

IMPROVING THE PERFORMANCE OF DESALINATION USING GO-POLYMER NANOCOMPOSITES

P.Rajakani¹, A.Mubeena Fathima², S.Muthu Pavithra³, P.Nafiza Parvin⁴

Abstract-Graphene oxide (GO) nanosheet and GO-Polyaniline (PA), GO-Polyglycine (PG) and GO-Poly o- toluidine (POT) nanocomposites are synthesized successfully by Hummer's method. FTIR spectra showed the incorporation of polymer into GO. The size and morphology of the GO and GO-Polymer are characterised by SEM images. TGA-DTA is used for the quantitative analysis and thermal stability of the synthesised nanocomposites. pH meter and conductivity bridge are used to find out the improvement of Desalination process while using GO-Polymer nanocomposite than GO.

1. INTRODUCTION

Desalination is one of the most promising approaches to supply new fresh water in the context of a rapidly growing global water gap. But although oceans and seas contain about 97% of the world's water, desalination today only accounts for a fraction of a percent of the world's potable water supply [1]. But thermal desalination methods such as multistage flash and multiple-effect distillation are several times more energy-intensive [1,2]. Graphene like nano porous materials have a greater deal to offer over existing technologies for desalination[3]. Nanotube membranes may prove to be effective for water filtration and desalination processes that would require substantially less energy than reverse osmosis.^[4]

There is a huge scope for graphene-based materials to be used as membranes for desalination. A very recent study has confirmed that 100% salt rejection can be achieved for commonly used ions by utilizing single layer nonporous grapheme. However, the cost effective fabrication procedure for graphene oxide membranes with precise control of pore size can offer a practical solution for filtration if one can achieve 100% percent salt rejection [5].

Besides, these diverse functional groups also provide a foundation for composite constructions such as graphene oxide-polymer composites, which are found to reinforce the mechanical stability and further enhance the membrane properties. In addition, the oxygenated functional groups endow graphene oxide with hydrophilicity and pH sensitivity[6,7]. Since the hydrophobic region regulates the water flow, the functional group density should be well controlled during the fabrication. In the present paper, attempts have been made to synthesize graphene oxide and Go-polymer nano composites to desalinate the salt water. At present a conventionally modified hummer's method is the primary method for preparing GO.

2. EXPERIMENTAL TECHNIQUE

2.1. MATERIALS & INSTRUMENTATION

The Graphene, aniline, o-toluidine and glycine used were analytical reagent (AR) grade from Sigma-Aldrich Co. FTIR spectroscopy (Model: SHIMADZU) of GO & GO-polymer were studied in the frequency range of 400–4000 cm^{-1} . UV-Vis spectra of the samples were recorded on a JASCO V530 UV-Vis spectrophotometer. Morphological study of the GO & GO-polymer were carried out using scanning electron microscopy (SEM Model: JEOL JSM 6360) operating at 25 kV. X-ray diffraction (XRD) was carried out using the Bruker AXS D8 Advance using CuK_α radiation source energized at 40 KV ($\lambda=0.154$ nm). Samples were scanned at a rate $29.5^\circ \text{sec}^{-1}$ from 1° to 80° in 2θ .

2.2. SYNTHESIS OF GO & GO-POLYMER NANOCOMPOSITE

Graphene oxide (GO) is synthesized from graphite powder using modified Hummer's method. In brief, 1 g of graphite and 0.5 g of sodium nitrate are mixed together followed by the addition of 23 ml of conc. sulfuric acid under constant stirring. After 1 h, 3g of KMnO_4 is added gradually to the above solution while keeping the temperature less than 20°C to prevent overheating and explosion. The mixture is stirred at 35°C for 12 h and the resulting solution is diluted by adding 500 ml of water under vigorous stirring. To ensure the completion of reaction with KMnO_4 , the suspension is further treated with 30% H_2O_2 solution (5 ml). The resulting mixture are washed with HCl and H_2O respectively, followed by filtration and drying, graphene oxide sheets were thus obtained.

Graphitic oxide is prepared by the oxidation of pure graphite using Hummers' method. This prepared GO is further factionalized by treating it with concentrated HNO_3 acid for 2 hours followed by washing with water to reach pH 7. This treatment provides oxygen containing functional groups at the factionalized graphene oxide decorated by polymers with nitrogen using a chemical route.

¹ Department of Chemistry, V.O Chidambaram College, Tuticorin –628008, Tamilnadu.

² Department of Chemistry, V.O Chidambaram College, Tuticorin –628008, Tamilnadu.

³ Department of Chemistry, V.O Chidambaram College, Tuticorin –628008, Tamilnadu.

⁴ Department of Chemistry, V.O Chidambaram College, Tuticorin –628008, Tamilnadu.

