Nanofiltration membranes composed of carbonized giant cane and Pongamia meal binder for ion sieving in water and molecular sieving in organic solvents

K.R. Balaji*a,ψ, Mohamed H. Abdellahb,ψ, V.G. Dileep Kumar*a, M. S. Santoshac, Roopa Reddyd,
Surender Kumar*e, Gyorgy Szekelyb

a Coal to Hydrogen Energy for Sustainable Solutions (CHESS) Division, CSIR - Central Institute of Mining and Fuel Research (CIMFR), Digwadih Campus, Dhanbad – 828108, Jharkhand, India.
b Advanced Membranes and Porous Materials Center, Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology, (KAUST), Thuwal, 23955-6900, Saudi Arabia
c Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India.
d Centre for Incubation, Innovation, Research and Consultancy (CIIRC), Jyothy Institute of Technology, Thataguni, Off Kanakapura Road, Bangalore - 560082, Karnataka, India.
e CSIR-Advanced Materials and Processes Research Institute (AMPRI), Bhopal - 462026, Madhya Pradesh, India.
ψ M.A. and K.R.B. contributed equally to this study.

gyorgy.szekely@kaust.edu.sa; www.szekelygroup.com

Published in Sustainable Materials and Technologies, Elsevier: https://doi.org/10.1016/j.susmat.2022.e00517

Abstract: Climate change and other environmental problems necessitate the use of renewable resources and the development of sustainable technologies. Thus, giant cane, which is naturally abundant, and a plant-based binder extracted from Millettia pinnata seeds were used to fabricate carbon-based composite membranes. A continuous and uniform layer of a carbonized giant cane was formed on a porous support using a simple filtration method. The hardness of the membranes increased with the carbon content. The increase in the carbon content in the membrane yielded a looser and more selective nanofiltration membrane; the water permeance increased from 13 to 19 L m⁻² h⁻¹ bar⁻¹ and the NaCl/MgSO₄ selectivity doubled from 10 to 20. Similarly, the rejection of five different salts and seven organic molecules decreased in water and acetone, respectively. The
acetone permeance and molecular weight cutoff increased from 7 to 12 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) and from 577 to 795 g mol\(^{-1}\), respectively. The long-term performance tests on the membranes indicated a stable rejection of higher than 99% for rose bengal and a stable steady-state flux over a week of continuous filtration. The membranes exhibited good stability and high permeance in different organic solvents, including a harsh polar aprotic solvent, i.e., \(N,N\)-dimethylformamide. The toxicity of the giant cane carbon and the binder was examined via a cytotoxicity assay using NIH 3T3 cells. No toxicity was observed for either material. This study proposes a sustainable route for preparing aqueous and organic solvent nanofiltration membranes using natural nontoxic resources.

**Keywords:** giant cane; Millettia pinnata; membrane; nanofiltration; carbon

1. **Introduction**

The constantly growing industrial development is adversely affecting human health and the entire ecosystem, resulting in water, air, and soil pollution [1]. Membrane separations are promising processes for water purification and separation in organic solvents. Compared with traditional separation methods, membrane technology is considered an environmentally friendly technique that conserves energy, is cost-effective, and is easy to operate (either as a single or a hybrid process).

The success of membrane technology in aqueous systems has encouraged its use in organic streams, what is now known as organic solvent nanofiltration (OSN). OSN is considered a promising alternative to energy-intensive separation processes such as distillation and evaporation. The primary advantage of OSN over conventional thermal separation processes is that OSN does not involve any phase change, which reduces energy requirements of this process [2]. This
emerging technology has considerable potential in several industries, such as pharmaceuticals and petrochemicals, in which it can separate solutes having a molecular weight of 100–2,000 g mol$^{-1}$ in organic media [3]. Commercial membranes available on the market are typically made of hydrocarbon-based polymers and toxic solvents such as \(N\)-methylpyrrolidone, \(N,N\)-dimethylformamide, and \(N,N\)-dimethylacetamide, which have a negative impact on the environment [4].

Sustainable materials and processes that do not adversely affect human health and the environment are necessary for fabricating membranes. Thus, hydrocarbon-based polymers and harmful solvents should be replaced with bioderived ones to fabricate efficient membranes that offer good selectivity and permeance with minimum environmental impact.

