Synthesis, characterisation and water purification properties of carbon nanotube membranes (buckypapers)

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SYNTHESIS, CHARACTERISATION AND WATER PURIFICATION PROPERTIES OF CARBON NANOTUBE MEMBRANES (BUCKYPAPERS)

A thesis submitted in partial fulfilment of the requirements of the award of the degree

DOCTOR OF PHILOSOPHY

From
UNIVERSITY OF WOLLONGONG

By
MD. HARUN-OR RASHID

School of Chemistry
September, 2016
Certification

I, Md. Harun-Or Rashid, declare that this thesis, submitted in partial fulfilment of the requirements for awarding the degree of Doctor of Philosophy, in the School of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Md. Harun-Or Rashid

September, 2016
Abstract

Several different series of novel, self-supporting carbon nanotube (CNT) membranes, known as buckypapers (BPs), were successfully synthesised by vacuum filtration of dispersions containing multi-walled carbon nanotubes (MWNTs), functionalised MWNTs (MWNT–COOH and MWNT–NH₂), or single-walled carbon nanotubes (SWNTs). The formation of these dispersions was achieved by subjecting samples containing CNTs and various dispersant molecules, including a surfactant (Triton X-100 (Trix)), macrocyclic ligands (meso-tetra(4-sulfonatophenyl) porphyrin dihydrogen chloride, phthalocyanine tetrasulfonic acid or 4-Sulfonic calix[6]arene hydrate), and biopolymers (bovine serum albumin, lysozyme, chitosan, gellan gum and DNA) to ultrasonic energy. Absorption spectrophotometry and optical microscopy was used to monitor the formation of the dispersions, and determine the optimum sonication time for their formation.

Microanalytical data obtained from the MWNT and SWNT BPs confirmed the retention of significant amounts of the various dispersant molecules within their structures. The electrical conductivities of the MWNT and substituted MWNT BPs varied between 24 ± 16 and 58 ± 11 S cm⁻¹, while the SWNT/gellan gum and SWNT/chitosan BPs exhibited the highest electrical conductivities observed (68 ± 4 and 75 ± 6 S cm⁻¹, respectively). All MWNT and functionalised MWNT BPs possessed hydrophilic surfaces, with contact angles ranging from 28 ± 2 to 57 ± 5°. In contrast, the SWNT BPs possessed less hydrophilic surfaces (contact angles = 63 ± 7 to 88 ± 3°). Measurement of the mechanical properties of MWNT BPs prepared using Trix or one of the macrocyclic ligand dispersants showed that their tensile strengths varied between 1.6 ± 0.7 and 13 ±
2 MPa. In contrast, tensile test measurements performed on MWNT or SWNT BPs containing biopolymers revealed that they were typically much tougher materials, as reflected in tensile strengths between 12 ± 2 and 81 ± 14 MPa.

The surface areas of MWNT BPs prepared using macrocyclic ligands or biopolymers were determined through BET analysis of nitrogen adsorption/desorption isotherms, and found to vary between 136 ± 1 and 380 ± 2 m² g⁻¹. Nitrogen gas porosimetry showed that the MWNT/biopolymer BPs have highly porous internal structures, while scanning electron microscopy (SEM) revealed that their surfaces possess numerous pore openings, with the average surface pore diameter varying between 33 ± 9 and 54 ± 12 nm. The surface and internal morphologies of MWNT BPs containing macrocyclic ligands were also similar to each other (e.g., surface pore diameters ranging from 55 ± 18 to 88 ± 23 nm), accounting for the lack of variation observed between their measured permeabilities towards water. In contrast, the average surface pore diameters of the SWNT/biopolymer BPs were smaller, ranging between 10 ± 4 and 22 ± 7 nm. The five SWNT/biopolymer BPs all had surface areas less than 48 m² g⁻¹, highlighting another significant difference between the morphological properties of BPs prepared from SWNTs and MWNTs.

The water permeabilities of MWNT BPs were measured using a dead-end membrane filtration setup, and revealed that all were permeable towards water at low applied pressures (< 1 bar). This is attributable to the porous nature of each of these membranes. In the case of the MWNT/biopolymer BPs, the measured water permeabilities varied between 10 and 22 L m⁻² h⁻¹ bar⁻¹. These values are comparable to those obtained for
BPs composed of MWNTs and low molecular weight dispersants. For example, MWNT BPs prepared using phthalocyanine tetrasulfonic acid exhibited an average water permeability of 23 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). These results show that incorporation of biopolymers into MWNT BPs resulted in materials that exhibited improved mechanical properties, whilst still retaining a significant degree of permeability towards water. Surprisingly, the analogous series of SWNT/biopolymer BPs exhibited very low water permeabilities ranging from only 1 to 6 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). These values are much lower than those reported in published studies investigating SWNT BPs prepared using low molecular weight dispersants, which may be an indication that variations in the SWNTs used to prepare these membranes can have a major effect on their permeability characteristics.

The permeability of selected BPs towards inorganic salts and dissolved trace organic contaminants (TrOCs), including pharmaceuticals, personal care products, and pesticides was investigated through a range of filtration experiments. In the case of MWNT/Trix, MWNT–NH\(_2\)/Trix and MWNT–COOH/Trix BPs, the extent of bisphenol A (BPA) removal was more than 90%. In addition, MWNT/Trix BPs showed removal efficiencies greater than 80% for 11 out of the 12 TrOCs present in a test solution. On the other hand, BPs prepared from dispersions containing MWNTs and phthalocyanine tetrasulfonic acid, exhibited lower removal efficiencies towards this mixture of 12 TrOCs, possibly due to the smaller specific surface area of these membranes. A total of nine of the TrOCs present in the test solution were rejected to an extent of more than 95% by MWNT/chitosan BPs, which also demonstrated a significant ability to reject both NaCl (30 to 55%) and MgSO\(_4\) (40 to 70%) in experiments involving a cross-flow RO/NF filtration apparatus, and solutions involving both salts.
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understanding, particularly when I left you at home for a long time while I was doing
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<td>Acetaminophen</td>
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<tr>
<td>ACN</td>
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<td>Activated carbon</td>
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<td>Å</td>
<td>Angstrom</td>
</tr>
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<td>AAO</td>
<td>Anodic aluminum oxide</td>
</tr>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
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<td>Australian Nuclear Science and Technology Organisation</td>
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<td>β–CD</td>
<td>β-cyclodextrin sulfated</td>
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<td>BJH</td>
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<td>BPA</td>
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<td>Buckypaper</td>
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<td>Bundle diameter</td>
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<td>BSA</td>
<td>Bovine serum albumin</td>
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<td>[Bmim][BF₄]</td>
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<td>CO</td>
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<td>(D_{\text{bun}})</td>
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<td>Chemically converted graphene</td>
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<td>Colony forming unit</td>
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<td>Dalton</td>
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<tr>
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<td>Distribution coefficient</td>
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<td>Dissolved organic material</td>
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<td>Direct contact membrane distillation</td>
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<td>Disinfection by-product</td>
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<td>Electron volt</td>
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<td>$E. coli$</td>
<td><em>Escherichia coli</em></td>
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<tr>
<td>ETBE</td>
<td>Ethyl tert-butyl ether</td>
</tr>
<tr>
<td>GG</td>
<td>Gellan gum</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular activated carbon</td>
</tr>
<tr>
<td>HiPCO</td>
<td>High pressure carbon monoxide disproportionation</td>
</tr>
<tr>
<td>HEPA</td>
<td>High efficiency particulate air</td>
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<td>HPLC</td>
<td>High performance liquid chromatography</td>
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<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>HK</td>
<td>Horvath-Kawazoe</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
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<tr>
<td>HA</td>
<td>Humic acid</td>
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<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma-Optical Emission Spectrometer</td>
</tr>
<tr>
<td>$d_{BET}$</td>
<td>Internal pore size (determined by BET)</td>
</tr>
<tr>
<td>IBU</td>
<td>Ibuprofen</td>
</tr>
<tr>
<td>J</td>
<td>Joule</td>
</tr>
<tr>
<td>K</td>
<td>Degree Kelvin</td>
</tr>
<tr>
<td>l</td>
<td>Length</td>
</tr>
<tr>
<td>L</td>
<td>Litre</td>
</tr>
<tr>
<td>LC-MS</td>
<td>Liquid chromatography mass spectrometry</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>LSZ</td>
<td>Lysozyme</td>
</tr>
<tr>
<td>MFI</td>
<td>Mordenite Framework Inverted</td>
</tr>
<tr>
<td>MPD</td>
<td>m-phenylenediamine</td>
</tr>
<tr>
<td>f</td>
<td>Membrane permeability</td>
</tr>
<tr>
<td>MD</td>
<td>Membrane distillation</td>
</tr>
<tr>
<td>MBR</td>
<td>Membrane bioreactor</td>
</tr>
<tr>
<td>m</td>
<td>Metre</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
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<td>Mole</td>
</tr>
<tr>
<td>MF</td>
<td>Microfiltration</td>
</tr>
<tr>
<td>M</td>
<td>Molar concentration (mol L⁻¹)</td>
</tr>
<tr>
<td>MWNT</td>
<td>Multi-walled carbon nanotube</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight (g mol⁻¹)</td>
</tr>
<tr>
<td>MWCO</td>
<td>Molecular weight cutoff</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>Ω</td>
<td>Ohm</td>
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<tr>
<td>K&lt;sub&gt;ow&lt;/sub&gt;</td>
<td>Octanol–water distribution coefficient</td>
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<tr>
<td>OP</td>
<td>Organophosphate</td>
</tr>
<tr>
<td>OPH</td>
<td>Organophosphate hydrolase</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>Pa</td>
<td>Pascal</td>
</tr>
<tr>
<td>J</td>
<td>Permeate flux</td>
</tr>
<tr>
<td>PPCP</td>
<td>Pharmaceuticals and personal care products</td>
</tr>
<tr>
<td>PAC</td>
<td>Powdered activated carbon</td>
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<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>PES</td>
<td>Polyethersulfone</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>PSf</td>
<td>Polysulfone</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PEO</td>
<td>Polyethylene oxide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethyleneimine</td>
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<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
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<tr>
<td>PTS</td>
<td>Pthalocyanine tetrasulfonic acid</td>
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<td>rGO</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>R</td>
<td>Retention</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
<tr>
<td>P/P&lt;sub&gt;o&lt;/sub&gt;</td>
<td>Relative pressure</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>α</td>
<td>Separation factor</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>S</td>
<td>Siemen</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-walled carbon nanotube</td>
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<tr>
<td>AgNPs</td>
<td>Silver nanoparticles</td>
</tr>
<tr>
<td>A&lt;sub&gt;BET&lt;/sub&gt;</td>
<td>Specific surface area</td>
</tr>
<tr>
<td>SDBS</td>
<td>Sodium dodecylbenzenesulfonate</td>
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<tr>
<td>C&lt;sub&gt;f&lt;/sub&gt;</td>
<td>Solute concentration in the feed</td>
</tr>
<tr>
<td>C&lt;sub&gt;p&lt;/sub&gt;</td>
<td>Solute concentration in the permeate</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecylsulfate</td>
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<td>SA</td>
<td>Sodium alginate</td>
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<td>SOC</td>
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<td>C6S</td>
<td>4-sulfonic calix[6]arene</td>
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<td>D&lt;sub&gt;SEM&lt;/sub&gt;</td>
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<td>SILM</td>
<td>Supported ionic liquid membrane</td>
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<td>SRFA</td>
<td>Suwannee River fulvic acid</td>
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<td>σBreak</td>
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<td>TBA</td>
<td>tert-butyl alcohol</td>
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<td>TSP</td>
<td>meso-tetra(4-sulfonatophenyl) porphyrin</td>
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<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>TFC</td>
<td>Thin film composite</td>
</tr>
<tr>
<td>TFN</td>
<td>Thin film nanocomposite</td>
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<tr>
<td>3-D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>-------------</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium dioxide</td>
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<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>T</td>
<td>Toughness</td>
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<tr>
<td>TrOC</td>
<td>Trace organic contaminant</td>
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<td>Trix</td>
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<td>TMC</td>
<td>Trimesoyl chloride</td>
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<td>Triclosan</td>
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<td>Two-dimensional</td>
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<td>Volts</td>
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<td>Watt</td>
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<td>Young’s modulus</td>
</tr>
<tr>
<td>ZP</td>
<td>Zeta potential</td>
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Chapter 1

General Overview of Membrane Filtration and Adsorption Separation Processes

This chapter describes the principles underpinning membrane filtration and adsorption processes for separating and purifying mixtures of substances. It includes a discussion of the most widely used materials for both types of separation processes, as well as the differences between the main types of filtration membranes, and the mechanism through which they exhibit solute selectivity. A discussion of advantages and disadvantages associated with new classes of filtration media, such as zeolite membranes and mixed matrix membranes containing nanoparticles is included. The chapter concludes with a description of key challenges to further developing new membrane materials and membrane filtration processes, along with a discussion of how these are being met through the use of nanotechnology.
1.1 Separation processes

In general, separation is a process in which constituents of a mixture are separated into at least two different fractions.\textsuperscript{1} Since ancient times, people have used methods of separating and purifying chemical substances for improving their quality of life. During the industrial revolution, the ability to separate and purify chemical substances became of great importance. The past few decades have continued to see chemical separation techniques becoming an integral feature of the scientific and industrial landscapes.\textsuperscript{2-4} There is a huge range of separation techniques available, due to the variety of separation goals, the diversity of samples that need to be separated, and the assortment of physical and chemical phenomena that can be used to effect the separation. Separation methods include adsorption, chromatography, distillation, electrophoresis, dialysis and membrane filtration, with the method chosen for a specific separation task depending on the final application and the exact molecules involved.\textsuperscript{5} Despite the wide range of separation techniques available today, they all have the same end goals, which are to maximise the speed of the process and the volume of material which can be separated, whilst minimising energy input to make the process as economically viable as possible. Of all the separation techniques available currently, adsorption and filtration are the most simple and thus the most widely used. In the following sections the basic principles underpinning these methods are described, before recent work exploring the potential of new nanotechnology-inspired membranes is discussed.
1.2 Adsorption

Adsorption is a mass transfer process in which substances present in a liquid phase are deposited onto, or accumulated on a solid phase and thus removed from the liquid (Figure 1.1). Adsorption processes, such as those using powdered activated carbon (PAC) or granular activated carbon (GAC), are used in drinking water treatment for the removal of taste and odour-causing chemical compounds, synthetic organic chemicals (SOCs), colour-forming organics, and disinfection by-product (DBP) precursors.\(^5\)-\(^9\) Inorganic compounds, including some that pose a health hazard such as arsenic, perchlorate, and some heavy metals, can also be removed by adsorption.\(^10\)-\(^12\)

![Figure 1.1: Schematic illustration of the adsorption process.](image)

