GO. The TGA analysis has shown that 10 wt.% of PAN was loaded on GO. The Raman Spectroscopy results revealed an increase in the I_D/I_G index and suggested physical functionalization of double-layer GO with PAN. From TOC analysis it has been determined that 6% of IL is leaching from GO after 7 hours of continuous stirring. Adsorption coefficient increased around 3 times for lower concentrations of CaCl₂ and MgCl₂ and 10 % for higher concentrations of these inorganic salts. However, for NaCl the adsorption capacity increased higher than 40 % for 1000 ppm of salt solution and did not changed for lower concentration of NaCl. GO modified with IL generally showed better adsorption capability for both concentrations of NaCl, MgCl₂ and CaCl₂ salts compared to GO alone.

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