Recently, studies demonstrated that membranes prepared using sustainable and environmentally friendly raw materials are comparable to those prepared using hydrocarbons [4–12]. Many biomass-based materials, e.g. date-seed agricultural waste [7], shrimp-farming waste chitosan [8], biosourced fully recyclable polyesters [4], oils and fats [13], plant-based monomers [14], bamboo [15], cellulose [16], polyhydroxyalkanoate [17], and alginate [18], were successfully used to fabricate robust nanofiltration membranes for separation in both aqueous and organic solvents. Recently, green monomers, polymers, and solvents are being increasingly used for membrane fabrication. In particular, green solvents such as dimethyl carbonate [15], deep eutectic solvents [19], PolarClean [4], dimethyl isosorbide [20], eucalyptol [8], TamiSolve [21], \(p\)-cymene [14], \(\alpha\)-pinene [5,6], and Cyrene [17] were used for membrane preparation. Moreover, TamiSolve was proposed for activating thin-film composite OSN membranes [22]. The activated membranes exhibited comparable and even superior performance to hydrocarbon-based membranes for oil separation and organic solvent applications.
Activated carbon (AC) materials are characterized by their high surface area, significant chemical stability, tunability of the surface and structure, and ease of production. They can be derived from biomass sources such as coconut shells [23], banana peel [24], straw [25], fungal mycelium [26], tannery waste [27], and cassava rhizome [28]. Moreover, they have been used for various applications, including electrode preparation [29], water treatment [30], air purification [31], resource recovery [32,33], and separation processes [34]. AC materials are often used as adsorptive fillers in membranes [35–38]. However, they are rarely used in transport membranes [39,40] and have not been previously reported in organic solvent nanofiltration. In this study, AC-based OSN membranes were developed for the first time.

In this study, carbon-based composite nanofiltration membranes with different carbon contents were prepared (Figure 1). The membranes were composed of a carbonized natural Arundinaria gigantea cane (commonly known as giant cane, GC) and Pongamia meal extract as a natural binder. The nanofiltration performance was evaluated in aqueous and organic streams by measuring the rejection of salts in water and organic solutes in acetone, respectively. Moreover, the long-term performance of membranes and their stability in various organic solvents were investigated. Finally, cytotoxicity studies were performed to evaluate the toxicity of the prepared membranes.
2. Experimental

2.1. Materials. The GC was obtained from the Agriculture Science Campus, Hebbal, Bangalore, India. Hydrochloric acid (HCl), potassium hydroxide (KOH), sodium chloride (NaCl), sodium sulfate (Na$_2$SO$_4$), calcium chloride (CaCl$_2$), magnesium chloride (MgCl$_2$), magnesium sulfate (MgSO$_4$), and organic markers including styrene dimer (236 g mol$^{-1}$), estradiol (272 g mol$^{-1}$), methyl orange (327 g mol$^{-1}$), losartan (423 g mol$^{-1}$), remazol brilliant blue (627 g mol$^{-1}$), roxithromycin (837 g mol$^{-1}$), and rose bengal (974 g mol$^{-1}$), were purchased from Merck, Germany. Solvents, including acetone, acetonitrile, toluene, heptane, benzene, ethanol, methanol, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-pyrrolidone (NMP), and tetrahydrofuran (THF), were obtained from Sigma Aldrich. All chemicals were used as received without further modification. A nylon support, with porosity of 0.22 µm and thickness of 0.13 mm, was obtained from Pall Corporation.
2.2. **Carbonization of giant cane.** A known amount of GC was thoroughly washed using distilled water and then dried. The dried GC was carbonized in a tubular furnace at 450 °C for 2 h under an inert nitrogen atmosphere. The resulting carbon was then treated with a 10 wt% KOH solution (1:3 g GC g⁻¹ solution) for 12 h, followed by drying at 110 °C for 12 h. The dried GC was then carbonized at 800 °C for 2 h under an inert atmosphere. Finally, the carbon powder obtained was thoroughly washed with distilled water and 0.1 M HCl to neutralize the pH.

2.3. **Preparation of the Pongamia meal binder.** The natural binder, which is a byproduct obtained during the oil extraction from Millettia pinnata seeds, was recovered as a meal. This meal was dissolved in 0.1 M NaOH, and stirred overnight to obtain a homogenous solution. Next, the solution was thoroughly filtered to remove any traces of impurities and used as a natural binder in the membrane preparation. The solution was placed in a tightly sealed plastic container and stored at room temperature for subsequent use.