Primary adsorbent materials used for drinking water treatment are PAC and GAC.\(^13\) Both materials are examples of a large group of activated carbons that can be produced from sources such as coconut shells, wood char, petroleum coke, lignite, coal and peat. Activated carbon possesses graphitic and highly porous structures, with diameters of the same order as molecular dimensions.\(^14\),\(^15\) Activated carbon has been the most popular and widely used adsorbent for water purification, due to its porous structure, high specific surface area, and special surface reactivity.\(^16\) For nearly 100 years, adsorption processes employing activated carbon have been used for drinking water purification to remove organic solutes. Initially, chemical compounds responsible for unwanted tastes and odours were the main target solutes. Subsequently activated carbon was shown to
be highly effective for the removal of a wide range of other trace organic contaminants (TrOCs), such as phenols, chlorinated hydrocarbons, pharmaceuticals, pesticides, and personal care products, as well as inorganic contaminants.\textsuperscript{17-20}

Despite these outstanding properties, activated carbon materials are often expensive, non-selective and non-reusable once their capacity has been reached. There is therefore a shift towards the use of new, lower cost adsorbents, including zeolites, molecular sieves, clay minerals and biosorbents such as algae, bacteria and chitosan.\textsuperscript{14,16,21} The ability to adsorb analytes is not limited to microporous materials, but also extends to many conventional polymer membranes. Some nanofiltration membranes, for example, have been shown to remove trace organic pollutants by hydrophobic adsorption mechanisms, while others are able to reject polar compounds owing to unfavourable electrostatic interactions.\textsuperscript{22,23}

1.3 Membrane Filtration

Membrane filtration processes are modern physiochemical techniques that use differences in permeability of sample components as a separation mechanism. It allows the passage of some molecules present in the sample through a membrane material, while others present in the initial mixture are retained.\textsuperscript{4} During filtration, water is pumped against the membrane surface, resulting in the production of permeate (product) and waste streams, as shown in Figure 1.2. The membrane is typically less than 1 mm thick. During the filtration process, permeable components pass through the membrane while those which are impermeable or less permeable are retained on the feed side. As a
result, the permeate is relatively free of impermeable components, which are instead concentrated in the waste stream.\textsuperscript{24}

![Diagram of membrane filtration](image)

**Figure 1.2:** Schematic illustration of molecular separation employing a semipermeable membrane.

Membrane filtration technologies have been widely adopted by different industries. This is partially because membrane separation processes are often more capital and energy efficient when compared with conventional separation processes.\textsuperscript{25} In addition, many of the materials used for membrane separations are considerably more environmentally benign than those used with other separation techniques, and have the potential to be reused after cleaning, thus helping to overcome wastage issues. The high durability and flexibility of membrane materials ensures there is enormous scope for developing novel separation systems for applications involving large quantities of complex mixtures. For these key reasons industry has rapidly adopted many membrane separation approaches to replace other more cumbersome techniques.
Nowadays, membrane filtration technology can be found in many industrial areas, including food and beverages, dairy, pharmaceutical, biotechnology, metallurgy, pulp and paper, textile, automotive, and chemicals. In addition, membrane processes are becoming increasingly important for water treatment for domestic and industrial consumption. Among the various water treatment technologies available, membrane filtration is considered as a good alternative to conventional water treatment for secondary and tertiary treatment.\(^{26}\) For example, more than 500 commercial membrane bioreactors (MBRs) are in use globally today, and are suitable for treating surface water, ground water and waste water.\(^{27}\) The selectivity and productivity of a membrane filtration process determine its efficiency. Membrane selectivity is expressed as a parameter called the retention \((R)\) or separation factor \((\alpha)\), while the productivity of a membrane process is expressed as the membrane flux or flux rate. For dilute aqueous mixtures, consisting of a solvent and a solute, the retention of a membrane is given by

**Equation 1.1:**

\[
R = \frac{C_f - C_p}{C_f} = 1 - \frac{C_p}{C_f}
\]

where \(C_f\) is the solute concentration in the feed solution and \(C_p\) is the solute concentration in the permeate. The selectivity of a membrane towards mixtures of gases or organic liquids is instead usually expressed as a separation factor, \(\alpha\). For a mixture containing components \(A\) and \(B\), the selectivity factor \(\alpha_{A/B}\) is given by **Equation 1.2,**

\[
\alpha_{A/B} = \frac{y_A/y_B}{x_A/x_B}
\]

where \(y_A\) and \(y_B\) are the concentrations of components \(A\) and \(B\) in the permeate, and \(x_A\) and \(x_B\) are the concentrations of the same components in the feed solution.
The volume of solute flowing across a membrane per unit area and time is commonly referred to as its flux rate or permeability ($f$). The flux rate is an important characteristic of a membrane, and can be calculated using the relationship shown in Equation 1.3. This shows that the flux rate is directly proportional to the mass or volume of solute transported across the membrane per unit time ($J$), and inversely proportional to the membrane surface area ($A$) and pressure difference applied across the membrane ($\Delta P$). The flux rates of different membranes can be compared, as it takes into account differences between the conditions used for performing filtration experiments. It is therefore one of the most important properties of a membrane.

\[
f = \frac{J}{A \times \Delta P}
\]

Equation 1.3

The permeability or flux rate of membranes varies markedly in response to differences in their composition, pore structure, method of preparation, and applied pressure used during filtration experiments. Table 1.1 illustrates the range of applied pressures and permeabilities exhibited by commercial membranes. Inspection of the data in the table shows that membranes with larger pore sizes require a much lower pressure range for operation, and provide a much higher flux of solvent.

Table 1.1: Typical permeabilities and operating pressures for pressure driven membrane separation processes.

<table>
<thead>
<tr>
<th>Membrane process</th>
<th>Pressure range (bar)</th>
<th>Permeability (L m(^{-2}) h(^{-1}) bar(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
<td>0.1 – 2.0</td>
<td>&gt; 50</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>1.0 – 5.0</td>
<td>10 – 50</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>5 – 20</td>
<td>1.4 – 12</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>10 – 100</td>
<td>0.05 – 1.4</td>
</tr>
</tbody>
</table>
Membrane filtration is a broad field often subdivided into four different categories depending on the size of the pores present in the membrane used, and the pressure differences applied across the membrane. These four categories are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Each process is different as a result of variations in the sizes of pores present in the membranes used, which facilitates removal of different classes of contaminants (Figure 1.3).

**Figure 1.3:** Schematic illustration of the four main classes of pressure-driven membrane processes.

MF and UF can be broadly defined as processes that separate suspended particles from a liquid phase by passage of the suspension through a porous medium with pores having diameters in the 0.01 – 0.1 µm range. In both processes the feed stream may contain sediment, bacteria, viruses, algae, protozoa or colloid particles. In contrast, RO membranes are used to remove dissolved solutes such as sodium, chloride, nitrate, calcium and magnesium ions, as well as dissolved natural organic matter (NOM), and specific dissolved contaminants such as pesticides, arsenic and radionuclides.
The primary goal of RO membranes is to minimise the concentration of these solutes in the product water. RO membranes are used to produce potable water from ocean or brackish water, while NF membranes are used to soften hard water samples (remove calcium and magnesium ions), treat brackish water and municipal waste water, and reduce the concentration of NOM in water supplies to control DBP formation.\textsuperscript{3,34,35}

1.3.1 Microfiltration

MF is one of the oldest pressure-driven membrane separation processes, and is used for removing micron-sized particles including bacteria, yeast cells, algae, protozoa and colloids.\textsuperscript{36,37} A typical MF membrane has pore sizes ranging from 0.1 \( \mu \)m to 10 \( \mu \)m, and exhibits negligible osmotic pressure.\textsuperscript{38} The trans-membrane pressure drop which drives the MF process is also relatively small (typically 0.069 to 3.45 bar). As a result of these characteristics, the membrane pore size and permeability (\( > 50 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1} \)) are typically larger for MF processes than either UF or RO. Very small, dissolved species such as monovalent ions (\( \text{Na}^+ \), \( \text{Cl}^- \)), dissolved NOM, and some viruses are able to pass through MF membranes, and require the use of membranes with much smaller pore sizes in order to achieve their separation. MF membranes can be synthesised using both polymeric and inorganic materials with either symmetric or asymmetric structures. For the symmetric membranes, the internal pore diameters do not vary over the entire cross section of the membrane, and the membrane thickness determines its flux. MF membranes can also be asymmetrically structured, depending on the manufacturing technique used, but the pores of the active surface are not much smaller than those of the supporting layer.
MF can be carried out using one of two types of system configurations, known as dead-end and cross-flow. In dead-end filtration, the permeate flow of water is perpendicular to the membrane, while all or most of the particles are retained (Figure 1.4). The driving force is the pressure drop across the membrane that results from the hydrostatic pressure of the feed solution, and from applying either pressure to the feed side or suction to the permeate side, or both. During the past two decades, the cross-flow configuration has been increasingly used as an attractive alternative to the dead-end configuration. Cross-flow microfiltration is also sometimes referred to as tangential-pass filtration. The filtration method is similar to that of UF and RO in that the bulk suspension is made to flow tangential to the surface of the membrane (Figure 1.4).

Figure 1.4: Schematic illustration of the difference between dead-end filtration and cross-flow filtration processes.
1.3.2 Ultrafiltration

UF is a size exclusion based and pressure-driven membrane separation process, that typically employs membranes with pore sizes in the range between 0.01 to 0.1 μm. UF processes are the most widely used, apart from dialysis and MF. UF membranes reject a variety of species including biomolecules, polymers, bacteria, viruses and colloidal particles, and have been in industrial use since the 1960s for a variety of applications. These include the treatment of oily wastewater, surface water samples, the separation of whey proteins, and the treatment of process streams from pulp and paper mills.

The selectivity of an UF membrane is commonly described by its molecular weight cutoff (MWCO), which can be defined as the molecular weight of the solute that achieves a 90% rejection by the membrane. The MWCO of typical UF membranes is in the range from 1 to 300 kDa. A larger MWCO indicates that the membrane has a larger pore size and lower rejection ability. UF membranes typically have an asymmetric structure to maximize their permeability. This consists of a very thin (0.1 – 1 μm) active layer with fine pores supported by a highly porous 100 – 200 μm thick substructure. In these materials the pore diameters may vary from the active layer of the membrane to the other supporting layer by a factor of 10 – 1000. The separation characteristics and permeability of these membranes are determined mainly by the features of the active layer (e.g., thickness, pore size and pore-size distribution), while the porous sublayer serves only as a mechanical support. Because of their asymmetric structure, UF membranes show excellent separation performance, and possess considerable strength. The permeabilities of UF membranes typically vary from 10 to 50 L m⁻² h⁻¹ bar⁻¹, while their normal operating pressure range is from 1.0 to 5.0 bar.
1.3.3 Reverse Osmosis

Reverse osmosis a purification method that came into existence with the development of new types of semi-permeable membranes with extremely narrow diameter pores. RO membrane technology has grown widely in recent years, and has become the technique of choice for the removal of cations, anions, and other soluble organic and inorganic compounds from wastewater samples, saline water and industrial leachates. Reverse osmosis membranes have effective pore sizes between 0.001 and 0.01 μm owing to the presence of interstitial voids between polymer chains that constitute the membrane film. Reverse osmosis membranes enable the separation and concentration of dissolved species due to the presence of a hydraulic gradient across the semi-permeable membrane. In the RO process an external pressure is applied to overcome the naturally occurring osmotic pressure across the membrane (Figure 1.5).

This forces water to pass through the membrane, effectively resulting in the removal of salts. A solution–diffusion mechanism mainly controls water transport through this class of membranes, which are effectively non-porous, and can exclude particles and even low molecular weight species such as simple cations and anions. The ability of RO membranes to separate selectively, and simultaneously, organic and inorganic solutes from aqueous systems without a phase change offers flexibility in the design of separation processes and substantial energy savings. Reverse osmosis is often found to be more cost effective for the removal of toxic substances than other conventional techniques, such as activated carbon adsorption.
There are two main types of RO membranes commercially available: (1) asymmetric cellulose acetate (CA) membranes prepared by phase inversion, and (2) thin film composite (TFC) polyamide membranes formed by an interfacial polymerisation process. Cellulose acetate RO membranes have hydrophilic and smooth membrane surfaces, and exhibit low resistance to hydrolysis and biodegradation. However, their permeability and rejection properties are inferior to that of modern TFC polyamide RO membranes.

Reverse osmosis membranes are used for many important water purification processes to produce fresh water from sea water, brackish water and other contaminated water sources. For example, the removal of 15 major pesticides from an aqueous industrial waste sample, containing chlorinated hydrocarbon and organophosphorus compounds,
has been demonstrated.\textsuperscript{53} Reverse osmosis membranes have also been used frequently to remove dissolved organic materials (DOMs) from surface waters.\textsuperscript{54,55} The extent of rejection of bacteria, viruses and other microbes by RO membranes is 100\%. Therefore, these membranes are used for the preparation of ultrapure water for use in the pharmaceutical industry, and are an integral part of today’s most economic process for saline water treatment to produce potable water.\textsuperscript{56,57}

1.3.4 Nanofiltration

Nanofiltration is a pressure-driven membrane separation process with characteristics in between those of RO and UF. The nominal MWCO for a NF membrane is in the range from 100 to 1000 Da, as a result of the approximate pore size for these materials being 1 nm.\textsuperscript{58} NF offers several advantages such as low operation pressure, high flux, high retention of multivalent anion salts and organic molecules with molar masses above 300, and relatively low initial investment and ongoing operation and maintenance costs. Because of these advantages, the applications of NF worldwide have increased dramatically.\textsuperscript{59} The history of NF dates back to the 1970s, when RO membranes which exhibited high water fluxes at relatively low pressures were developed. Eventually these low-pressure RO membranes became known as NF membranes.\textsuperscript{60} By the second half of the 1980s, NF had become firmly established, as the first applications of NF membranes were reported.\textsuperscript{61,62} NF membranes can be prepared using both cellulose acetate and polyamides. In addition, other polymers (e.g., polyvinyl alcohol (PVA) and sulfonated polysulfone) and inorganic materials (e.g., some metal oxides) can also be used for the synthesis of NF membrane.\textsuperscript{63} In contrast to typical RO membranes, these TFC-NF membranes exhibited lower levels of NaCl rejection (~ 90 – 95\%), and higher water
permeability (10 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)). TFC-based NF membranes exhibit negative surface charges, and produce similar contact angles to TFC–RO membranes.\(^{63}\)

Nanofiltration is a promising membrane technology for removing low molar mass solutes, such as salts, lactose, glucose and various organic micro-pollutants, from contaminated water.\(^{64,65}\) NF membranes selectively reject contaminants as well as enable the retention of nutrients in water, which is an advantage compared to the RO process. Nanofiltration membranes can also reject bivalent ions (e.g. Ca\(^{2+}\), Mg\(^{2+}\)) in significant amounts to reduce water hardness.\(^{28,66}\) For example, in one study NF membranes exhibited rejection efficiencies of 90% for multivalent ions such as SO\(_4^{2-}\), Ca\(^{2+}\) and Mg\(^{2+}\), and 60 – 70% for monovalent ions such as Na\(^+\) and Cl\(^-\).\(^{57}\) During the NF process, electrostatic interactions between the negatively charged membrane and charged species in solution appear to be an important factor in determining solute rejection. Monovalent ions tend to be rejected to a lower extent, unless they are retained to maintain charge neutrality with adsorbed multivalent counter ions.\(^{68}\)

### 1.4 Membrane separation mechanisms

Depending on the physicochemical properties of the solute and the membrane, separation can be achieved by one or more of several mechanisms, including size exclusion, electrostatic interactions and sorption diffusion.\(^{69}\) The word ‘physicochemical’ means that rejection can be due to physical selectivity (such as size exclusion, charge repulsion or steric hindrance) or chemical selectivity (solvation energy, hydrogen bonding or hydrophobic interaction). Consequently the mechanism of separation for a specific analyte can also be strongly influenced by its molecular weight,
structure, geometry and hydrodynamic radius. These interactions are complex, and the transport of analytes across a membrane is an interesting topic which to date, is not fully understood. The following section provides an overview of the current state of understanding of membrane filtration mechanisms.

