

# Studies on Enhanced Permeability of Graphitic Carbon Nitride Incorporated Polysulfone Composite Membranes

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## Abstract

Nanomaterial incorporated fabrication of Composite membranes and application of these membranes to Water treatment and for removal of monovalent and divalent ions from water can simultaneously improve hydrophobicity. In the present research work, a novel carbon based nanomaterial, Graphitic carbon nitride ( $gC_3N_4$ ) was adopted in polysulfone based composite membranes  $gC_3N_4$  in order to enhance the hydrophilicity through membrane permeability. The  $gC_3N_4$  was synthesized using thermal oxidation etching process and polysulfone membrane were synthesized using non-solvent phase inversion process. Pure water flux was measured for the fabricated membranes in dead-end filtration setup. The composite membranes with 1% and 1.75%  $gC_3N_4$  showed a good enhancement in hydrophilicity and hence an increased flux. However, the membrane with 2.5%  $gC_3N_4$  exhibited lower flux which may be attributed to the blockage of pores with increased wt. % of nanomaterial. The C/N atomic ratio of 0.7453 in  $gC_3N_4$  was observed which was close to the actual value of 0.75.

**Keywords:** Graphitic carbon nitride, Composite membranes, Hydrophilicity, Permeability

## 1.0 Introduction

Nanostructures such as zeolites, metal organic frameworks, ceramics and carbon-based materials have attracted considerable attention as alternative membrane materials to replace polymeric membranes due to good chemical resistance, high flux and high rejection rates. In majority of membrane applications, the most important challenge is to overcome irreversible fouling of the membranes which consequently increases the operating costs of membrane separation processes [1-5]. Also materials such as Graphene Oxide (GO) present limitations in the form of low dispersibility in the polymer phase, environment neutrality and deformation of nanopore edges at high operating pressures (~10MPa) [6]. Researchers have been focusing on more environmentally stable substitute which opened the doors to graphene 'like' nanomaterials. This

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is a new class of filler material for fabrication of novel polymeric nanocomposite membranes. It exhibits sheet like 2D structure similar to GO and has excellent mechanical properties, chemical stability and thermal stability. It is an environmentally neutral material and its synthesis requires low cost raw materials.

As a promising 2D graphene-like material, graphitic carbon nitride ( $gC_3N_4$ ) has been highlighted as a low-cost, robust, earth-abundant, and metal free semiconductor in fields including visible-light-active photocatalysis, energy conversion, and optoelectronics.  $gC_3N_4$  has a layered structure which is held together by van der Waals interaction. The carbon nitride layer comprises aromatic tri-s-triazine units connected by tertiary amines. The  $gC_3N_4$  offer a stable channel for small molecules such as water and hydrogen to rapidly pass through, while bigger molecules are retained.

The bulk  $gC_3N_4$  can be easily synthesized by adopting one step synthesis methods such as thermal oxidation etching process. Also  $gC_3N_4$  has good dispersibility in the polymer phase thus making it a favourable filler material for membrane fabrication [7]. These nanocomposite membranes are still in their development phase and thus only a few commercial membranes have been reported in the literature. Chen et al. [8] incorporated  $gC_3N_4$  nanosheets incorporated in skin layer of nanocomposite membranes with polyethersulfone base through the interfacial polymerization technique. The authors concluded that the membranes consisting of  $gC_3N_4$  nanosheets in the skin layer exhibited improved membrane throughput and also enhanced antifouling behavior with respect to Bovine serum albumin and humic acid rejection when compared with pristine Polyamide membranes.

Wang et al. [9] fabricated a hybrid membrane of  $gC_3N_4$  and polyacrylic acid (PAA) by creating a  $gC_3N_4$  and PAA dispersion and vacuum filtering the dispersion on polycarbonate membranes. The membranes were reported to exhibit significant increase in water flux though the membranes and higher rejection rates to Evan's Blue dye. Gao et. al.[10] reported the incorporation of  $gC_3N_4$  and acidified  $gC_3N_4$  ( $aC_3N_4$ ) nanoparticles into the skin layer of polyamide based thin film nanocomposite (TFN) membranes. The TFNs were fabricated through interfacial polymerization technique in which the  $gC_3N_4$  and  $aC_3N_4$  were dispersed along with the m – Phenylenediamine solution and then the skin layer of polyamide was cast on Polysulfone support membranes. The TFN membranes fabricated exhibited a generous increase in water flux and high rejection rates for NaCl removal in the Reverse osmosis range.

The membranes also showed an enhanced anti fouling tendency towards protein and natural organic foulants. The present research aims at incorporating  $gC_3N_4$  nanoparticles in polysulfone membranes fabricated by non-solvent based phase separation process and utilize the same to study the influence of nanomaterials on hydrophilicity of membranes through permeability studies.

## **2.0 Experimental Details**

### **2.1 Materials**

Melamine (99%) and Polysulfone (Avg. molecular weight – 35,000 by LS, avg. Mn – 16,000 by MO, pellets (Transparent)) and N – Methyl Pyrrolidone (99.5 %) were purchased from Sigma Aldrich, USA. DI water is used in sonication of  $gC_3N_4$ , in coagulation bath as anti – solvent, for storing membranes and to run the pure water flux tests on membranes.