2.4. **Fabrication of carbonized giant cane composite membranes (GCM).** The membranes were prepared on a porous nylon support (diameter = 47 mm) using a vacuum-supported filtration method. The carbonized GC (0.1, 0.5, and 0.75 mg mL⁻¹) was dispersed in the natural binder solution to yield different membranes, which were designated as GCM-10, GCM-50, and GCM-75, respectively. The dispersion was sonicated using a probe-sonicator for 0.5 h, followed by stirring at 650 rpm for 12 h to obtain another dispersion. The obtained dispersion was filtered on the support and allowed to dry at 50 °C for 24 h. Composite membranes, with diameter of 40 mm, were then obtained.

**Evaluation of the membrane performance.** The nanofiltration performance was investigated using crossflow membrane cells having an effective membrane area (A) of 12.57 cm². The experiments were performed at a transmembrane pressure (ΔP) of 5–30 bar, a temperature of 25
°C, and a solution flow rate of 10 L min⁻¹ to mitigate concentration polarization. The nanofiltration performance of membranes in aqueous and organic streams was evaluated by measuring the permeance of solvents, as well as the rejection of different salts in water (1000 ppm) and organic markers in acetone (100 ppm). The permeate flux was allowed to stabilize before the measurement by running the filtration for at least 16 h. The permeate volume (V) was then measured over time (t) and used to calculate the flux by Eq. (1). The solute rejection (R) was calculated based on the solute concentration in the permeate (Cp) and feed (Cf) streams using Eq. (2). The solvent permeance (P, L m⁻² h⁻¹ bar⁻¹) was calculated based on the normalized values of the flux and the transmembrane pressure (Δp). Salt permeance (Ps, g m⁻² h⁻¹) during the nanofiltration process was calculated as per Eq. (3), and the permeation selectivity (α) of NaCl to MgSO₄ was estimated using Eq. (4).

\[
F (L\ m^{-2}h^{-1}) = \frac{V}{A \times t} \quad \text{Eq. (1)}
\]

\[
R (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad \text{Eq. (2)}
\]

\[
Ps (g\ m^{-2}h^{-1}) = F \cdot C_p \cdot (1 - R) \quad \text{Eq. (3)}
\]

\[
\alpha = \frac{P_{NaCl}}{P_{MgSO_4}} \quad \text{Eq. (4)}
\]

2.5. **Membrane characterization.** The morphology and thickness of membranes were examined using surface and cross-sectional scanning electron microscopy (SEM) on a Magellan
instrument at an acceleration voltage of 5 kV and current of 0.1 pA. Before imaging, the samples were submerged in liquid nitrogen, fixed on the stub using a Cu tape and coated with a 4 nm-thick Pt layer using Quorum Q150TES under Ar atmosphere to make them electrically conductive. At least five measurements were conducted on each sample at different locations. These measurements were then used to determine the average thickness using ImageJ. The water contact angle of membranes was obtained by the Kruss EasyDrop instrument using the sessile drop method. Dried membrane samples were fixed on a clean glass plate by double face tape and used for analysis. Water droplets (volume = 4 μL) were gently placed on different locations of each sample, and the contact angle was determined using the Young–LaPlace fitting model. FTIR analysis (32 scans) was conducted within a range of 600–4000 cm$^{-1}$ using the Alpha-P instrument (Bruker Instruments). The surface roughness of the membranes was analyzed using atomic force microscopy (AFM) on a BioAFM Burker Multimode 8 instrument. The imaging was conducted at 25 °C on an area of 20 × 20 μm using the standard tapping mode in air at a scanning rate of 1 Hz. The average mean squared roughness ($R_q$) was analyzed using Gwyddion.

The crystallographic arrangements of the composite carbon powder were examined using a powdered X-ray diffractometer (Bruker D8 ADVANCE) over an angular range (2θ) of 5°–80°. X-ray photoelectron spectroscopy (XPS) analysis was conducted using an Axis Ultra Hybrid spectrometer (Kratos Analytical) equipped with a monochromatic Al Kα X-ray source with a base vacuum pressure of 5 × 10$^{-9}$ mbar ($hν = 1486.6$ eV, spot size = $300 \times 700$ μm, and emission = 10 mA at 150 W). Charge neutralization was achieved using a filament. Binding energy scale calibration was performed for each sample using C–C in the C 1s photoelectron peak at 285 eV. Data analysis and curve fitting were achieved using CasaXP 2.3.24. The mechanical hardness of membranes was assessed by the nanoindentation technique using a NanoTest Vantage instrument.
with a pyramidal diamond indenter. Membrane samples (1 cm²) were cut and fixed to a Si wafer using superglue. At least four indentions were obtained per specimen, and the average value of the hardness was recorded.