1.4.1 Size exclusion

Size exclusion is a simple mechanism of solute rejection that is believed to play an important role for many solutes. According to this mechanism, solutes larger than the pore size of the membranes are retained (Figure 1.6), while those which are smaller are transferred to the permeate.

Figure 1.6: Schematic illustration of different mechanisms of solute separation used by filtration membranes.
The process can be described using a number of simplified assumptions. To begin with, it is usually assumed that the membrane consists of a bundle of cylindrical capillaries, with the pore size being the internal capillary diameter, and that solutes are spherical in shape. An average pore size and an estimated equivalent solute sphere diameter can then be used to model the separation process. While size exclusion is particularly effective for the retention of colloids and particulates by membranes, it can also be used for the retention of salts where the hydrated ion radius is large. As many organic solutes do not have a spherical shape, other models have been developed, such as the friction model and the pore model, to explain the variations in permeability exhibited by membranes. These models have been verified using a number of non-polar neutral organic molecules, and show that the extent of rejection of neutral compounds increases with increases in molar mass. This implies that uncharged compounds with a molecular size larger than the pore size of the membrane will be efficiently rejected.

1.4.2 Electrostatic interactions

Electrostatic interactions between a porous membrane and charged solutes have been reported to be an important rejection mechanism. In these instances the extent of solute rejection depends on its charge as well as its size. For example, neutral organic molecules, colloidal particles and other large molecules may be rejected depending on the relationship between solute and pore size, while ionic components and charged, lower molecular weight organic molecules are simultaneously rejected due to repulsive electrostatic interactions with the membrane surface (Figure 1.6). The existence of a negative charge on a membrane surface is usually caused by the presence of sulfonic and/or carboxylic acid groups, that are deprotonated at neutral pH. The polarity and
magnitude of the surface charge can be quantified by zeta potential measurements, which have been shown to be influenced by solution pH.\textsuperscript{79,81} In general, the zeta potential for a membrane becomes increasingly negative as the pH of the surrounding solution is increased, resulting in deprotonation of acidic functional groups.\textsuperscript{82-84} Altering solution pH not only changes the net charge present on the membrane surface, it also affects the dissociation state of some electrolyte solutes, as well as their solubility.\textsuperscript{72,85} Most solutes have at least one ionisable group that is affected by solution pH. Therefore by modifying the pH of the solution the charge of the solute can be changed in order to enhance its extent of rejection by a membrane.\textsuperscript{86}

1.4.3 Adsorption mechanism

Adsorption has been identified as the first step in the mechanism of transport of water and some solutes across a membrane in the sorption-diffusion model.\textsuperscript{87} According to this model, the flux of water across a membrane is dependent on its ability to form hydrogen bonds with hydrophilic groups present in the membrane polymer. Therefore hydrogen bonding can play a major role in determining the level of retention of solutes by a membrane. This view is supported by the results of a study that showed there was a 60% drop in the water flux due to the presence of 2,4-dinitrophenol in the water sample, owing to the ability of this organic molecule to compete for hydrogen bonding sites on the membrane surface.\textsuperscript{87}

Adsorption of solute molecules onto a membrane surface can also be accomplished via hydrophobic interactions, which therefore can play an important role in determining the extent of rejection of some micropollutants. Most membranes used for high pressure
filtration applications have been shown to be hydrophobic, based on measurement of their contact angles.\textsuperscript{88,89} Furthermore several studies have reported that membranes with larger contact angles can reject and adsorb greater quantities of a hydrophobic compound, than a membrane with a smaller contact angle.\textsuperscript{88,89} It has been reported that the rejection of hydrophobic compounds increases with increasing affinity of the solute for the membrane, can be expressed through the octanol–water distribution coefficient ($K_{\text{ow}}$).\textsuperscript{90} In another investigation the relationship between the extent of adsorption, and various properties of solutes including dipole moment, dielectric constant, $K_{\text{ow}}$, polarity, and molecular size, was examined.\textsuperscript{91} It was concluded that the value of $K_{\text{ow}}$ was the best predictor of the extent of adsorption of hydrophobic compounds to the membranes, although molecular size also played a significant role.

1.5 **Current issues with membrane filtration technologies**

1.5.1 Membrane fouling

Membrane technologies are currently used for a wide range of drinking water, wastewater, and industrial effluent purification applications.\textsuperscript{92–94} A major barrier for the efficient application of membranes for water treatment, however, is the phenomenon of fouling by inorganic salt scaling, colloidal particles, adsorption of protein or DOM and biofilm formation.\textsuperscript{95–98} In addition to increasing hydraulic resistance, the adsorption of DOMs can form a conditioning layer that promotes bacterial adhesion and eventually leads to the development of a biofilm with low permeability.\textsuperscript{95,99} Fouling therefore results in deterioration of membrane performance, leading to increased energy consumption and operation costs, as well as shortening membrane lifetimes.\textsuperscript{95,96}
Protein is one of the most important membrane foulants, which is known to cause a significant decrease of membrane permeability.\textsuperscript{100,101} Many investigations into protein fouling have been performed using MF and UF membranes. These studies demonstrated that the extent of protein fouling is affected by hydrodynamic conditions (permeate flux and cross-flow velocity), feed water characteristics (solution pH, ionic composition, and foulant concentration) and membrane properties (hydrophobicity, roughness, and charge density).\textsuperscript{102–104} For porous MF and UF membranes pore blocking has been reported to be an important fouling mechanism, but is less likely to be important for non-porous RO and NF membranes.\textsuperscript{105} Previous studies have suggested that smooth, hydrophilic membranes with a favourable surface charge exhibit the best anti-fouling performance.\textsuperscript{106,107} For example, one study showed that membranes with a significant negative charge were less prone to fouling if the feed water supply contained negatively charged organic molecules or colloidal particles.\textsuperscript{108}

Many techniques have been developed for mitigation of membrane fouling, including pretreatment of the feed solution, optimisation of process conditions, changing membrane configuration, and modification of membrane properties.\textsuperscript{109,110} Due to the presence of various types of foulants in natural water supplies and secondary effluent sources, the physical and chemical interaction mechanisms that various foulant molecules participate in needs to be further investigated in order to develop improved methods for mitigating membrane fouling. In addition, there is a critical need to develop new membrane materials with intrinsic anti-fouling properties.
1.5.2 Pore size and pore size distribution

Traditional fabrication methods offer little control over the average size, size distribution and morphology of the effective pores present in membranes.\textsuperscript{44,111} For porous membranes (MF or UF), the pore size and pore size distribution affects both the flux of water and solute separation characteristics. Consequently, the distribution of pore sizes becomes one of the most important properties of a membrane. Membranes with a large distribution of pore sizes can be susceptible to pore breakthrough, which results in unwanted solutes passing through the membrane.\textsuperscript{112} For example, some studies have shown that small, uncharged organic compounds such as urea, as well as other small molecules such as methanol and formaldehyde, can be difficult to remove effectively using RO or NF membranes owing to this phenomena.\textsuperscript{113} A narrower pore-size distribution allows a membrane to exhibit better overall rejection and more predictable separation performance.\textsuperscript{113} Therefore, it is important to be able to fabricate membranes with a pore size distribution tailor-made for the specific application at hand.

1.5.3 Chlorine degradation

As noted above, the application of membrane technology for water treatment is limited by the gradual deterioration of performance due to membrane fouling.\textsuperscript{97,98} Among the strategies used to reduce membrane fouling, disinfection and chemical cleaning are the most prevalent and utilise a large number of different chemical agents.\textsuperscript{114-116} Chlorine has been widely used as a disinfectant for membrane systems. However, it can cause significant degradation to many commercial polymer-based (polyamide) RO and NF membranes, resulting in poorer levels of performance.\textsuperscript{117-119} The specific reason for this has been identified as structural changes within the polymers caused by the introduction of chlorine substituents.\textsuperscript{120} This can lead to changes to hydrogen bonding behaviour, as
well as altered flexibility of polymer chains.\textsuperscript{121} Owing to the combination of these effects, exposure to chlorine results in deterioration of membrane performance, and is a limiting factor in the lifespan of RO and NF membranes.\textsuperscript{51}

### 1.6 Nanotechnology-based membranes for filtration applications

Membrane-based water purification methods are now among the most important and multipurpose technologies for drinking water production, ultrapure water production, wastewater treatment, desalination and water reuse.\textsuperscript{92,94} Despite this, there are a number of disadvantages associated with commercial membrane filtration processes, including short membrane life-times, high energy consumption, limited chemical selectivity, membrane fouling, and sensitivity towards chlorine.\textsuperscript{95,96,117} Nanotechnology may provide answers to many of these issues. For example, it may be possible to immobilise nanomaterials within a membrane to improve its separation performance, chemical, thermal, or mechanical stability. The following sections briefly review some emerging nanotechnology-based membrane materials intended for use in the water purification industry.

#### 1.6.1 Zeolite membranes

Zeolites are naturally occurring aluminosilicate minerals with uniform subnanometer and nanometer size crystalline structures. These can be converted into zeolite membranes using hydrothermal synthesis methods or other approaches, including in situ layer-by-layer crystallisation, and dry gel conversion in the presence of a template-water vapor.\textsuperscript{122-124} The chemical and thermal stability of zeolite membranes are extremely
Zeolite membranes are composed of a three-dimensional (3D) cross-linked \((\text{Si/Al})\text{O}_4\) tetrahedral framework, which contains precisely defined cavities that allow for the movement and containment of ions and water molecules.\(^{125}\) Figure 1.7 shows the framework structure of a Mordenite Framework Inverted (MFI)-type zeolite and the SEM image of a zeolite membrane on a porous \(\alpha\)-alumina support.

![Figure 1.7: (A) Framework structure of a MFI-type zeolite and (B) SEM image of a MFI-type zeolite membrane.](image)

Zeolite membranes have been studied widely for more than 20 years, with a primary focus on gas separation and liquid pervaporation processes.\(^{126}\) In 2001, molecular dynamics simulations showed that zeolite membranes are also theoretically suitable for removing ions from aqueous solutions by reverse osmosis.\(^{127}\) The simulations revealed that 100% rejection of sodium ions could be achieved using a single crystal zeolite membrane and RO. Since then, a number of studies have showed that thin zeolite
membranes are effective for achieving desalination of brackish water and a variety of wastewater samples, and in particular exhibit promising levels of rejection of salts and organic molecules.\textsuperscript{122,123,129}

The density and size of the pores present within a zeolite membrane are the primary factors that determine its effectiveness for water separation applications. The size of the pores determines the selectivity of the membrane towards different ions, while the density of pores determines its overall water permeability. Incorporation of atoms other than Si and Al into the structure of a zeolite via ion exchange can potentially be exploited to alter the charge and structural properties of the resulting membrane, including the widths of its internal channels. This would be expected to significantly change the sieving properties of a zeolite membrane.\textsuperscript{130}

The above studies demonstrate that zeolite membranes offer promise as an economically viable, alternative material for high-flux RO membranes with enhanced chemical, thermal, and mechanical stability. However, there are several issues associated with using zeolites that make them a difficult membrane platform to use. For example, most zeolites exhibit a low flux of water in comparison to current NF and RO membranes.\textsuperscript{125,131} In addition, their long-term stability when incorporated into an RO system is questionable, because they are susceptible to degradation under slightly acidic, aqueous conditions.\textsuperscript{132}
1.6.2 Self-assembled block copolymer membranes

Block copolymers are macromolecules containing different polymeric segments with the ability to self-assemble into highly ordered nanostructures.\textsuperscript{133} By varying the conditions under which self-assembly occurs, various nanostructures can be formed, including densely packed nanoporous membranes ideal for water filtration.\textsuperscript{134} Block copolymers are promising materials for making MF and UF self-assembled membranes with novel properties.\textsuperscript{134-137} For example, the addition of a specific hydrophilic component can be used to enhance a membrane’s resistance to fouling. The self-assembly of block copolymers can produce membranes with high porosities and narrow pore-size distributions, which is a distinct advantage over many current UF membranes with polydisperse pore sizes.\textsuperscript{138,139} Such membranes show potential for UF because the monodispersed pores should result in high solute selectivity, and their close packing should allow high fluxes. In addition, flat surfaces can be readily produced, suggesting that fouling will be reduced. The challenge remains to produce block copolymer membranes with precisely controlled nanosized pores, which enable these materials to function as RO membranes. In addition, greater control over the self-assembly process must be developed in order to produce large, defect-free materials suitable for use in a pilot scale setting.

1.6.3 Inorganic-organic TFN membranes

Another approach to developing new materials with novel separation capabilities centres on dispersing a filler material, such as various nanoparticles, into a polymer matrix to produce a mixed matrix membrane. Such materials are already finding use for a variety of membrane processes, including those which utilise fuel cells, as well as
pervaporation and gas separations. More recently, mixed matrix nanocomposite membranes have also been explored for potential use in water purification applications. This has been spurred on by investigations that examined the effect of depositing nanoparticles onto the surface of RO membranes, or encapsulating the nanoparticle within RO thin films. The resulting materials exhibited higher permeabilities towards water and salts, and in some cases also showed significant antimicrobial activity.

In another investigation, Jeong et al. produced zeolite-polyamide thin film nanocomposite (TFN) membranes by interfacial polymerisation. The zeolites were dispersed in the initiator solution prior to interfacial polymerisation, and resulted in nanocomposite films that were nearly twice as permeable to water, but still able to reject salts and low molecular weight organic solutes. When the loading of nanoparticles in the membranes was increased, the latter became increasingly hydrophilic, more negatively charged, and smoother than the corresponding materials produced without the nanoparticles.