SYNTHESIS OF GO-POLYMER NANOCOMPOSITE

In this method, the graphene oxide - poly aniline (GO-PA) nanocomposite is synthesized by bulk polymerization method of aniline using $K_2Cr_2O_7$ in a solution of 1 M HCl. Similarly graphene oxide- poly-o-toluidine (GO-POT), graphene oxide- poly glycine (GO-PG) are synthesized in the same method. The nanocomposite material is then filtered and washed with a large amount of water and subsequently with ethanol to remove the residual oxidant. Finally, all nanocomposites were washed with acetone and dried at 60°C.

3. RESULTS & DISCUSSION

3.1. FOURIER TRANSFORM INFRARED ANALYSIS

Fig.1 and table 1 shows the FTIR spectra of GO and GO-Polymer nanocomposites. The broad bands appeared at the range of $3442 \pm 7 \text{ cm}^{-1}$ is known that it is -OH stretching, C=O and C-O are proved that the GO is present in the nitrogen containing polymer nanocomposites. The nitrogen is present in the GO nanocomposite which is confirmed by C=N stretching and N^+H stretching appeared at $1459\text{-}1461 \text{ cm}^{-1}$ and $1115 - 1118 \text{ cm}^{-1}$.

3.2. UV- VIS SPECTROSCOPY

Two characteristic peaks are observed in GO and GO-polymer nanocomposites. The first maximum absorption peak at $\sim 237 \text{ nm}$ attributable to $\pi\text{-}\pi^*$ transition of the atomic C-C bonds^[8]. Second shoulder peak at $\sim 300 \text{ nm}$ due to $n\text{-}\pi^*$ transitions of aromatic C=O bonds^[9]. The graphene oxide λ_{max} values are confirmed by the UV characteristic peaks. The λ_{max} value is slightly shifted to 235 to 242nm while adding polymer into GO and the absorption peak intensity also increased which is predicted that polymer is incorporated into the GO nanosheet.

3.3. SCANNING ELECTRON MICROSCOPY

The SEM images of GO (Fig.3a) shows that the structure resulting in the form of nanosheet. The image (Fig. 3b) shows GO-PN which clearly displays, the polyaniline is spread around the surface it look like a foams are spread on rocks. GO-POT (Fig. 3c), the POT is formed as a layer in between the nanosheet graphene oxide. Polyglycine is incorporated into the GO nanosheet (Fig.3d) it look like a growth of algae on the rock. From the above information, it can be concluded GO is formed as a nanosheet and polymer perfectly incorporated into the GO nanosheet which is confirmed that in our nanocomposite systems there is a good compatibility between the organic and inorganic compounds.

3.4. X-RAY DIFFRACTION STUDY

In the XRD spectrum two peaks are observed in the GO and GO-polymer nanocomposite in Fig.4. The first peak appeared in the range $20\text{-}30^\circ$ which is broad in the case of GO. While adding the polymer into GO, the intensity of the first peak become narrow and very sharp. This information proved that the polymer incorporated into the GO nanosheet.

3.5. TGA/DTA STUDY

The TG curve of GO (fig.5) shows a significant weight loss up to 210 which is attributed to the loss of CO and CO_2 from the decomposition of the oxygen-containing functional groups and carbon oxidation, respectively. The graphene oxide nanosheets show an obvious mass loss in the temperature range of $200\text{-}300^\circ\text{C}$, illustrating a much lower thermal stability compared to natural flake graphite. [10, 11]

The mass loss below 200°C can be attributed to the evaporation of absorbed water. A slight mass loss appears between 200°C and 500°C presumably owing to the decomposition of some residual oxygen containing group. The first weight loss $\sim 20\%$ ($200^\circ\text{C}\text{-}500^\circ\text{C}$) is the oxygen containing groups of GO and GO-polymer nanocomposite and partly to thermal decomposition of composite matrix [12]. The second weight loss $\sim 40\%$ ($500^\circ\text{C}\text{-}800^\circ\text{C}$) is ascribed to the weight loss of composite matrix [13]. GO polymer-nanocomposite have a better thermal stability than GO.

4. APPLICATION

Graphene Oxide were studied for desalination of seawater using reverse osmosis. Graphene oxide membrane highly used to purify the water. In our research, synthesized GO and GO with different polymer are using to find out the effect of desalination.

4.1 USING PH METER

Sea water is collected from the Indian Ocean. This water is desalinated by vapour collection method as discussed in earlier experimental section 3.3.6. About 0.02g of synthesized GO is added to the 20mL of sea water. The reaction mixture is boiled approximately 30 minutes and the resulting vapours are collected in the test tube. Similarly this process are carried out GO-PN, GO-POT and GO-PG nanocomposite.

The desalinated sea water is confirmed by pH value and conductivity. The pH of sea water 7.70 which is slightly basic in nature. After desalination of sea water with GO, the pH range is 7.16. Desalination process was also carried out by GO-PN, GO-POT and GO-PG. The pH value of GO-PN is 6.83, GO-POT is 6.51 and GO-PG is 7.50 which is confirmed the sea water is desalinated by this method.