Thermogravimetric analysis (TGA) of the GC carbon and their composite membrane was performed using a Jupiter STA 449 F1 instrument at a 10 °C rate of increase in the temperature within a range of 25–600 °C under N₂ atmosphere. The specific surface area of the carbonized GC was studied using a Brunauer–Emmett–Teller (BET) surface analyzer (BELSORP Max) after degassing the samples at 180 °C for 6 h.

**2.6. In-vitro cytotoxicity studies.** The cytotoxicity of the Pongamia meal and the carbonized GC was determined using a 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) assay. NIH 3T3 cells were cultured in Dulbecco's Modified Eagle Medium (DMEM, Hi-Media Laboratories Pvt Ltd, India) supplemented with fetal bovine serum (10 wt%, Hi-Media Laboratories Pvt Ltd, India), and the cells were maintained at 37 °C in a 5 v% CO₂ incubator. The stock solution of the cells (100 µL, 1 × 10⁵ mL⁻¹) was seeded in 96 well plates and incubated overnight at 37 °C. The stock solutions for all three test samples were prepared at a concentration of 1 mg mL⁻¹ in a sterile Milli-Q water followed by sonication for 15 min. It was then diluted to 100, 50, and 10 µg mL⁻¹. Sterile water was used as a control solution. After overnight incubation of these cells, samples (100 µL) from each concentration of the carbonized GC, Pongamia meal, and the control samples were inoculated in triplicate wells in 96 well plates and incubated for 48 and 96 h. At the end of each incubation time, the media containing these samples were aspirated and carefully washed using phosphate buffered saline (PBS). A 100 µL volume of the MTT solution (1 mg mL⁻¹) was added to each well, followed by incubation for 3 h. After incubation, the MTT reagent was carefully aspirated, and 100 µL DMSO was added and incubated for 10 min.
to dissolve the purple formazan crystals. The purple color of the dissolved crystals was spectrophotometrically analyzed by measuring its optical density (OD) at 570 nm using a microplate reader (Thermofisher Multiskan GO).

3. Results and Discussion

3.1. Structural and morphological analysis. The XRD analysis of the carbonized GC demonstrated a strong peak at $2\theta = 24.62^\circ$, which corresponds to the (002) plane (Figure 2a). This confirms that the formed carbon has an amorphous structure and randomly stacked layers [41]. Figure 2b shows the FTIR spectra of the carbonized GC, binder, nylon support, and the membranes. The intensity of the distinguished peaks of nylon at 3300 cm$^{-1}$ (N–H), 2930 cm$^{-1}$ (–CH$_2$), 1640 cm$^{-1}$ (C=O), and 1538 cm$^{-1}$ (N–H) decreased because the surface of the nylon support was covered with the carbonized GC and binder. The broad peak of the GC membranes at 3000–3600 cm$^{-1}$ corresponds to the overlapping of the O–H group of the binder with the N–H group of the nylon support. All membranes exhibited strong peaks at 1630, 1540 and 1050 cm$^{-1}$, which correspond to the C=O, N–H, and C–O stretching, respectively, in the carbonized GC and the binder. The small peak at 2930 cm$^{-1}$ in all membranes can be attributed to the C–H stretching, which confirms the presence of the binder and nylon support.
Figure 2. X-ray diffraction patterns of the carbonized giant cane; b) FTIR spectra of the carbonized giant cane, binder, nylon substrate, as well as the GCM-10, GCM-50, and GCM-75 membranes; c) TGA analysis of the giant cane carbon, binder, membranes, and nylon substrate; and d) high-resolution XPS analysis of the membranes.