Silver nanoparticles were incorporated into a thin polyamide film during interfacial polymerisation to produce composite membranes which exhibited good antibacterial properties, and selective rejection of solutes (e.g. 96-97% rejection of 2000 ppm MgSO₄) reminiscent of NF membranes. It has also been reported that incorporation of titanium dioxide (TiO₂) nanoparticles into polyamide thin films increased the permeability of the resulting membranes owing to enhanced hydrophilicity.
Although the above examples show that incorporation of nanomaterials into membranes can result in significant benefits for membrane filtration applications, this approach is not free from limitations. Issues that have been identified with this class of materials include thermal and mechanical instability, effectiveness only at high pressures, fouling, pollutant precipitation, pore blocking, and decreases in water flux. Low levels of reusability and unknown risks for ecosystems are also major concerns. Thus, alternative membrane materials that are reliable, safe, environmentally sensitive and cost-effective are still required for water purification and desalination.
1.7 References


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Chapter 2

Carbon Nanotubes and Membranes Derived from Carbon Nanotubes

This chapter commences with an overview of the structure and properties of CNTs. In addition, it provides a review of published work which has explored the potential for CNT materials, including membranes and composites, to act as selective adsorbents or filtration media for analytical and environmental applications. The chapter concludes with the overall aims of this research project.
2.1 Introduction

Recent years have witnessed impressive developments towards the application of nanostructured materials, including CNTs, in the field of membrane technology. CNTs are promising nanomaterials for the development of the next generation of membranes which exhibit high flux, high selectivity, and low fouling capabilities.\(^1\) In addition, CNTs are relatively easy to modify by adding different functional groups or even entire molecules to the outside of individual tubes, which may result in increased levels of, or variations in, molecular selectivity.\(^2,3\) Most importantly, the internal diameters of CNTs are very narrow and comparable in size to that of many small molecules, which raises the prospect of size-based exclusion and separation of chemical compounds.\(^4\) Molecular dynamics simulations showed that gas and water transport through the central channels of individual CNTs would be extraordinarily fast, owing to their extremely smooth, defect-free walls.\(^5,6\) These predictions are supported by the results of experimental studies, which found that the rates of transport of gases and liquids through membranes composed of aligned CNTs were exceptionally fast.\(^7,8\) These results highlight the need for further exploration of this new class of membrane materials. This is reinforced by the results of investigations into the cytotoxic properties of CNT membranes, which show these materials are less prone to biofouling and exhibit increased membrane lifetimes by killing and removing bacterial and viral pathogens.\(^9\) In addition, the high surface areas of CNT membranes confer advantages on these materials for applications involving rejection or adsorption of TrOCs and ions present in liquid samples.\(^10,11\)
2.2 Structure and properties of carbon nanotubes

Since their discovery by Iijima in 1991, CNTs have attracted much attention from academia and industry because of their unprecedented mechanical, electrical, and thermal properties.\textsuperscript{12-14} An immense range of potential applications for CNTs have been proposed (some realised), that include high-strength conductive composites, field emission displays, hydrogen storage devices, sensors, and membrane materials.\textsuperscript{4,7,15,16} Because of their very small diameters (as low as $\sim 0.7$ nm), these fascinating hollow cylinders exhibit chemical and physical properties which are very different from those of other carbon-based nanostructures. Carbon nanotubes possess high flexibility, low mass density, and large aspect ratios (typically ca. 300 – 1000).\textsuperscript{17,18} Some nanotubes are more conductive than copper, stronger than steel and lighter than aluminium. For example, theoretical and experimental studies on individual single-walled carbon nanotubes (SWNTs) showed they exhibit extremely high Young’s moduli (640 GPa to 1 TPa) and tensile strengths (150 – 180 GPa).\textsuperscript{19,20} Their mechanical robustness originates from the strength of the C–C bonds in their constituent graphene sheets. In addition to the exceptional mechanical properties associated with CNTs, they also exhibit superior electrical and thermal properties. They are thermally stable up to 2800 °C in a vacuum, exhibit thermal conductivities about twice as high as that of diamond, and display electrical conductivities 1000 times higher than that of copper wire.\textsuperscript{21}

Carbon nanotubes are essentially long cylinders composed of covalently bonded carbon atoms. The ends of the nanotube cylinders may or may not be capped by hemifullerenes. Depending on whether they consist of a single tube or multiple tubes, carbon nanotubes can be classified as single-walled carbon nanotubes (Figure 2.1A),
double-walled carbon nanotubes (DWNTs) or multi-walled carbon nanotubes (MWNTs, Figure 2.1B). SWNTs can be considered as single graphene sheets rolled into seamless cylinders. MWNTs composed of nested graphene cylinders coaxially arranged around a central hollow core, with interlayer separations of \( \sim 0.34 \) nm. DWNTs consist of two concentric graphene cylinders. They are expected to exhibit higher flexural moduli than SWNTs due to the presence of two concentric nanotubes, and greater toughness than regular MWNTs due to their smaller size.\(^{22}\) The inner diameter of SWNTs ranges from 0.7 – 1.6 nm, while their outer diameters vary from 1 – 2 nm. In contrast, the inner diameter of MWNTs vary between 1 and 3 nm, and their outer diameter can be up to 10 nm.\(^{23}\) The properties of SWNTs and MWNTs depends on their exact structure, as there are many ways a planar graphene sheet can be rolled up to form armchair, zigzag, or chiral nanotubes. The chirality of nanotubes has a significant impact on their properties, including electrical conductivity. For example, graphite is considered to be a semi-metal, but it has been shown that CNTs can be either metallic or semiconducting, depending on their chirality.\(^{24}\)

\[\text{Figure 2.1: Schematic illustration of: (A) a single-walled carbon nanotube, and (B) a multi-walled carbon nanotube. Reprinted with permission from John Wiley and Sons.}\]
2.3 Production of CNTs

CNTs can be synthesised using different methods with varying yields and purities. The primary methods of synthesising SWNTs and MWNTs include arc-discharge, laser ablation, gas-phase catalytic growth from carbon monoxide (CO), and chemical vapour deposition (CVD) from hydrocarbons. Both the arc-discharge and laser-ablation techniques are limited in the volume of CNTs they can produce. In addition, the product obtained often contains significant amounts of impurities in the form of catalyst particles, amorphous carbon, and non-tubular fullerenes. Therefore purification is always necessary to separate the tubes from undesirable by-products. These limitations have motivated the development of gas-phase synthesis techniques, such as CVD methods, where nanotubes are formed by the decomposition of a carbon-containing gas. These gas-phase techniques are amenable to the continuous production of large quantities of nanotubes since the carbon source is continually supplied by a flowing gas. In addition, the purity of the as-produced CNTs is quite high, minimizing subsequent purification steps. By using a modified CVD method, SWNTs with purities of up to 90% (w/w) have been synthesised in the gas phase using Fe(CO)₅ and CO in what has become called the high-pressure carbon monoxide disproportionation (HiPCO) process. The synthesis of CNTs by CVD-HiPCO appears to be a promising approach in comparison with other methods, owing to its comparatively low cost, the high purity of the resulting nanotubes, use of relatively simple equipment, and ability to produce nanotubes on a large-scale.


2.4 Surface modification of CNTs

While their extraordinary properties make CNTs attractive candidates for a diverse range of nanotechnology based applications including membrane filtration, their lack of solubility and processability in most common solvents has imposed limitations on their development for specific applications. CNT bundles typically form large aggregates due to van der Waals interactions and, as a result, they are insoluble in common organic solvents and aqueous solutions.\(^{28}\) CNTs can be dispersed in some solvents by ultrasonication, but precipitation immediately occurs in most cases when this process is interrupted. Surface modification of CNTs through covalent attachment of functional groups, and non-covalent wrapping or adsorption of various functionalised molecules onto the surfaces of CNTs, have both proven to be popular methods for facilitating their dispersion into solution.\(^3\)

Covalent surface modification involves functionalisation of a CNT surface with various moieties such as –COOH, –COH, –NH\(_2\), and –OH groups that are attached by covalent bonds (Figure 2.2).\(^{29}\) Direct covalent sidewall functionalisation is associated with a change of hybridisation of carbon from sp\(^2\) to sp\(^3\), and a simultaneous loss of π-conjugation in the graphene layer. The above functional groups endow CNTs with a rich chemistry, enabling their use as precursors for further chemical reactions, such as silanation, polymer grafting, esterification, thiolation, alkylation, arylation and attachment of biomolecules.\(^3,30,31\) CNTs functionalised in this way are soluble in many organic solvents, because their normally hydrophobic nature is changed to hydrophilic as a result of the attachment of polar functional groups. Chemically functionalised CNTs can produce strong interfacial bonds with many polymers, allowing the
preparation of CNT based nanocomposites that exhibit exceptional mechanical properties. Despite the utility of the covalent functionalisation method, a major drawback of this approach is that considerable damage to the sp\(^2\) hybridised carbon structure occurs as a result of the introduction of functional groups. Therefore, considerable effort has been devoted to developing alternative methods for solubilising CNTs that are convenient to use and cause less damage to their structure.

**Figure 2.2:** Surface functionalisation of CNTs through thermal oxidation, followed by subsequent esterification or amidation of the carboxyl groups.

Non-covalent surface modification is an alternative method for tuning the interfacial properties of CNTs. This approach is attractive because it does not compromise the physical properties of CNTs, but does improve their solubility and processability. Non-covalent functionalisation mainly involves wrapping the outside of CNTs with polymer, biomacromolecular or surfactant molecules. The ability to disperse CNTs into solution using polymers such as poly(phenylene vinylene) and polystyrene, was reported to be the result of wrapping of the latter molecules around the tubes to form supramolecular complexes.\(^\text{32,33}\) The polymer wrapping process involves van der Waals and \(\pi-\pi\) stacking...
interactions between the CNTs and polymer chains containing aromatic rings. This leads to the inter-tube van der Waals interactions between CNTs weakening, thereby increasing their ability to disperse into aqueous solution.

A number of studies have shown that a range of proteins, including bovine serum albumin and lysozyme, are also capable of forming stable aqueous dispersions of CNTs.\textsuperscript{34,35} The use of protein dispersants is of particular interest due to their lack of toxicity compared to surfactant and other typical dispersant molecules, as well as their biocompatibility.\textsuperscript{35} In addition, proteins contain a number of different types of reactive functional groups such as hydroxyls, carboxylic acids, amines and thiols, which effectively provide sites for further surface modification of CNTs when the protein is wrapped around the nanotubes.\textsuperscript{36} The dispersion of CNTs into aqueous solutions by protein molecules involves an electrostatic interaction mechanism, and is therefore highly dependent on the charge distribution present along the length of the protein and solution pH.\textsuperscript{34,35}

Carbohydrates such as chitosan and gellan gum have also been shown to be highly effective at wrapping themselves around CNTs to facilitate formation of aqueous dispersions of the latter.\textsuperscript{37} As biopolymers are generally either protonated or deprotonated in aqueous solution, their adsorption onto the surface of CNTs minimises re-aggregation of the latter through a combination of electrostatic repulsion and steric hindrance mechanisms.\textsuperscript{38} Chitosan was found to be very useful for separating SWNTs on the basis of differences in their size, as only the smaller diameter nanotubes could be non-covalently functionalised by the biopolymer and therefore dispersed in aqueous solution.\textsuperscript{39} It has been reported that chitosan chains wrap along the nanotube axis as
shown schematically in Figure 2.3. Evidence for this conclusion was provided by transmission electron microscopy studies on individual nanotubes which had been coated with polysaccharide (Figure 2.4).

![Figure 2.3](image)

**Figure 2.3**: Schematic illustration of chitosan helically wrapping around the outside of a CNT. The structure of chitosan is also shown. Reproduced from Journal of Membrane Science, 300, Fubing Peng, Fusheng Pan, Honglei Sun, Lianyu Lu, Zhongyi Jiang, Novel nanocomposite pervaporation membranes composed of poly(vinyl alcohol) and chitosan-wrapped carbon nanotube, 13, Copyright (2007), with permission from Elsevier.

Gellan gum is another polysaccharide that has been reported to be an extremely good dispersant for both SWNTs and MWNTs in aqueous solution. For example, in one study solutions containing gellan gum at concentrations as low as 0.0001% (w/v) were reported to be effective for dispersing MWNTs. DNA has also been shown to be capable of dispersing CNTs into aqueous solution. This was attributed to the ability of the DNA bases to bind to the nanotubes through π–π interactions, which then exposed the polar backbone of the DNA molecule to the solvent.
Due to their unique amphiphilic nature, surfactants have proven to be highly effective dispersing agents for CNTs.\textsuperscript{42-44} For example, surfactants with ionic, hydrophilic head groups, such as sodium dodecylsulfate (SDS) can stabilise a CNT dispersion by a mechanism involving electrostatic repulsion between micellar domains.\textsuperscript{45} In contrast, polyoxyethylene octylphenylether (Triton X-100), a commonly used non-ionic surfactant, facilitates the dispersion of CNTs by attaching itself around the individual nanotubes and using its hydrophilic moieties to form a large solvation shell around the assembly.\textsuperscript{46} The type of interaction between surfactant molecules and CNTs depends on the structure and properties of the surfactant, including its alkyl chain length, headgroup size, and charge. For example, both Triton X-100 and sodium dodecylbenzene sulfonate (SDBS) exhibit stronger interactions with the surfaces of nanotubes than SDS, because of the presence of the benzene rings in the former surfactants.
Having access to methods that enable solutions containing dissolved CNTs to be prepared is critical if scientists are to harness their many extraordinary properties. However, in order to take advantage of these discoveries, it is also necessary to have methods for then fabricating CNT dispersions into macroscopic structures such as films or membranes, which can then be incorporated into devices. Two such fabrication processes are the production of aligned CNT membranes and the synthesis of BP membranes. The following two sections describe how these materials are prepared, along with their properties, and present the results of studies that have examined their potential as membrane filtration media.

### 2.5 Aligned CNT membranes

Aligned carbon nanotube membranes consist of highly ordered, vertically aligned arrays of individual CNTs (Figure 2.5). As a consequence, aligned CNT membranes possess a regular pore structure consisting of very narrow internal cavities within individual tubes, which are of the order of c.a. 5 nm in the case of MWNTs. This inner core diameter is similar to the size of many proteins and other biological macromolecules. This suggests that aligned CNT membranes could be suitable for water desalination and decontamination applications. The size of their pores can be precisely determined by controlling the size of the catalytic particles used during nanotube growth, whilst the polarity of the pores can be fine-tuned through selective functionalisation.
Figure 2.5: (A) Scanning electron microscope (SEM) image of a vertically aligned array of CNTs produced using an Fe-catalysed CVD process. (B) Schematic illustration of the structure of an aligned CNT membrane. Reproduced with permission from American Association for the Advancement of Science.

Aligned CNT membranes are synthesised by either embedding CNTs into a matrix, or growing them directly onto a substrate, utilising a CVD process. For example, highly ordered nanoporous CNT membranes can be prepared by filling in the gaps between a vertically aligned ‘forest’ of CNTs with polymers such as polystyrene, followed by opening of the ends of the nanotubes. With the CVD approach catalytic particles (e.g. Co or Ni) are first deposited onto a support material such as quartz or silicon in a regular array to serve as growth sites for the CNTs (Figure 2.6). Gas-phase chemical vapour deposition is then used to grow the nanotubes by the decomposition of a carbon-containing gas. During synthesis, the walls of the growing nanotubes interact with their neighbours via Van der Waals forces to form rigid bundles of tubes aligned perpendicular to the substrate. The length of the nanotubes can be controlled to be within 10 – 240 μm, by varying the CVD reaction time.
The aligned CNTs that grow on the surface of the substrate are then treated with a range of polymer binders (such as polystyrene), or with silicon nitride, to fill in the interstitial voids between the individual CNTs.\(^5\)\(^,\)\(^6\) The membrane composed of aligned CNTs is then removed from the underlying substrate by using hydrofluoric acid, after which the ends of the closed CNTs can be opened, for example, by oxidation with a water plasma, to expose their entrances to gas or solvent molecules (Figure 2.6). The above preparation method was used by Majumder et al. to produce vertically aligned MWNT membranes with pore diameters of 7 nm, that were 4 – 5 orders of magnitude more permeable towards water than a simple macroscopic membrane.\(^5\)
Alternatively, free-standing aligned CNT membranes can be produced without a supporting material. Again a flat or microporous substrate such as quartz or alumina is required. The CNT forests that are produced using this method are as highly aligned as those made by the previous technique.\textsuperscript{52,53} However, the synthetic procedure does not involve sealing of the interstitial pores using a polymer. Therefore the final material can contain larger voids which extend up to tens of nanometres in diameter throughout its structure. Once complete, the aligned CNT film can be removed from the substrate using chemical methods as described previously, to leave behind a free-standing material.