### **2.2. Synthesis of graphitic carbon nitride**

Graphitic carbon nitride was synthesized by thermal oxidation ‘etching’ process [10]. In this process, melamine is heated at  $520^{\circ}C$  for 3 hours in a silica crucible to produce graphitic carbon nitride. The obtained graphitic carbon nitride is ground to a fine powder. The powdered  $gC_3N_4$  is calcined at  $500^{\circ}C$  for 2 hours. Thus obtained product is dispersed in DI water and sonicated for an hour. The obtained bulk  $gCN$  is dried, grounded and stored.

### **2.3 Fabrication of mixed matrix membranes**

18ml of N – Methyl Pyrrolidone (NMP) was taken in a reagent bottle and known amounts of  $gC_3N_4$  is added and the mixture is sonicated for 30 min. 4g of PSf was added slowly and the mixture was stirred for 24 hours to prepare the casting solution. After 24 hours, the stirring was stopped and the solution was kept in ultrasonic bath for around 30 minutes to degas the casting solution. A glass plate was washed with water and wiped with acetone to get a clean and smooth surface. Casting solution was slowly poured at one end of the plate and the membrane film was casted using glass rod in one single stroke. The cast film was exposed to air for about 20 seconds and then immersed in DI water bath. The membrane obtained, was kept in DI water for 24 hours for removal of residual solvent and then stored in a container of fresh DI water till subsequent use. All the other membranes were fabricated in a similar manner. The weight percentages of the nanoparticles added for the desired membranes are shown in Table 1.

**Table 1.** Membrane Composition

Membrane	PSf (g)	NMP (ml)	gC <sub>3</sub> N <sub>4</sub> (mg)	Composition (wt. %)
M0	4	18	0	-
M1	4	18	40	1.0
M2	4	18	70	1.75
M3	4	18	100	2.5

## 2.4 Characterization

The microstructural analysis of gC<sub>3</sub>N<sub>4</sub> was carried out in SEM (Hitachi SU 3500) equipped with EDS. X-ray Diffraction technique was adopted to investigate the crystalline structure of gC<sub>3</sub>N<sub>4</sub>. The nature of gC<sub>3</sub>N<sub>4</sub> was characterized using Bruker, D8 Advance Eco. The chemical structure of gC<sub>3</sub>N<sub>4</sub> synthesized was investigated using FTIR (Shimadzu IRAffinity-1S with HATR)

## 2.5 Permeability studies

Pure water flux studies were carried out to measure the flux and permeability of the membranes. A dead end filtration setup was used in order to perform the filtration-based studies. The feed inlet tank of filtration setup is filled with DI water. A membrane was fit into the membrane holder and fastened using a washer. Feed water was passed through the membrane at 2, 4, 6, 8 and 10 bar of pressures and permeate was collected for 10 minutes in order to determine the flux under steady state condition. At each pressure, permeate was collected for 3 trials each and the flux was computed using Equation (1). The average flux for the membrane at each of stated pressures was computed.

$$Q = \frac{V}{At} \quad (1)$$

where, Q = pure water flux in l/m<sup>2</sup>h, V = amount of water collected in litre, A = membrane area in m<sup>2</sup> and t = time in hr.

## 3.0 Results and Discussion

SEM micrograph of Fig. 1 indicates distributed form of gC<sub>3</sub>N<sub>4</sub> particle aggregates and particle size ranging from 700 nm to 2 μm. Smaller aggregates were due to bath sonication. It resulted in larger specific area and hence better dispersion in solvents and uniform distribution of nanomaterials in the membrane matrix. Table 2 presents elemental composition in the synthesized gC<sub>3</sub>N<sub>4</sub> particles. The C/N atomic ratio of 0.7453 in gC<sub>3</sub>N<sub>4</sub> was observed which is close to 0.75 of [8]. XRD results

of Fig. 2 indicated two characteristic peaks at  $2\theta$  angles of 27.10 and 12.50 which confirm the synthesis of  $gC_3N_4$  [9]. The strong peak at 27.53 ( $2\theta$  degrees) can be attributed to the conjugated aromatic planes stacking (0 0 2). Relatively weak peak is observed at 12.94 ( $2\theta$  degrees), which is attributed to in-plane structural packing motif of tri-s-triazine units (1 0 0).