Figure 2c shows the thermal properties of the materials. The initial weight loss up to 100 °C in all samples can be attributed to water loss. The carbonized GC exhibited a mass loss of 24% up to 800 °C, which can be attributed to the loss of high-boiling-point components. This indicates the good thermal stability of GC carbon. The binder remained stable up to 200 °C, followed by a mass loss of approx. 67% up to 800 °C. The nylon support exhibited good thermal stability up to 375 °C before it completely decomposed. The composite membranes demonstrated a similar trend with a gradual decrease in weight, which could be attributed to the loss of high-boiling-point components, before they decomposed at 375 °C. This indicates the good thermal stability of the composite membranes. Figure 2d shows the deconvolution of C 1s, N 1s, and O 1s high-resolution XPS spectrum. The composite membrane demonstrated a C–O peak stronger than that of the nylon.
support; however, the intensity of the C=O peak decreased with the increase in the carbon content in the membrane. This suggests a uniform coverage of the nylon surface with a continuous layer of carbonized GC and agrees with the C–N peak (at 400 eV) in the N 1s spectrum, which demonstrated a decrease in the intensity with the increase in the carbon content in the membrane. Similarly, the intensity of the C=O peak (at 533 eV) decreased and overlapped with the C–O peak (at 531.5 eV) of the composite membranes.

In the EDAX pattern (Figure S1), a small peak can be observed, which corresponds to Na. This Na peak can be attributed to the NaOH solution (0.1 M) used in the preparation of the binder solution. The adsorption–desorption isotherm of the carbonized GC was obtained based on BET analysis (Figure S2a). A type-I isotherm, which reflects the microporous nature of the sample, was observed. The surface area was calculated to be 768.95 m² g⁻¹. This high surface area of the carbon can be attributed to the evaporation of mineral salts, which creates the pores on the sample surface. The average diameter of the microspores was calculated as 1.67 nm based on the Barrett–Joyner–Halenda (BJH) plot (Figure S2b).

The surface SEM images show the coverage of the porous nylon support with the composite membrane comprising carbonized GC and a natural binder (Figure 3a–d). The cross-sectional images (Figure 3e–h) indicate that the composite top layer is dense with no pore intrusion in the support. The thickness of the carbon top layer increased with the increase in the concentration of the carbonized GC (Figure 3h). During membrane casting, several factors such as the concentration of the casting solution, drying temperature, coating method, and particle size of the carbon. The GC membranes thickness ranged from 1 to 4.4 μm. The AFM images (Figure 3i–l) agree with the SEM surface images, showing that the nylon support, which is covered by the composite membrane, has a pore-like texture. The surface roughness of membranes decreased from 747 to
178 nm with increase in the carbon content. Compared with the nylon support, the water contact angle of composite membranes increased with the addition of carbon, which increases the hydrophobicity of membranes (insets of Figure 3a–d). The mechanical stability of membranes was examined by measuring the hardness of the coating layer. The hardness of the composite membrane increased with increase in the thickness of the carbon film and was estimated to be 7.9 ± 1, 8.9 ± 1, and 14.1 ± 2 MPa for GCM-10, GCN-50, and GCM-75, respectively, compared with 5.8 ± 1 MPa for the nylon support.

Figure 3. a–d) Representative SEM images of the surface; (e–h) cross-section and (i–l) AFM images of the nylon support, GCM-10, GCM-50, and GCM-75, respectively. The insets in Figure 3a–d are the water contact angles of the membranes.
3.2. **Membrane performance in aqueous nanofiltration.** A stable water permeance was obtained by the composite membranes regardless of the solute. The permeance increased with increase in the carbon content in the membrane. An average permeance of $13.0 \pm 0.1$, $15.3 \pm 0.1$, and $18.7 \pm 0.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ was obtained using GCM-10, GCM-50, and GCM-75, respectively (Figure 4a). The surface area of membranes increased with increase in the carbon content because of the porous nature of the carbonized GC, which was demonstrated by the BET results (Figure S2). These pores act as channels, which facilitate the mobility of solvents and enhances the solvent permeance. Moreover, the membrane rejection decreased with the increase in the carbon content in the membrane (Figure 4b). The decrease in rejection, which reflects an increase in the ion transport, can be attributed to the increase in the number of pores because of the higher carbon content. The sequence of the salt retention for all membranes, irrespective of the carbon content, was as follows: $R(\text{Na}_2\text{SO}_4) \approx R(\text{MgSO}_4) > R(\text{CaCl}_2) \approx R(\text{MgCl}_2) > R(\text{NaCl})$, which agrees with the literature on polymer membranes using similar separation mechanisms. [42–44]. This rejection sequence does not follow the sequence based on Donnan exclusion, which assumes that the rejection sequence of a negatively charged membrane is $R(\text{Na}_2\text{SO}_4) > R(\text{NaCl}) \approx R(\text{MgSO}_4) > R(\text{MgCl}_2)$, whereas that of a positively charged membrane is $R(\text{MgCl}_2) > R(\text{NaCl}) \approx R(\text{MgSO}_4) > R(\text{Na}_2\text{SO}_4)$ [42]. This suggests that the ionic sizes and diffusivity of these salts in water have a major effect on their rejection (Tables S1 and S2). For example, the low retention of NaCl cannot be explained based only on the charge effects and can be attributed to its higher diffusivity compared with other salts. The high retention of MgSO$_4$ could be attributed to (i) its lower diffusivity compared with Na$_2$SO$_4$ and (ii) the larger radius of Mg compared with that of Na.
The increase in the transmembrane pressure resulted in a slight drop in the membrane permeance and a slight improvement in the rejection of different salts, which could be attributed to the limited compaction of the membrane upon applying pressure (Figure 4c and 4d). Membrane compaction is commonly observed in polymer membranes and results in an increase in the membrane resistance, which reduces its permeability and improves its salt rejection. The slight increase in the salt rejection with the pressure suggests that the ion transport through the membrane is primarily governed by the diffusion process, which is independent of pressure. Similar results have been reported by other researchers [46,47]. The composite membrane is composed of AC, which is
hardly compressible compared to a typical polymer-based membrane. Thus, the compaction of the developed membrane is negligible.