Aligned CNT membranes have been shown to selectively filter solute molecules present in aqueous solutions.\textsuperscript{8,47} For example, aligned MWNT membranes with internal diameters of c.a. 6.5 nm were prepared using a method similar to that described above, and found to allow the passage of [Ru(bipy)$_3$]$^{2+}$ (bipy = 2,2'-bipyridine) molecules and gold nanoparticles with average diameters of 2 and 5 nm respectively, but not larger gold nanoparticles with an average diameter of 10 nm.\textsuperscript{47} In another study, macroscopic hollow cylinders composed of radially aligned MWNTs were shown to retain the heavier components of a hydrocarbon mixture, as well as bacteria and viruses present in contaminated solutions.\textsuperscript{54} More recently, Baek et al. compared the flux, rejection performance, and biofouling capabilities of aligned CNT membranes to that of a commercial UF membrane.\textsuperscript{55} The aligned CNT membranes exhibited a water flux approximately three times higher than that for the UF membrane, and showed greater resistance to biofouling, with only an approximately 15% reduction in permeate flux and significantly lower levels of bacterial attachment.\textsuperscript{55}
Although aligned CNT membranes have a number of properties which make them very attractive for specific filtration applications, there are two major drawbacks associated with using these materials for this purpose. First, the aligned forest of CNTs must often be removed from an underlying substrate, which can involve vigorous chemical etching methods using hazardous reagents such as HF. Secondly, the ends of the CNTs must be opened, which also requires harsh conditions such as plasma oxidation. Both steps are also quite complex to optimise and costly to perform. In addition, most aligned CNT membranes produced to date only have a relatively small surface area, require a lengthy fabrication process, exhibit poor mechanical stability and low CNT packing density, and also show little resistance to fouling. In view of these issues there has been significant attention devoted to producing CNT membranes by alternative, less complicated and hazardous procedures, that can be more readily scaled up as required.

### 2.6 Buckypaper membranes

Carbon nanotube BPs ([Figure 2.7](#)) are a simple type of CNT membrane architecture that consists of a self-supporting entangled assembly of CNTs. Buckypapers are often flexible materials, however they also exhibit a significant degree of chemical and physical stability. Due to their inherent thermal, electronic, and mechanical properties, BPs have been proposed for various applications including nanoactuators, sensors, radio frequency filters, and cold-field emission cathodes. Buckypapers have been used to prepare artificial muscles because of their flexibility and structural integrity. They are typically synthesised from dispersions of CNTs, which are themselves obtained by applying ultrasonic energy to samples containing nanotubes.
Figure 2.7: (A) Digital photograph of a MWNT buckypaper, and (B) an SEM micrograph of a SWNT buckypaper.\textsuperscript{65}

and a suitable dispersant molecule. Filtration of these dispersions onto a support membrane, using either vacuum or positive pressure, then results in formation of the buckypaper.\textsuperscript{60,66,67} Due to their simple and inexpensive preparation procedures, it is generally possible to produce BPs on a larger scale than aligned CNT membranes. Buckypapers possess a highly disordered structure (Figure 2.7B), which consists of CNTs bound together by van der Waals forces and π–π interactions, at the tube-tube junctions.\textsuperscript{68} The internal structure of BPs consists of a combination of small and large pores which correspond to the spaces within and between bundles of CNTs, respectively. Their pore size distribution is dominated by larger pores with diameters of 100 nm or above.\textsuperscript{69} Overall the pores in BPs contribute 60 – 70\% of their total volume, rendering them suitable as filtration membranes.\textsuperscript{66} Despite this only a small number of studies have investigated the filtration properties of BP membranes.

In order for BPs composed of CNTs to become attractive options for filtration applications, it will be essential to improve upon their mechanical properties, as they are often brittle due to weak connections between nanotube bundles. One method for overcoming this issue is to reinforce the BPs, e.g. by polymer intercalation.\textsuperscript{66,70} For
example, Coleman et al. infiltrated PVA, polyvinyl pyrrolidone (PVP), and polystyrene (PS) into BPs.\textsuperscript{70} They found that this resulted in increases in Young’s modulus, tensile strength, toughness, and strain to break for the infiltrated BPs. The increase in mechanical properties was attributed to the improvement in inter-bundle load transfer caused by polymer bridging. In a further study, Frizzell et al. showed that the mechanical properties of BPs fabricated from dispersions of SWNTs in aqueous solutions containing Triton X-100, were significantly improved by soaking the BPs in solutions containing PVP.\textsuperscript{66} It has also been demonstrated that the intercalation of high molecular weight polymers was better for improving the modulus and strength of BPs, while low molecular weight polymers resulted in greater overall toughness.\textsuperscript{66} In addition, Boge et al. showed that incorporation of biopolymers, including proteins and polysaccharides, into BPs can improve their mechanical properties.\textsuperscript{71} The materials investigated in this study were fabricated from aqueous dispersions of SWNTs that also contained lysozyme, bovine serum albumin, chitosan or gellan gum. Microanalytical data showed that some of the biopolymers were retained in the BP after they were prepared by vacuum filtration, owing to their ability to interact in a non-covalent fashion with the SWNTs.\textsuperscript{71} In the following section the results of investigations into the suitability of BPs as filtration media will be summarised and evaluated.

### 2.7 Filtration applications of CNT BPs and composite membranes

#### 2.7.1 Air filtration

One of the first demonstrations of the potential of carbon nanotubes for filtration applications involved composite materials consisting of a 2 μm ultrathin MWNT BP film supported on a cellulose filter.\textsuperscript{72} Fine aerosol particles ranging between 50 – 500
nm in diameter were removed by the composite BP, with efficiencies that exceeded the standards set out by the USA government for HEPA (high efficiency particulate air) filters. It was suggested that the composite BPs could also be used as filters for removing contaminants such as viruses from bioreactor feed streams.

In a more recent study, the suitability of a MWNT/ceramic composite membrane for air filtration applications was investigated. A CVD method was used to prepare the MWNT/ceramic composite filter by growing MWNTs on a porous alumina ceramic membrane. The ability of both the pristine ceramic membrane and the composite membrane to function as particulate filters was investigated using a sample of SO$_2$ with an average particle size of 296 nm. Under the same conditions, the pristine ceramic membrane showed a retention rate of 79.88%, while for the MWNT composite membrane it was 99.99% for the most penetrating particle size. These results showed that the latter membrane meets the criteria for both HEPA and ultra-low penetration air filters, according to the specifications of the USA Department of Energy. Experiments were also conducted to evaluate the antibacterial properties of both the pristine membrane and the MWNT composite membrane. It was shown that the presence of the MWNTs strongly inhibited the propagation of the bacterium E. coli on the filters, owing to inactivation of the cells, with an antibacterial rate of 97.86%. The authors believed that these results demonstrated that the MWNT/ceramic composite membrane showed great promise for multifunctional air filtration applications.

In an attempt to prepare high performing air filters, Nasibulin et al. developed an aerosol CVD synthesis method, which is a very simple and rapid fabrication technique for preparing free-standing films. SWNT films were prepared first by collecting
nanotubes downstream of the reactor on a microporous filter (0.45 µm pore diameter), and then dry transferring them to a flexible polyethylene terephthalate (PET) substrate. The free-standing SWNT films were found to be exceptionally good air filters, with an efficiency of 99.99% towards 11 nm Fe aerosol particles. The excellent performance of the filters was attributed to the high surface area of the SWNTs.

2.7.2 Bacterial filtration

The antimicrobial properties of BPs, and their ability to efficiently remove bacteria and viruses from contaminated water samples, were demonstrated by Brady-Estévez and coworkers. Initially these authors examined BPs prepared from dimethylsulfoxide (DMSO) solutions containing SWNTs but no dispersants molecules. The BPs were not removed from the underlying poly(vinylidene fluoride) (PVDF) support membrane they were deposited on, prior to evaluating their ability to remove E. coli and MS2 bacteriophage virus particles from water. Filtration experiments showed that the majority of the bacterial cells were retained, while measurements of their metabolic activity indicated that only 6% of E. coli cells remained metabolically active after retention (Figure 2.8). Exceptionally high viral removal capabilities were also shown by the hybrid SWNT/PVDF BPs.
Recently Sweetman et al. measured the permeability towards water, and determined the effectiveness for bacterial filtration, of self-supporting SWNT BPs prepared from dispersions containing macrocyclic ligands and antibiotics.\textsuperscript{65,76} It was shown that incorporation of the macrocyclic ligands into the SWNT BPs in some instances increased their water permeability up to ten-fold, compared to BPs prepared from dispersions containing Triton X-100.\textsuperscript{65} The most dramatic increase in permeability was exhibited by SWNT/PTS (PTS = phthalocyanine tetrasulfonic acid) BPs, which displayed an average membrane flux of $2400 \pm 1300 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which was almost 30 times greater than the average obtained for SWNT/Trix BPs ($83 \pm 5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$). The membrane flux observed for the SWNT/PTS BPs was even greater than that for commercial 0.22 mm PTFE membranes ($1900 \pm 300 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) measured under the same conditions. In addition, each of the above BPs was found to be $> 99\%$ effective for removing \textit{E. coli} from aqueous suspensions.\textsuperscript{76} This study therefore demonstrated that free-standing BP membranes can be just as effective for removing
Silver nanoparticles (AgNPs) are currently amongst the most efficient and well-known antibacterial agents. Studies have confirmed that AgNPs can deactivate microorganisms during water filtration processes. The antimicrobial properties of AgNPs can be attributed to their capacity to damage cellular protein and DNA, to interrupt electron transport chains and disturb cellular functions.\textsuperscript{77,78} Recently a new approach was used to synthesise a silver-doped MWNT composite membrane, with the aim of fully utilising the antibacterial properties of MWNTs and silver.\textsuperscript{79} In the first step towards the preparation of the composite membranes, MWNTs were impregnated with different loadings of silver (1, 10 and 20 wt.%\%) via a wet chemistry technique. Both MWNTs and AgNO\textsubscript{3} were dissolved in ethanol and ultrasonicated to obtained homogeneous mixtures. Impregnated MWNTs were then compacted at 200 MPa and sintered at 800 °C to prepare compact disk membranes. The resulting silver doped-MWNT composite membranes showed a high water permeate flux and exhibited strong antibacterial properties. \textbf{Figure 2.9} shows how the amount of bacteria remaining in the filtrate varied as a function of time after passing through Ag/MWNT composite membranes with different silver loadings. It was observed that for suspensions containing the same initial amount of bacteria, the membrane with 10% silver content showed tremendous antibacterial properties. For example, almost 100% of bacteria were removed or killed by this particular membrane after 1 h.
2.7.3 Gold nanoparticle filtration

Buckypapers prepared from MWNTs have recently been successfully used as nanofilters to remove gold nanoparticles (Au NPs) from colloidal solutions. The nanotubes were first dispersed in isopropyl alcohol, and subsequently filtered through a PVDF membrane to eventually prepare self-supporting MWNT BPs. Measurements performed using SEM images of the surface of the BPs (Figure 2.10a) revealed that the interstitial pores were 33 ± 15 nm in diameter. Despite the presence of such large pores, the BPs were able to intercept and remove much smaller particles because of the highly tortuous paths that liquid samples have to take while traversing the membrane. As a consequence, 100% removal of Au NPs was observed from a colloidal solution containing 0.25 mM gold. Figure 2.10b shows that these Au NPs were trapped on the surface of the BP after filtration. These particles were shown by High Resolution Transmission Electron Microscopy (HRTEM) to have an average diameter of 14.7 ± 0.7...
nm (Figure 2.10b). The complete rejection of Au NPs was demonstrated by the total disappearance of the characteristic plasmon resonance peak from the nanoparticles at 520 nm, in a UV–visible absorption spectrum of the permeate (Figure 2.10c).

Figure 2.10: (a) SEM micrograph of the surface of a self-supporting MWNT BP prepared from a dispersion of the nanotubes in isopropyl alcohol. Scale bar is 100 nm. (b) SEM micrograph of the surface of the BP after filtration of gold NPs. Scale bar is 100 nm. The inset is an HRTEM image showing the Au NPs. (c) UV–visible absorption spectrum of the colloidal solution of Au NPs before and after filtration through a MWNT BP. Reprinted with permission from Journal of Physical Chemistry C, 2012, 116 (35), 19025. Copyright (2012) American Chemical Society.

2.7.4 Organic compound filtration

Further evidence that BPs may be useful for water purification applications was provided by Harris and co-workers. Their studies involved BPs made from MWNT dispersions prepared in ethanol, without the assistance of surfactant or dispersant molecules. These BPs proved to be useful for the removal of humic acid (HA) from water samples, with recovery efficiencies > 93% being obtained. The authors demonstrated that carboxylic acid and hydroxyl functional groups were present on the surfaces of the CNTs, and concluded that the increased hydrophilicity they bestow on the nanotubes was an important contributor to their effectiveness as filtration media.
Self-supporting and electrochemically active MWNT BP filters have been shown to be effective for the adsorptive removal, and electrochemical oxidation, of a number of water-soluble dyes including methylene blue and methyl orange.\textsuperscript{82} In addition, the BPs were able to effect the oxidation of chloride and iodide ions in aqueous solution.\textsuperscript{82} The MWNTs were first dispersed in DMSO using probe sonication. Vacuum filtration of the resulting dispersions through 5 μm PTFE membranes was then used to eventually afford the self-supporting MWNT BPs. In the absence of an applied electrical potential, the MWNT BP filter completely removed methylene blue and methyl orange from an influent solution, until a monolayer of dye molecules had become adsorbed to the MWNT filter surface. In a separate experiment, application of an electrical potential (2 V) to a buckypaper resulted in oxidation of > 98% of influent dye molecules after a single pass through the membrane. The efficient removal and oxidation of the dye molecules was attributed to their planar aromatic structures, which promotes adsorption to the anodic MWNT surface. The electrochemical MWNT BP filter was also able to oxidize chloride and iodide ions present in aqueous solutions with only a minimal overpotential required. These results highlight the potential of electrochemically active MWNT BPs for the adsorptive removal and oxidative degradation of aqueous contaminants.

Among the membrane separation technologies that are currently available, pervaporation is one of the most developed and energy-efficient processes for separating azeotropic mixtures, isomers or close-boiling mixtures that cannot be separated through conventional filtration processes.\textsuperscript{83} Pervaporation is a process for the separation of the mixtures of liquids by partial vaporisation through a membrane. In this
process, at first the feed is heated up to the operating temperature and then brought into contact with the membrane. The permeate passes through the membrane and is continuously removed in the form of a vapour. The continuous removal of the permeate creates a concentration gradient across the membrane which acts as a driving force for the process. To date, most studies have reported on the pervaporation of binary mixtures involving a combination of water with either ethanol or ethyl tert-butyl ether (ETBE), using polymeric membranes or mixed matrix membranes.\textsuperscript{83-85} For example, Choi \textit{et al.} incorporated MWNTs into a PVA membrane for the dehydration of a water/ethanol mixture.\textsuperscript{83} The pervaporation properties of the membrane were observed to be affected by the amount of MWNTs in the membranes, with 4\% (w/w) MWNTs determined to be the optimum nanotube content.