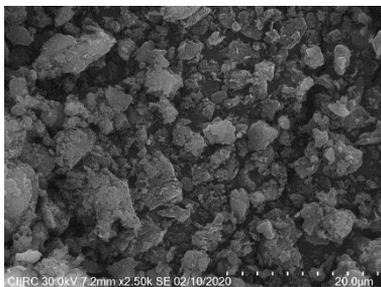


Fig. 1. SEM micrograph of sonicated  $gC_3N_4$

Table 2. Elemental composition of sonicated  $gC_3N_4$

Element	wt, %	Atomic %
C K	37.33	41.20
N K	58.42	55.28
O K	4.25	3.52

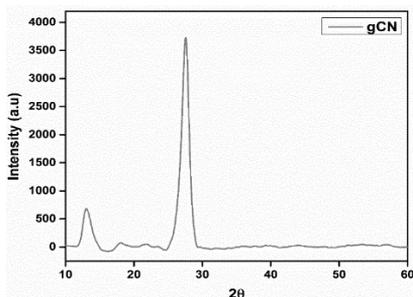


Fig. 2. XRD result of  $gC_3N_4$

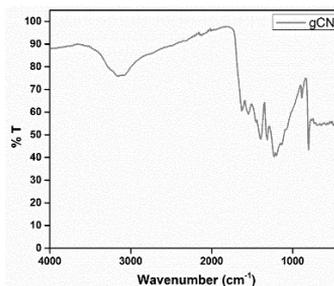


Fig. 3. FTIR result of  $gC_3N_4$

In case of  $gC_3N_4$ , the absorption bands at  $810\text{ cm}^{-1}$ ,  $1000\text{ to }1800\text{ cm}^{-1}$ ,  $2900\text{ to }3600\text{ cm}^{-1}$  wavenumbers have been observed in the literature [9]. In the sample of synthesized (Fig.3)  $gC_3N_4$ , absorption bands at  $802.38\text{ cm}^{-1}$ ,  $1000\text{ to }1850\text{ cm}^{-1}$  and  $2950\text{ to }3500\text{ cm}^{-1}$  wavenumbers were observed which predicts that synthesized  $gC_3N_4$  is in agreement with available  $gC_3N_4$  literature. The sharp absorption band at  $802.38\text{ cm}^{-1}$  represents bending vibrations of tri-s-triazine rings. The absorption band in  $1000\text{ to }1850\text{ cm}^{-1}$  corresponded to stretching vibration of connected

units of C-(C)-C (full condensation) or bridged C-NH-C (partial condensation). The absorption band at 2950 to 3500 $\text{cm}^{-1}$  can be attributed to hydrogen bonding interactions and N-H stretching vibration.

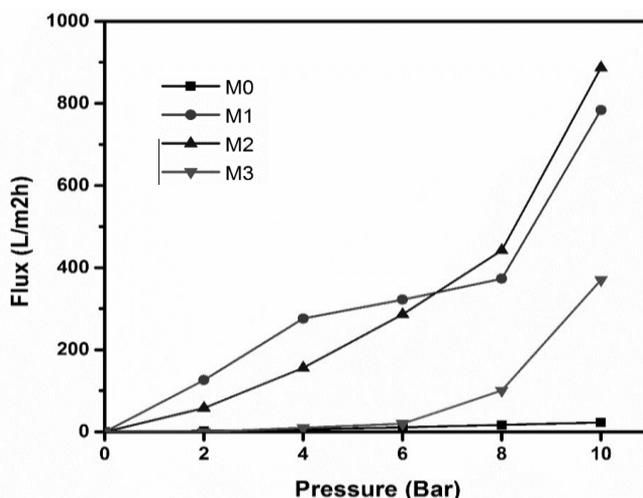


Fig. 4. Pure water flux studies of composite membranes

The variation of flux with pressure for all types of membranes (M0, M1, M2, and M3) is as shown in Fig. 4. The slope of each of the curves represents the permeability of the membrane. The flux of the membrane varied linearly with pressure ranging from 2 to 10 bar. As evident from the plot, the presence of  $\text{gC}_3\text{N}_4$  in the membranes improved the hydrophilic nature of the inherently hydrophobic polysulfone membranes. The composite membranes with 1% and 1.75%  $\text{gC}_3\text{N}_4$  showed good improvement in hydrophilicity and hence an increased flux. The membrane with 2.5%  $\text{gC}_3\text{N}_4$  showed a decreasing trend in flux which may be attributed to the fact that the increased nanomaterial might block the pores of the membrane thereby decreasing the flux of the membranes. The sudden increase in flux after 8 bars for M1, M2 and M3 membranes may be attributed to the widening of pores in membranes due to application of high pressure.

## 4.0 Conclusions

Influence of  $\text{gC}_3\text{N}_4$  nanoparticles on the hydrophilicity of the polysulfone composite membranes is reported. The  $\text{gC}_3\text{N}_4$  incorporated PSf membranes were fabricated by non-solvent induced phase separation process. The composite membranes with 1% and 1.75%  $\text{gC}_3\text{N}_4$  showed a good improvement in hydrophilicity and hence an increased flux. However, the membrane with 2.5%  $\text{gC}_3\text{N}_4$  showed a decreasing trend in

flux which may be attributed to the fact that the increased nanomaterial might block the pores of the membrane thereby decreasing the flux of the membranes. The sudden increase in flux beyond 8 bars for M1, M2 and M3 membranes may be attributed to the widening of pores in membranes due to application of high pressure. Thus, gC<sub>3</sub>N<sub>4</sub> incorporated PSf composite membranes have enhanced hydrophilicity and improved permeability than the pristine polysulfone membranes and can be further employed for filtration applications.

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