The selectivity of NaCl to MgSO₄ in GCM-10 remained almost unchanged at 10.17 ± 0.06 with increase in the pressure from 5 to 30 bar (Figure 4e). However, with increase in the carbon content in the membrane, the selectivity of NaCl to MgSO₄ in GCM-50 and GCM-75 increased to 16.39 and 19.67, respectively. This indicates that the relative transport of NaCl and MgSO₂ remains unchanged with increase in pressure, which suggests that ion mobility through the membrane can primarily be attributed to diffusion. The increase in salt selectivity with the increase in the carbon content could be attributed to the following: i) the higher relative diffusivity of NaCl compared with MgSO₄, and ii) the increase in the ion mobility with the increase in the carbon content, which increases the surface area. The combination of these two effects resulted in a relatively higher permeability of NaCl than MgSO₄ with a subsequent increase in selectivity. Compared to previous studies, the proposed membranes fabricated from sustainable resources have comparable performance to that of conventional ion-sieving nanofiltration membranes and have the potential to exceed the reported upper bound (Figure 4f) [45].

3.3. Membrane performance in organic solvent nanofiltration. The acetone flux through the composite membranes demonstrated a nonlinear increase with pressure, resulting in an average permeance of 7.1 ± 0.5, 9.8 ± 0.4, and 12.0 ± 0.3 L m⁻² h⁻¹ bar⁻¹ for GCM-10, GCM-50, and GCM-75, respectively (Figure 5a). This nonlinear increase in the flux with the pressure is commonly observed with pressure-driven polymer membranes and can be primarily attributed to the pressure-induced compaction of the membranes [48,49]. The drop in the flux increased with the increase in the pressure for all membranes (Figure 5b). The membranes with different carbonized GC contents
demonstrated different decline percentages in the flux. Carbonized materials resist compaction, which is the reason for the lower flux decline in GCM-75 with the higher carbon content.

The molecular weight cutoff (MWCO) of GCM-10, GCM-50, and GCM-75 was 577, 737, and 795 g mol⁻¹, respectively (Figure 5c). The rejection profiles demonstrate how the composite membranes get looser with increase in their carbon content. This phenomenon can be attributed to the decrease in the number of pores with the decrease in the carbon content. These pores allow the passage of the solute molecules from the feed side to the permeate side. Thus, the decrease in the number of pores resulted in a decrease in the rejection of the solutes. The long-term filtration performance of GCM-10 was investigated for 120 h of continuous filtration of rose bengal in an acetone solution (Figure 5d). The acetone flux initially declined over the first 10 h of the continuous operation from 60 to 37 L m⁻² h⁻¹ because of the initial membrane compaction, and the flux then stabilized at 37 L m⁻² h⁻¹. However, the rejection of rose bengal remained almost unchanged at 99.7% over the 5 days of continuous filtration. These results indicate the excellent chemical stability of the composite membranes and the requirement for compacting the membranes before using them, which is the case for most polymer-based membranes.