Recently it has been reported that BPs can be used in a pervaporation process to separate organic compounds from azeotropic mixtures in water.\textsuperscript{86,87} In one such study, self-supporting MWNT BPs were used, which were prepared from dispersions of MWNTs in ethanol. The BPs were coated with a thin layer of PVA to form a new type of asymmetric MWNT/PVA membrane.\textsuperscript{86} The PVA-coated BP membranes exhibited improved mechanical properties relative to those of a pure PVA membrane. They were then used for the dehydration of a multi-component azeotropic reaction mixture obtained from ethanol and tert-butyl alcohol (TBA), via a pervaporation process. When the purified MWNT/PVA membranes were used for pervaporation, they exhibited permeation fluxes and separation factors two and four times greater than those of a pure PVA membrane. This was believed to be due to the presence of hydrophilic groups on the oxidised MWNTs, and the existence of nanochannels within the pre-selective layer.
of the MWNT buckypaper, which favoured the permeation of water molecules. It was also assumed that the MWNT/PVA BP could serve as a catalytic membrane in systems designed to separate water and by-products of the etherification reaction, and thereby achieve high yields of ETBE (Figure 2.11).  

Figure 2.11: Schematic illustration of pervaporation of an azeotropic mixture: (A) Feed solution containing a mixture of ETBE, TBA and ethanol; (B) intermediate and (C) final stages of pervaporation using a MWNT/PVA BP. Reproduced from Journal of Membrane Science, 453, Kian Fei Yee, Yit Thai Ong, Abdul Rahman Mohamed, Soon Huat Tan, Novel MWCNT-buckypaper/polyvinyl alcohol asymmetric membrane for dehydration of etherification reaction mixture: Fabrication, characterisation and application, 546, Copyright (2013), with permission from Elsevier.  

Composite materials have often been used in investigations into the filtration properties of CNTs, owing to their superior mechanical properties in comparison to stand alone nanotube membranes. An alternative method of endowing improved strength upon free-standing BPs involved the preparation of a BP supported ionic liquid membrane (SILM). The synthesis of this material first required 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]) to be blended with polyvinyl alcohol. The [Bmim][BF₄]/PVA blend was then infiltrated into the interstitial pores of a MWNT BP, endowing improved mechanical stability on the resulting BP/SILM composite material.
The structure of the composite, in which the membrane and support layers were merged into a single layer, different from that of conventional asymmetric membranes. In addition, the BP/SILM membrane exhibited lower levels of resistance to mass transport, as well as enhanced thermal and mechanical stability. When used in a pervaporation process to dehydrate an aqueous solution containing ethylene glycol, the new membrane displayed significantly greater separation performance compared to that of other PVA membranes reported in the literature. In addition, the BP/SILM membrane exhibited enhanced permeability, with a permeation flux of 102 g m⁻² h⁻¹. The BP/SILM composite membrane also demonstrated robust pervaporation performance over a period of 120 h, further confirming its potential for industrial applications.

Organophosphates (OPs) are among the most toxic substances synthesised to date, and are used as pesticides and nerve agents. Recently a new ‘one-pot’ methodology was developed for the rapid and straightforward fabrication of an enzymatically active MWNT BP to be used for OP bioremediation. This new type of BP was prepared from carboxylated MWNTs (MWNTs–COOH), which were ultrasonically dispersed in an
aqueous solution containing Triton X-100. The resulting dispersion was then filtered under vacuum onto a support membrane to produce a MWNT BP membrane. Organophosphate hydrolase (OPH) was subsequently covalently immobilised onto the nanotube surface to produce an enzymatically active OPH/MWNT BP membrane. To demonstrate its potential for bioremediation, an aqueous solution of methyl paraoxon (used as a model OP contaminant) was filtered using the OPH/MWNT buckypaper (Figure 2.13). A significant decrease in the concentration of methyl paraoxon was achieved, which was ascribed to its in situ hydrolysis by the immobilised OPH during the filtration process. The authors proposed that this result provides proof of concept for a new generic approach to the design of bioactive CNT BP scaffolds, which can be tailored for a range of applications from environmental remediation to biomedical devices.

Figure 2.13: Schematic illustration of the structure of a biocatalytic MWNT BP containing an immobilised organophosphate hydrolase (OPH). A model OP solution was filtered through the BP membrane, resulting in a decrease in OP concentration owing to its in situ hydrolysis by the enzyme during the filtration process. Reproduced from Journal of Materials Chemistry B 2014, 2, 915, with permission of The Royal Society of Chemistry.90

In a recent study, a promising hybrid NF membrane was obtained by loading reduced graphene oxide (rGO) that was intercalated with CNTs (rGO/MWNTs) onto an anodic
aluminum oxide (AAO) MF membrane via a vacuum-assisted filtration process. The as-prepared rGO/MWNT hybrid NF membranes were then used to purify drinking water by retaining Au nanoparticles and a wide range of organic compounds including dyes, proteins, organophosphates, sugars, and humic acid. The as-prepared rGO/MWNT hybrid NF membranes exhibited high performance with regard to the rejection of fulvic acid from aqueous solutions (Figure 2.14). This could be observed qualitatively, with the yellow colour of the feed solution being converted into a clear and transparent permeate. This indicated that the fulvic acid had been completely rejected by the rGO/MWNT hybrid NF membranes.

![Figure 2.14: Performance of rGO/MWNT hybrid NF membranes for removing fulvic acid (initial feed concentration 50 ppm) from water. Reprinted from Nanoscale 2016, 8, 5696, with permission of The Royal Society of Chemistry.](image)

The rGO/MWNT hybrid NF membrane was highly effective at retaining Au nanoparticles, bovine serum albumin (BSA) and phoxim (an organophosphate insecticide), whilst retaining a high degree of permeability towards solvent water
molecules. The former conclusion was supported by the measured retention values for Au nanoparticles, BSA and phoxim being 99.2%, 99.5% and 99.8%, respectively in experiments involving a single solute (Figure 2.15). During these experiments the permeability of water was determined to be between 22 and 30 L m$^{-2}$ h$^{-1}$ bar$^{-1}$, which is markedly larger than what has been reported for graphene NF membranes in the literature.$^{92}$

![Figure 2.15: Performance of rGO/MWNT hybrid NF membranes during experiments involving feed solutions containing Au nanoparticles, BSA and phoxim. Reprinted from Nanoscale 2016, 8, 5696, with permission of The Royal Society of Chemistry.$^{91}$](image)

Introduction of nanomaterials such as CNTs into other membranes has been used as a method for altering the selectivity of the later, without greatly affecting their intrinsic permeability. This has been demonstrated by a number of authors, who showed that the transport and separation properties of such modified membranes is dependent on both the identity and mount of incorporated nanomaterial.$^{93,94}$ In one such study, the effect on ability to recover low molecular weight micropollutants, of modifying polyacrylonitrile (PAN) membranes with SWNTs was investigated.$^{95}$ The composite membranes were prepared by a phase inversion method in which SWNTs were first dispersed in DMF
using ultrasonication. Polyacrylonitrile was then added to the DMF solution, and the solution cast onto a glass plate and subsequently immersed in a coagulation bath containing deionised water and isopropanol. After the membranes had precipitated, they were stored in deionised water to ensure complete phase separation. It was observed that the structure of the membranes changed significantly depending on the amount of nanotubes added, with those having the highest content of CNTs exhibiting the highest capacity towards micropollutants.

Figure 2.16 illustrates the effect of changing the amount of SWNTs incorporated into PAN membranes on their ability to remove BPA and nonylphenol (4-NP), as well as their permeate flux. Also included are data for a composite PAN membrane containing 1% SWNT–COOH. The permeate flux of a PAN membrane containing 1% SWNTs was about 80% higher than that for an unmodified PAN membrane. Increasing the amount of SWNTs present in the membranes from 0 to 0.2%, and then 0.5%, resulted in a significant enhancement in the ability to remove both types of micropollutants. Somewhat surprisingly, however, further increasing the amount of SWNTs incorporated to 1.0% adversely affected recovery levels, but not the permeate flux. Figure 2.16 also shows that the ability of a composite membrane containing 1.0% SWNT–COOH to recover both micropollutants was greater than for the corresponding materials containing the same amount of SWNTs.⁹⁵
Pharmaceuticals and personal care products (PPCP) have been widely used in modern society and are persistently released into aquatic environments. There is therefore an urgent need for energy-efficient technologies that can be used to control levels of PPCP pollution. One recent study examined the effectiveness of nanocomposite membranes, consisting of a layer of SWNTs or MWNTs deposited on PVDF, for removal of triclosan (TCS), acetaminophen (AAP), and ibuprofen (IBU) from aqueous solutions. The extent of removal of the PPCP ranged from 10 – 95%, and was found to increase as the number of aromatic rings in the pollutant molecules increased. In addition, the greater specific surface area of membranes containing SWNTs was found to be advantageous for higher PPCP recoveries. The membranes were prepared by first dispersing SWNTs, MWNTs or carboxylated MWNTs in 10 mL of ultrapure water using ultrasonication, and then filtering the resulting suspensions slowly through a flat piece of PVDF contained in a glass syringe. This resulted in composite materials with a CNT loading of 22 g m\(^{-2}\) membrane surface area.
In order to determine the adsorption capacities of the different CNT membranes towards mixtures of TCS and IBU, the amounts of these two pollutants that had adsorbed onto the membranes was measured. The results obtained showed that adsorption of TCS by the virgin PVDF membrane quickly reached saturation within 40 min. In contrast, the amount of TCS adsorbed by the composite SWNT/PVDF and MWNT/PVDF membranes increased in an almost linear fashion for up to 200 min, regardless of whether or not Suwannee River fulvic acid (SRFA) was also present (Figure 2.17A). These results indicated that the adsorption of TCS by the CNT membranes had not reached saturation under the conditions studied. Similar trends were observed during experiments in which the adsorptive filtration of IBU by the composite CNT membranes was examined (Figure 2.17B).

![Figure 2.17: Effect of time on the adsorption of: (A) triclosan and (B) ibuprofen by SWNT/PVDF and MWNT/PVDF composite membranes both in the absence and presence of SRFA. Reprinted from Journal of Membrane Science, 479, Yifei Wang, Jiaxin Zhu, Haiou Huang, Hyun-Hee Cho, Carbon nanotube composite membranes for microfiltration of pharmaceuticals and personal care products: Capabilities and potential mechanisms, 165, Copyright (2015), with permission from Elsevier.](image-url)
2.7.5 Desalination

Several groups have demonstrated that it is possible to desalinate water samples with relatively low salinity (< ~5000 mg L\(^{-}\) of NaCl), by using electrodes containing CNTs and carbon nanofiber (CNT/CNF) composite films as the electrochemically active layers, in conjunction with a capacitive de-ionisation apparatus.\(^{97,99}\) This application takes advantage of the electrical conductivity and high porosity offered by electrodes consisting of both CNTs and CNFs. The capacitive de-ionisation apparatus used in these experiments consisted of two electrodes to form a capacitor, across which a voltage was applied to adsorb ions of opposite polarity from a stream of salty water. When the applied potential was reversed the salt was then released as a concentrated brine.

A self-supporting BP was first used in conjunction with a direct contact membrane distillation (DCMD) apparatus for the rejection of salt from an aqueous solution by Dumee et al.\(^{100}\) These researchers prepared buckypapers from dispersions of MWNTs in propan-2-ol, and were able to use these membranes to reject 99% of the salt present in water samples. The highly hydrophobic BPs were used to separate a feed solution consisting of hot sea water or brackish water, from a permeate solution comprised of cold fresh water. While liquid could not cross the membrane, water vapour was able to pass through the pores from the hot feed solution to the cold permeate, driven by the difference in partial vapour pressure (Figure 2.18). This vapour then condensed on the permeate side creating fresh water. The inherent hydrophobicity of CNTs, combined with the high porosity of the buckypaper membrane, made the latter ideal for this application. This was reflected in water vapour permeabilities up to \(3.3 \times 10^{-12} \text{ kg m}^{-1} \text{s}^{-1} \text{ Pa}^{-1}\) being observed using a small scale rig.\(^{100}\) Although some issues were encountered such as a decline in flux with time, and delamination of the BPs owing to
the formation of micro-cracks, this work provided proof of concept that BPs can be used for water desalination. In a subsequent study, the same authors prepared poly(tetrafluoroethylene) (PTFE) coated BPs with enhanced hydrophobicity, and improved mechanical stability.\textsuperscript{101} The PTFE-coated BPs also exhibited an improved lifespan, as well as excellent water permeability and salt rejection properties. For example, 99\% rejection of the salt was observed with feed solutions containing high NaCl concentrations (35 g L\textsuperscript{−1}).

![Figure 2.18: Schematic illustration of direct contact membrane distillation using a BP membrane. Reproduced from Journal of Membrane Science, 351, Ludovic F. Dumée, Kallista Sears, Jürg Schütz, Niall Finn, Chi Huynh, Stephen Hawkins, Mikel Duke, Stephen Gray, Characterization and evaluation of carbon nanotube Bucky-Paper membranes for direct contact membrane distillation, 36, Copyright (2010), with permission from Elsevier.\textsuperscript{100}](image)

Recently a novel class of hybrid nanofiltration membranes were fabricated via in-situ ionic cross-linking between sodium alginate (SA), polyethyleneimine (PEI), and MWNT–COOH.\textsuperscript{102} It was shown that the permeability towards water of these hybrid nanofiltration membranes doubled from 13.4 to 27.0 L m\textsuperscript{−2} h\textsuperscript{−1}, when the mass ratio of MWNTs to SA (X_{MWNT/SA}) was increased from 0.00 to 0.05. In addition, they showed
higher levels of MgCl$_2$ rejection (93.5%), and greater Na$^+$/Mg$^{2+}$ selectivity, compared to other NF membranes containing polyelectrolytes.