When comparing the GO and GO-polymer nanocomposite using desalination process, the GO- polymer nanocomposite show a better result than GO. Particularly GO-POT show a very good result for desalination.

4.2 USING CONDUCTIVITY BRIDGE

Superior electrical conductivity is the most important property of graphene. More generally desalination is refers to the

removal of salts and minerals from target substances. The conductivity value would prove the desalination. Various polymer such as GO-PA nanocomposite, GO-POT nanocomposite, GO-PG nanocomposite and seawater have been used as matrices to prepare electrically conductive GO-polymer nanocomposites. The table-3 shows the conductivity values of various polymer with graphene oxide and GO-polymer nanocomposite. The conductivity is measured after desalination using conductivity meter. The conductance of seawater is around 1.0 (mho^{-1}). The conductance of GO is 0.62. But the conductivity of GO-polymer nanocomposite slightly decrease from GO-PG to GO-POT. This conductivity measurements were that confirmed by desalinated of seawater because the H^+ concentration is reduced by desalination. So the conductance is also reduced. From the above result it can be concluded that the GO-POT show very good result in the desalinated process compare than other GO-PA, GO-PG nanocomposite and GO which is proved by the result of pH.

5. CONCLUSION

GO nanosheet and GO-PA, GO-POT and GO-PN nanocomposites are synthesized successfully by Hummer's method. Polymers are perfectly incorporated into GO which is confirmed by FTIR, UV, SEM and XRD. GO-Polymer nanocomposites are good thermal stability which is confirmed by TGA/DTA. The GO-POT is a very good desalinated nanocomposite. GO-PA is moderate desalinated nanocomposite compare than that of GO-PG nanocomposite and GO nanosheet which is proved by pH meter.

REFERENCE

- [1] Addams, L.; Boccaletti, G.; Kerlin, M.; Stuchtey, M. Group, 2. W.R.; McKinsey and Company Charting Our Water Future: Economic Frameworks to Inform Decision-making; 2030 Water Resources Group, 2009.
- [2] Spiegler, K.; El-Sayed, Y. Desalination 2001, 134, 109–128.
- [3] Suk, M.; Aluru, N. R. J. Phys. Chem. Lett. 2010, 10 (1), 1590–1594.
- [4] Cao, Liwei. "Patent US8222346 – Block copolymers and method for making same". Retrieved July 9, 2013.
- [5] B. Zhu, et al., Application of robust MFI-type zeolite membrane for desalination of saline wastewater, J. Membr. Sci., 2015, 475, 167–174.
- [6] B. Mi, Graphene oxide membranes for ionic and molecular sieving, Science, 2014, 343, 740–742.
- [7] B. Ganesh, A. M. Isloor and A. Ismail, Enhanced hydrophilicity and salt rejection study of graphene oxide-polysulfone mixed matrix membrane, Desalination, 2013, 313, 199–207.
- [8] S. Xu, L. Yong, P. Wu, ACS Appl. Mater. Interfaces, 2013 (5), 654.
- [9] L. Shahriary, Anjalía, Athawale, Int. J. Renew. Energy Environ. Eng. 2014 (2), 1.
- [10] G. X. Wang, J. Yang, J. Park, X. L. Gou, B. Wang, H. Liu and J. Yao, J. Phys. Chem. C, 2008, 112, 8192–8195.
- [11] S. Park, J. An, I. Jung, R. D. Piner, S. J. An, X. S. Li, A. Velamakanni and R. S. Ruoff, Nano Lett., 2009, 9, 1593–1597.
- [12] Bai X, Hu X, Zhou S, Li L, Compos. Sci. Technol. 2015;110:166-175
- [13] Hu X, Xu L. Polymer. 2000; 41:9147.

Table 1

S.No	FREQUENCY RANGE (cm^{-1})				FUNCTIONAL GROUP
	GO	GO-PA	GO-POT	GO-PG	
1	3442	3448	3449	3448	O-H stretching
2	2924	2924	2924	2924	Anti- sym $=\text{CH}_2$
3	2854	2853	-	2853	Symmetry $=\text{CH}_2$
4	2361	2362	2363	2363	CO_2 Stretching
5	1636	1637	1638	1637	-C=O Stretching
6	-	1461	1459	1461	-C=N Stretching
7	1383	1383	1383	1384	C-O Stretching
8	-	1117	1115	1118	$\text{N}^+\text{H}=\text{Stretching}$
9	874	838	752	839	C=C stretching
10	593	619	670	670	$=\text{C-H}$ Bending

Table 2

S.No	Nano composite	Particle size in nm
1	GO	12.331
2	GO-PA	15.471
3	GO-POT	16.565
4	GO-PG	16.972

Table 3

Compounds	Conductivity (mho ⁻¹)
Seawater	1.0
GO	0.62
GO-PA	0.04
GO-POT	0.02
GO-PG	0.42