Furthermore, the flux of the solvents, i.e., acetonitrile, acetone, DMF, ethanol, and toluene, which cover a wide range of polarity, was measured for GCM-10 at 5–30 bar with a 5-bar increment. An average permeance of 9.7 ± 0.5, 7.1 ± 0.5, 5.5 ± 0.4, 4.2 ± 0.2, and 1.8 ± 0.2 L m⁻² h⁻¹ bar⁻¹, respectively, was obtained (Figure 5e). The solvent permeance increased with the increase in the solubility parameter of the solvents (Figure 5f). Moreover, the stability of composite membranes was studied in different organic solvents over 30 days, and no damage or dissolution of the membranes was observed during the immersion test (Table S3).
Figure 5. Membrane performance in organic solvent nanofiltration: a) pure acetone flux as a function of pressure, b) decline in the acetone flux as a function of pressure, c) rejection of different solutes with different molecular weights in acetone at 5 bar, d) long-term flux and rejection of rose bengal in acetone at 5 bar using GCM-10, e) fluxes of different organic solvents as a function of pressure, and f) effect of the solubility parameter of different organic solvents on their permeance.

3.4. Cytotoxicity assay. The toxicity of the Pongamia meal and carbonized GC was determined in a dose- and time-dependent MTT assay (Figure 6 and Figure S3). A graph was plotted between different concentrations of the materials (100, 50, and 10 µg mL⁻¹) and the absorbance of the formazan solution at 570 nm. After treating the NIH 3T3 cells with the samples for 48 h, the absorbance of the different concentrations of carbon materials was similar to those of the control samples. Even after extending the incubation time to 96 h, no cytotoxicity was observed in any of the tested concentrations for all three samples. Figure 6a shows the corresponding bright-field images of 3T3 cells incubated with different concentrations of samples at 96 h. These results
suggest that the Pongamia meal and synthesized carbon materials were not cytotoxic to the 3T3 cells, which was confirmed at different concentrations over an extended incubation time (96 h).

Figure 6. a) Brightfield images of the NIH 3T3 cells treated with different concentrations of Pongamia meal and carbonized giant cane. The images were captured prior to the MTT assay after 96 h at 40x magnification using the EVOS imaging system. b) Cell viability of NIH 3T3 cells after exposure to Pongamia meal and carbonized giant cane in a dose- and time-dependent MTT assay. The toxicity of the samples was evaluated by increasing the concentration of the test samples over a period of 96 h. The values in the graph are representative of the readings from triplicates, and the data were represented as means with standard deviations.

Conclusions. In this study, carbonized GC was used to fabricate composite membranes by the vacuum filtration method using the Pongamia meal extract as a natural binder. The increase in the carbon content in the membrane from 0.1 to 0.75 mg mL$^{-1}$, which is associated with an increase in the surface area, increased the water permeance from 13.0 to 18.7 L m$^{-2}$ h$^{-1}$ bar$^{-1}$, respectively. However, the salt rejections decreased with the increase in the carbon loading and was relatively improved with the increase in the transmembrane pressure. The selectivity of NaCl/MgSO$_4$ remained constant with the increase in the pressure and was improved with the increase in the carbon loading up to 19.67, which is comparable to that of the state-of-the-art conventional hydrocarbon-based nanofiltration membranes. The membranes exhibited excellent thermal, mechanical, and chemical stability in various organic solvents. In acetone, the membrane
compaction decreased with the increase in the carbon content in the membrane. The membranes demonstrated an excellent selectivity in acetone with an MWCO ranging from 577 to 795 g mol\(^{-1}\) with a corresponding permeance of 7.1 to 12.0 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), respectively. Moreover, the membranes exhibited an almost unchanged rejection of rose bengal (>99%) over 120 h of continuous filtration; however, the flux stabilized at 37.4 L m\(^{-2}\) h\(^{-1}\) after the initial compaction of the membranes. The toxicity test of carbonized GC and the Pongamia meal revealed the nontoxicity of the materials, which makes the developed membranes suitable for pharmaceutical and food applications.

**Conflict of interest**

The authors declare no competing financial interest.

**Appendix A. Supporting information**

The supporting information is available free at www... The hydrated ionic radii of ions, the diffusion coefficient of various salts EDS pattern of GCM, adsorption isotherm of GCM, Membrane stability table, BJH plot of GCM, Brightfield images of NIH 3T3 cells, and toxicity of GC carbon and binder.

**References**