Graphene, a two-dimensional (2D) carbon material is a potential candidate for next generation membrane nanomaterials.$^{103,104}$ Recently it was shown that graphene membranes formed by stacked graphene oxide (GO), or chemically converted graphene (CCG), possess aligned nanochannel arrays that can efficiently separate molecules in the gas or liquid phase.$^{105-108}$ Although earlier graphene membranes had been reported to exhibit high water fluxes, their ability to reject pollutants was usually much lower than that of commercial NF membranes. Recently, however, Han et al. reported the preparation of a graphene nanofiltration membrane consisting of densely stacked CCG layers, which exhibited comparable rejection properties to a commercial NF membrane for both a simple salt (Na$_2$SO$_4$) and organic dyes.$^{92}$ One disadvantage, however, was that the graphene membrane exhibited a relatively low degree of permeability towards water (flux = 3.3 L m$^{-2}$ h$^{-1}$ bar$^{-1}$). It was hypothesized that the narrow space between graphene sheets in graphene membranes might be the main cause for their low water flux. To overcome this issue, the same research group later prepared graphene/CNT composite membranes by assembling rGO and MWNTs on a porous substrate. The rationale behind the design of these new membranes was that the reduced graphene oxide would facilitate molecular sieving interactions, while the MWNTs would expand the interlayer space between neighbouring graphene sheets resulting in higher water fluxes.$^{109}$ A series of these new NF membranes containing different amounts of MWNTs were prepared.
Electron microscopy studies on the membranes revealed that the MWNTs had been inserted into the graphene sheets without disturbing the morphology of the later. This was attributed to the flexibility of graphene oxide and excellent compatibility between graphene and CNTs. Transmission electron microscopic examination of the materials indicated that the MWNTs were well dispersed throughout the membranes. Nanofiltration experiments conducted in a dead-end filtration device with the rGO/MWNT NF membranes showed water fluxes up to 11.3 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), which was more than twice that of the neat graphene NF membrane. In addition, the rGO/MWNT membrane exhibited high levels of dye rejection (> 99% for Direct Yellow and > 96% Methyl Orange), and a significant ability to reject salt (83.5% rejection for Na\(_2\)SO\(_4\), 51.4% rejection for NaCl).\(^\text{109}\) Moreover, the rGO/MWNT NF membranes showed better antifouling ability than those composed solely of graphene due to lower levels of roughness and higher hydrophilicity.\(^\text{109}\)

2.8 Improved resistance to fouling

Recent interest in CNTs also stems from research which showed they can be used to improve the antifouling properties of commercial UF membranes. For example, in a recent study by Guo et al., the effects of modifying the surface of polyethersulfone (PES) UF membranes with buckypapers on susceptibility to fouling was investigated.\(^\text{110}\) The composite membranes were fabricated by filtering a suspension of MWNTs through a commercial PES membrane in a dead-end UF unit. The pure water flux of the composite material was shown to be significantly greater than that exhibited by a pure PES membrane. It was also shown that the BP could trap pollutants present in sewage effluent on the surface of the composite, thereby preventing them from reaching the underlying PES membrane. The ability of the BP modified membrane to remove humic
acid from aqueous solutions was also significantly greater than that of the unmodified PES membrane.

Another comprehensive investigation of the antifouling properties of composite membranes was performed by Bai et al.\textsuperscript{111} The composite membranes examined were prepared using MWNT–COOH or MWNTs that had been covalently functionalised with polyethylene glycol (MWNT–PEG). A PES UF membrane was coated with either the raw or functionalised MWNTs, resulting in composite materials that had rougher surfaces than the underlying support material. Investigations into the antifouling properties of each of the different types of composite materials were conducted using three natural organic matter models. These were humic acid, BSA and sodium alginate. In each case the composite membranes exhibited significantly improved antifouling properties compared to the PES membrane alone. This was attributed to decreased direct contact between the PES membrane and the foulant owing to the intervening BP layer.\textsuperscript{111} Figure 2.19 compares results obtained from fouling studies performed using humic acid. Each of the modified membranes showed significantly higher fluxes than a pure PES membrane after exposure to increasing amounts of humic acid. The charges present on the surface of the composite material, as well as its roughness were believed to be important factors affecting the antifouling properties. These results clearly illustrate that a potential application of BPs is to enhance the overall performance of commercial membranes by minimising fouling, thereby reducing running costs and increasing operational lifetimes.
2.9 Application of electric potential to inhibit fouling

To date there have been very few studies which have sought to take advantage of the electrical conductivity of BP membranes in order to achieve superior outcomes for a filtration process. One study that achieved this goal involved the use of robust and electrically conductive membranes prepared using MWNT−COOH and cross-linked PVA, which were designed to inhibit fouling by organic compounds. The first step towards preparing these membranes involved dispersing MWNT−COOH in aqueous solutions containing dodecylbenzenesulfonic acid (DDBS) using a horn sonicator. The resulting MWNT−COOH dispersion and a solution of PVA were then pressure deposited onto a commercial polysulfone (PS-35) ultrafiltration membrane. This resulted in the formation of modified membranes (PVA/MWNT−COOH/PS-35) that were then incorporated into an electrofiltration cell, in order to study the effects of applied potentials on the extent of membrane fouling in the presence of high...
concentrations (3 – 5 g L$^{-1}$) of negatively charged alginic acid. Higher fouling rates were observed for the unmodified PS-35 membrane compared to the PVA/MWNT–COOH/PS-35 membrane. It was shown that application of −3 V or −5 V to the modified membrane for 100 min resulted in much smaller reductions in operating pressure (33% and 51%, respectively) compared to when no voltage was applied (Figure 2.20). This was due to the application of negative voltages leading to significant inhibition of fouling, which was concluded to be a result of electrostatic repulsive forces between the negatively charged membrane and alginic acid.$^{112}$

![Figure 2.20: Effect of application of negative potentials to PVA/MWNT–COOH/PS-35 membranes on the extent of fouling caused by a solution consisting of 5 g/L alginic acid. Reduced levels of fouling lead to smaller increases in applied pressure being required to maintain membrane operation. Reproduced from Journal of Membrane Science, vol. 468, Alexander V. Dudchenko, Julianne Rolf, Kyle Russell, Wenyan Duan, David Jassby, Organic fouling inhibition on electrically conducting carbon nanotube–polyvinyl alcohol composite ultrafiltration membranes, 1, Copyright (2014), with permission from Elsevier.$^{112}$](image)

The effect of applied potentials on biofilm formation was also examined in a study involving polyamide/MWNT–COOH composite membranes.$^{113}$ The first step towards
producing these membranes involved preparing a dispersion of MWNT–COOH in an aqueous solution containing DDBS using a sonication probe. The MWNT–COOH dispersion was then deposited onto a PES support membrane. In the final step the MWNT–COOH covered PES support membrane was immersed in a solution containing $m$-phenylenediamine (MPD) and trimesoyl chloride (TMC) to produce a PES supported polyamide/MWNT–COOH composite membrane. The latter exhibited high electrical conductivity ($\sim 400$ S/m) and good NaCl rejection properties ($> 95\%$). In the case of plain polyamide membranes, a nonreversible decline in flux was observed in experiments involving a feed solution containing *Pseudomonas aeruginosa*, a model biofouling bacterium. This was attributed to biofilm formation, which could not be reversed by application of a cross-flow rinse with the feed solution. In contrast, the decrease in flux observed when polyamide/MWNT–COOH nanocomposite membranes were tested under the same conditions, and with an electrical potential applied to their surface, was only caused by deposition of bacteria, rather than bacterial attachment. This was shown by experiments in which the flux was restored to its initial levels following a short rinse with the feed solution, and without the use of added cleaning agents. Inhibition of biofilm formation on these polyamide/MWNT–COOH nanocomposite membranes was shown to be a long term effect, which did not decrease with membrane use, and was highly reproducible.

Membrane filtration technology provides feasible solutions for removing contaminants, but achieving high permeability, good selectivity, and antifouling ability still remains a great challenge for existing filtration technologies. Recently Fan *et al.* applied a new strategy in which membrane filtration is coupled with electrochemistry to enhance the
performance of a MWNT/Al$_2$O$_3$ composite membrane.\textsuperscript{114} The synthesis of the composite membrane was achieved by first dispersing oxidised MWNTs in DMF also containing 0.5 wt. % polyacrylonitrile (PAN). The resulting CNTs/PAN dispersion was then vacuum filtered onto a porous Al$_2$O$_3$ substrate, producing a MWNT/PAN/Al$_2$O$_3$ membrane which was then pyrolysed at 1000 °C under an atmosphere of hydrogen. The final membrane exhibited good pore-size tunability, mechanical stability, and electrical conductivity.\textsuperscript{114}

The MWNT/PAN/Al$_2$O$_3$ composite membrane exhibited a notable ability to remove contaminants smaller than the membrane pores.\textsuperscript{114} These results indicated that both the permeability and selectivity of MWNT composite membranes can be significantly enhanced by electrochemical assistance. As shown in Figure 2.21a, the total organic carbon (TOC) removal efficiency exhibited by the MWNT/PAN/Al$_2$O$_3$ membrane without any electrochemical stimulation was just 28.9%. However, this improved to 46.7%, 71.3%, and 87.7%, when the membrane was subjected to a constant applied potential of +0.5, +1.0, and +1.5 V, respectively.\textsuperscript{114} These results indicated that the extent of removal of NOM by the MWNT/PAN/Al$_2$O$_3$ membrane could be enhanced significantly by electrochemical assistance.
Figure 2.21: Effect of an applied electrochemical potential on the performance of a MWNT/PAN/Al₂O₃ membrane exposed to humic acid: (a) effect on TOC removal efficiency; and (b) normalised permeate flux. Reprinted with permission from *Journal of Environmental Science & Technology*, 2015, 49 (4), 2293. Copyright (2015) American Chemical Society.¹¹⁴

Figure 2.21b shows the effects of different electrochemical stimulation on the permeate flux of the MWNT/PAN/Al₂O₃ membrane. In the absence of an applied electrochemical potential, the normalised permeate flux of the MWNT/PAN/Al₂O₃ membrane decreased to 59.5% after 60 min of operation, owing to membrane fouling caused by humic acid accumulation.¹¹⁴ This was confirmed by observation of a layer of organic matter on the MWNT/PAN/Al₂O₃ membrane surface (Figure 2.22a). In contrast, permeate fluxes of 68.5%, 79%, and 92.6% were observed when applied potentials of +0.5, +1.0, and +1.5 V, respectively were used.¹¹⁴ These results demonstrated that the loss of permeability of the MWNT/PAN/Al₂O₃ membrane was mitigated through the use of an electrochemical signal. Consistent with this, the SEM image of the membrane used in the experiment performed using an electrochemical potential of +1.5 V showed much less accumulation of humic acid on its surface (Figure 2.22b).
Figure 2.22: SEM images of MWNT/PAN/Al₂O₃ membranes used in NOM filtration experiments for 60 min: (a) no electrical potential applied to the membrane; and (b) an applied potential of + 1.5 V used. Reprinted with permission from Journal of Environmental Science & Technology, 2015, 49 (4), 2293. Copyright (2015) American Chemical Society.¹¹⁴

Similar results were obtained by the same research group when using electropolarisation in conjunction with a conductive MWNT/ceramic composite membrane.¹¹⁵ The latter was prepared by first dispersing carboxylated MWNTs into a 0.5 wt % PAN/DMF solution by ultrasound sonication, and then coating a hollow fibre substrate with the dispersion using a vacuum filtration process. The resulting materials were heated at 250 °C for 3 h in air, and then subjected to pyrolysis at 1000 °C under a hydrogen atmosphere, to afford the desired MWNT/ceramic composite membranes. When an electrical potential was applied, the MWNT/ceramic composite membrane exhibited a permeate flux 8.1 times higher than that observed in the absence of electropolarisation, when used to filter a feed solution containing bacteria. In addition, the permeate flux of the composite membrane was 1.5 times larger when electropolarisation was used to filter an aqueous solution containing NOM. These results demonstrate the very good performance of the new membrane with respect to mitigating biofouling.
Figure 2.23 shows the effect of operating time on both the normalised water flux and ability to remove NOM, of this new type of composite membrane when subjected to different types of electrical potential. In each case where an electrical potential was applied, the results obtained were superior to those observed when no electrical stimulation was used. The highest permeate flux and NOM removal was observed when the membrane was operated under anodic, cathodic and alternating polarisation. The increases in permeate flux were ascribed to mitigation of fouling of the MWNTs/ceramic membrane by organic components, owing to the application of electropolarisation.

Figure 2.23: Effect of different types of electrochemical stimulation on the performance of a MWNT/ceramic membrane during filtration experiments performed using solutions containing NOM: (a) Effect of normalised permeate flux of water; and (b) effect on TOC removal efficiency. Reprinted from Water Research, 88, Xinfei Fan, Huimin Zhao, Xie Quan, Yanming Liu, Shuo Chen, Nanocarbon-based membrane filtration integrated with electric field driving for effective membrane fouling mitigation, 285, Copyright (2015), with permission from Elsevier.

Similar promising results were obtained from fouling mitigation experiments performed using the MWNT composite membranes and aqueous feed solutions that contained both NOM and *E. coli*. In the absence of any electropolarisation, the permeate flux was shown to be 846 L m⁻² h⁻¹ bar⁻¹. In contrast, values of 1065, 1410 and 1570 L m⁻² h⁻¹ bar⁻¹ were obtained after 60 min filtration, when increasing alternating biases of ± 0.5, ±
1.0 and ± 1.5 V, respectively were used. In addition, NOM removal efficiency was enhanced more than three-fold, when the membrane was cycled between ± 1.5 V.\textsuperscript{115}

The above results show that electrically conductive composite membranes containing CNTs show intriguing and potentially useful antifouling properties. Further evidence of this was provided by a recent investigation using a new type of dual-layer MWNT/PVDF membrane.\textsuperscript{116} When compared to a pristine PVDF membrane, the MWNT/PVDF dual layer membrane exhibited greater electrical conductivity and a 10% increase in water permeability.\textsuperscript{116} When an electrical potential of 1 V DC or 2 V DC was applied, the MWNT/PVDF membrane maintained a lower transmembrane pressure than the pristine PVDF membrane in experiments performed with solutions containing sodium alginate, BSA and humic acid. The lower transmembrane pressure was attributed to lower levels of fouling as a result of the applied electric field. With the MWNT/PVDF membrane serving as a cathode, it was hypothesized that the foulants in the feed solution were driven away from the membrane.

Composite membranes consisting of MWNTs and calcium alginate (CA) also exhibit low levels of fouling even in the absence of any electrochemical assistance. It had already been shown that CNT doped alginate composites exhibited good mechanical strength, and can be used to remove heavy metal ions, dye molecules and NOM from wastewater by acting as an adsorbent.\textsuperscript{117,118} In order to incorporate those characteristics into filtration membranes, Jie \textit{et al.} prepared MWNT/CA hydrogel NF membranes, by using Ca\textsuperscript{2+} to crosslink the CNTs and CA in the presence of polyethylene glycol 400 (PEG400), which served as a pore-forming agent.\textsuperscript{119} The strength, antifouling properties
and dye rejection capabilities of the MWNT/CA membranes were investigated. When the feed solution was changed from pure water to a solution containing BSA, the permeate flux reduced only slightly. Furthermore, after repeated operation, the permeate flux remained at ca. ~ 90% of the value obtained when pure water was used as the feed. These results were obtained without any washing operations being performed between experiments, indicating that the MWNT/CA filtration membrane exhibited excellent protein antifouling properties. In addition, the MWNT/CA composite membrane also showed 99% rejection of Congo Red, indicating that it can be used as a NF membrane to remove small organic molecules present in wastewater.

The ability to resist fouling by organic molecules of a new type of nanocomposite membrane, consisting of polysulfone (PSf) with embedded MWNTs, was recently investigated. Before embedding into the polymer matrix, the MWNTs were first treated with HNO₃ to introduce carboxylic groups on their surface, and facilitate modification with dodecylamine (DDA). The final nanocomposite membranes exhibited significantly higher permeability and protein fouling resistance than pristine PSf membranes, when used in filtration experiments using solutions containing BSA.

2.10 CNTs as adsorbents

In recent years CNTs have received considerable attention as adsorbents to solve environmental pollution problems. They possess chemically inert surfaces which are suitable for physical adsorption of a range of chemical compounds of interest, and high specific surface areas similar to that of activated carbons (ACs). Importantly, however,
CNTs are distinct from ACs in that their structure at the atomic scale is far more well-defined and uniform. The relationship between CNTs and other carbonaceous adsorptive materials can be viewed as similar to that between single crystals and polycrystalline materials. The following paragraphs provide a glimpse of the enormous range of investigations that have been performed into the suitability of CNTs for recovery of various types of pollutant species.

Raw carbon nanotubes have been shown to exhibit high adsorption capacities for such diverse classes of compounds as phenols, heavy metals and NOM. Functional groups (e.g., carboxyl, hydroxyl, and phenol) present on the surfaces of the nanotubes were stated to be the major adsorption sites for metal ions, and to facilitate electrostatic and other types of binding interactions. CNTs have proven to be particularly effective adsorbents for Cu$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, and Zn$^{2+}$. A significant advantage of using CNTs for recovery or reclamation of these metal ions was that the rates of adsorption were fast, owing to the presence of many highly accessible adsorption sites.

Other studies have shown that CNTs can be more effective adsorbents than activated carbon for removing organic compounds, due to the larger specific surface area of the nanotubes, and the diverse range of contaminant/adsorbent interactions they can participate in. Although activated carbons possess comparable specific surface areas to CNT bundles, they often contain a significant number of micropores inaccessible to large organic molecules such as antibiotics and pharmaceuticals. The absence of these micropores endows CNTs with higher adsorption capacities for some bulky organic molecules. A further drawback of activated carbons is their low
adsorption affinity for low molecular weight polar organic compounds. In contrast, CNTs strongly adsorb many polar organic compounds due to the diverse range of interactions that can occur between them, including hydrophobic forces, $\pi-\pi$ interactions, covalent bonding, hydrogen bonding and electrostatic interactions.\textsuperscript{131} For example, the $\pi$-electron rich CNT surface allows $\pi-\pi$ interactions with organic molecules containing C=C bonds or benzene rings, such as polycyclic aromatic hydrocarbons (PAHs) and polar aromatic compounds.\textsuperscript{122,132} In addition, organic compounds which have $-\text{COOH}$, $-\text{OH}$ and $-\text{NH}_2$ functional groups can also form hydrogen bonds with graphitic CNT surfaces, which effectively act as electron donors.\textsuperscript{133}

Contamination of the environment with radionuclides and toxic heavy metal ions is an area of growing concern throughout the world due to the development of nuclear weapons, exploitation of nuclear energy, coal combustion, application and production of phosphoric acid based fertilisers, and production of diagnostic and therapeutic nuclear medical agents.\textsuperscript{134} Radionuclides released into the environment progress through the food chain to eventually be ingested by humans, leading to detrimental impacts on health, such as kidney damage, liver damage and even death.\textsuperscript{135,136} Therefore, it is extremely important to remove radionuclides from wastewater before it is discharged into the environment.

A number of different methods have been employed for the elimination of radionuclides and toxic heavy metal ions from waste solutions, such as electrodeposition, solvent extraction, coagulation, membrane processing, reverse osmosis and adsorption.\textsuperscript{137-139} Among these approaches, adsorption has been widely employed to remove
radionuclides and heavy metal ions in industrial wastewaters because it is cost-effective, simple to use, and highly efficient. Carbon nanotubes have been shown to possess excellent adsorption capacities for the removal of heavy metal ions and radionuclides.\textsuperscript{140-142} In 2005 Wang \textit{et al.} first used MWNTs as adsorbents to study the adsorption of $^{243}\text{Am}$ from aqueous solutions at room temperature.\textsuperscript{142} The adsorption efficiency of the MWNTs, which had been pre-treated with nitric acid, towards $^{243}\text{Am}$ was shown to be $\geq 40\ \text{mg}\ \text{g}^{-1}$, and was attributed to a surface complexation mechanism. Fasfous \textit{et al.} examined the effects of initial concentration, contact time, pH, and temperature on the removal of U(VI) from aqueous solutions by MWNTs.\textsuperscript{143} The maximum sorption capacity of U(VI) ions onto the MWNTs increased from 24.9 to 39.1 mg g$^{-1}$ when the temperature was increased from 298K to 318K. The adsorption of a variety of other radionuclides, including those of Th, Eu, Ce and Sr by CNTs, has also been reported.\textsuperscript{141,144-148} These studies all concluded that conditions such as solution pH, concentration of CNTs and radionuclides, temperature and the degree of functionalisation (oxidation) of the nanotubes all dictated the sorption capacity of the CNTs used.

\section*{2.11 Project aims}

In the previous sections it was highlighted that BP membranes have recently attracted growing attention for a variety of filtration applications. Most of the BPs used did not vary widely in their composition or properties, as a result of typically being produced from dispersions made using an organic solvent (i.e. with no dispersant present), or from an aqueous dispersion containing one of a limited range of surfactants. As a consequence, it is unlikely these BPs will exhibit a significant degree of selective solute
permeability, as they do not possess a range of functional groups capable of interacting in a variety of ways with different solutes. A further disadvantage of BPs prepared from dispersions containing conventional surfactant molecules, is that they frequently exhibit poor mechanical properties. Consequently they are not suitable for filtration applications which require the use of high operating pressures. In order for BPs to become attractive options for filtration applications, it is essential to improve upon their mechanical properties and chemical diversity. As a consequence one of the principal aims of this project was to include molecules capable of selective molecular recognition, such as macrocyclic ligands, cyclodextrins or calixarenes, into BPs during their preparation, and examine the effects on the physical properties of the resulting membranes as well as their permeability and solute rejection characteristics.

An alternative means of achieving the above goals is to include a structurally diverse range of biopolymers, including proteins, DNA and polysaccharides, into either SWNT or MWNT BPs. Therefore a second overarching objective of this project was to prepare MWNT and SWNT BPs from dispersions containing biopolymers, and explore whether they exhibited selective permeability towards dissolved solutes, including trace organic contaminants (TrOCs) and simple salts.

In order to achieve the above overall objectives, the specific aims of this project were:

1. To investigate the ability of a variety of dispersant molecules (chitosan (CHT), bovine serum albumin (BSA), lysozyme (LSZ), DNA, gellan gum (GG), meso-tetra(4-sulfonatophenyl) porphyrin dihydrogen chloride (TSP), phthalocyanine tetrasulfonic acid (PTS) and 4-sulfonic calix[6]arene hydrate (C6S)) to disperse CNTs (SWNTs, MWNTs or functionalised MWNTs), and characterise the
resulting dispersions using optical microscopy and UV-vis-NIR spectrophotometry;

2. To synthesise BPs from the above dispersions, and compare their physical and morphological properties to those of BPs fabricated from dispersions containing the same type of CNTs and Triton X-100;

3. To investigate the effect of ageing on the mechanical stability of selected BPs;

4. To measure the permeability towards water of various CNT/biopolymer and CNT/macro cyclic ligand BPs using a dead-end or cross-flow NF/RO filtration system, and compare the measured permeabilities to each other and that of CNT/Trix BPs;

5. To investigate the ability of different BPs prepared from dispersions containing MWNTs or functionalised MWNTs (MWNT–COOH, MWNT–NH₂), and either Triton X-100 or selected macro cyclic ligands, to remove bisphenol A (BPA) and/or a mixture of twelve TrOCs from aqueous solution, using a dead-end filtration system;

6. To explore the ability of MWNT BPs containing a range of biopolymer dispersants to remove TrOCs from aqueous solutions using either a dead-end filtration cell or cross-flow RO/NF system; and

7. To explore the ability of selected MWNT BPs containing biopolymer dispersants to reject simple salts such as NaCl and MgSO₄, using a cross-flow NF/RO system;
2.12 References


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Chapter 3

Materials and Methods

This chapter provides details about the general experimental methods used in this project.
3.1 Materials

All chemical reagents were used as received from suppliers, without any further purification or modification. MWNTs (95+% C purity) and functionalised MWNTs (95+% C purity) used in this study were purchased from Nanocyl S.A. (Belgium). SWNTs (70+% C purity) were obtained from NanoIntegris Technologies (batch no. HR27004). All CNTs used in this study were synthesised using a chemical vapour deposition process. The range of nanotubes studied included MWNTs (Nanocyl-3100, batch nos. 110221P2 and 100825), amine-functionalised MWNTs (MWNT–NH$_2$; batch no. LMWS-P-NH$_2$), carboxylic acid functionalised MWNTs (Nanocyl-3151, MWNT–COOH; batch no. MEL110513) and SWNTs (batch no. HR27004). The average diameter of each of the above types of MWNTs is stated by the manufacturer to be 9.5 nm, while the average lengths are 1.5 μm in the case of MWNTs, and < 1 μm for MWNT–NH$_2$ and MWNT–COOH. The diameter of the SWNTs used in this project varied from 0.8 – 1.2 nm, while their lengths ranged from 100 to 1000 nm.

Triton X-100 (Trix), low molecular weight chitosan (batch no. MKBB4232), bovine serum albumin (fraction V, ≥ 96%, batch no. 067K0759), lysozyme (protein ≥ 90%, lot no. 100M1897V), and deoxyribonucleic acid (DNA) sodium salt were purchased from Sigma-Aldrich. CP Kelco provided food grade gellan gum (Kelcogel®, batch no. 7C9228A) for use in this study. Both meso-tetra(4-sulfonatophenyl) porphyrin dihydrogen chloride (TSP) and phthalocyanine tetrasulfonic acid (PTS) were obtained from Frontier Scientific. 4-Sulfonic calix[6]arene hydrate (C6S) was supplied from Alfa Aesar.
Unless otherwise specified, all solutions were prepared in Milli-Q water (resistivity 18.2 MΩ cm) at room temperature. Analytical grade bisphenol A (BPA), amitriptyline, trimethoprim, sulfamethoxazole, diclofenac, bezafibrate, caffeine, atrazine, primidone, carbamazepine, pentachlorophenol, linuoron and triclosan from Sigma-Aldrich were used as model TrOCs. Sodium chloride (98%) and anhydrous magnesium sulfate (99.5%) were also purchased from Sigma-Aldrich, and used in desalination studies. Other solvents used in this study included methanol (99.8%, Merck), ethanol (absolute, AJAX) and acetone (99.5%, AJAX).

3.2 Experimental methods

3.2.1 Preparation of dispersions

CNT dispersions were prepared in Milli-Q water using SWNTs, MWNTs and functionalised MWNTs (MWNT–COOH, MWNT–NH₂) with a concentration of 0.1% (w/v) in a typical volume of 15 mL. The ideal concentrations of dispersants for preparing homogeneous dispersions were determined by a series of absorption spectrophotometric experiments. Subsequently the concentration of Trix and C6S in samples used to prepare dispersions was always 1% (w/v), while for samples containing PTS or TSP the concentration of dispersant was 0.1% (w/v). In the case of biopolymer dispersants a range of different concentrations from 0.05 to 0.6% (w/v) were used to prepare BPs. All biopolymer solutions used for preparing dispersions were made using pure Milli-Q water with the exception of chitosan solutions, which were prepared using Milli-Q water containing 0.01% (v/v) acetic-acid (AR grade, AJAX). Both chitosan and gellan gum solutions were heated for 3 h at 80 °C with stirring, and then for a further 24 h stirred at room temperature until most of the biopolymer particles were dissolved. All
biopolymer solutions were then filtered using 5.0 μm PTFE membrane filters to remove any undissolved particles.

In a typical experiment, 15 mg of CNTs were dispersed in 15 mL of dispersant solution using a Branson 450 (400 W, Ultrasonics Corp.) digital sonicator horn with a probe diameter of 10 mm to apply ultrasonic energy (Figure 3.1A). The conditions used were an amplitude of 30%, 16 W power output, pulse duration of 0.5 s and pulse delay of 0.5 s. The total amount of sonication time was optimised using a combination of absorption spectrophotometry and optical microscopy. During sonication, the sample vial was placed inside an ice/water bath (Figure 3.1B) to minimize increases in temperature. The only exception to this was when gellan gum was used. In these cases the sample vial was placed in a warm water bath (c.a. 50 °C) to prevent gelation from occurring. The water and ice in the bath was changed every 10 – 20 min to minimise excessive heating of the mixture of reagents.

Figure 3.1: (A) Schematic illustration of the experimental setup used to prepare CNT dispersions. (B) Photograph of the actual experimental setup used.
3.2.2 Buckypaper preparation

Dispersions were formed into BP membranes using vacuum filtration. Depending on the filtration apparatus used, three different sized BPs were obtained. Small, circular BPs measuring approximately 35 mm in diameter were obtained using the following procedure. Two dispersions prepared as described above were combined and added to a further 50 mL of dispersant solution (1% (w/v) Trix or C6S, 0.1% (w/v) PTS, TSP, 0.05% (w/v) chitosan, GG or DNA, or 0.2% (w/v) BSA or LSZ), and then placed in an ultrasonic bath (Unisonics, 50Hz, 150W) for 3 min. This process resulted in homogeneous dispersions (80 mL) containing 0.038% (w/v) of CNTs. Milli-Q water was added to give a total volume of 250 mL (final CNT concentration after dilution 0.012% (w/v)), and the resulting dispersion was then vacuum filtered through a polytetrafluoroethylene (PTFE) membrane filter (5 μm pore size; Millipore) housed in an Aldrich glass filtration unit, using a Vacuubrand CVC2 pump that typically operated between 30 and 50 mbar. Plastic film was placed over the top of the filtration unit to minimise evaporative losses during the filtration process.

Large BPs used for water permeability and solute rejection experiments were prepared using a custom-made rectangular filtration cell containing an internal sintered glass frit measuring 5.5 cm × 8 cm. Initially six dispersions were prepared as described above, and then added to 50 mL of dispersant solution. The resulting mixture was subjected to further treatment in an ultrasonic bath for 3 min. The resulting homogeneous dispersions (140 mL) contained 0.064 % (w/v) of CNTs, and were diluted to a total volume of 1 L with Milli-Q water (final CNT concentration after dilution 0.009% (w/v)). These final dispersions were vacuum filtered through a piece of commercial
PVDF membrane (0.22 μm pore size; Millipore) housed in a custom-made filtration unit.

After the filtration process was completed, both the circular and rectangular BPs were washed with 250 mL of Milli-Q water and then 10 mL of methanol (99.8%, Merck) whilst still in the filtration unit. This was found to be sufficient to remove loosely bound dispersant molecules on the membrane surface, as evidenced by the disappearance of foam that appeared during the early stages of the washing process. After washing, the damp BP was allowed to dry overnight (~ 15h) after being placed between absorbent paper sheets under ambient temperature (c.a. 21 °C). The dry buckypaper was then carefully peeled away from the underlying commercial membrane filter to leave a self-supporting film.

A second type of rectangular BP (6 cm × 12 cm) was prepared for use in cross-flow permeability experiments using a custom-built filtration cell. In order to prepare a BP of this size 10 homogeneous dispersions measuring a total of 150 mL were required. The combined dispersions were diluted to a total volume of 1 L with Milli-Q water, before being filtered through large sheets of PVDF membrane. The resulting BP was then washed and dried using an analogous procedure to what was outlined earlier for the other membranes. Typically, small BPs contained at least 30 mg of CNTs, whereas the two larger rectangular BPs contained 90 mg and 150 mg of CNTs, respectively. All BPs were stored at room temperature in sealed glass or plastic petri dishes (c.a. 21°C). Figure 3.2 shows example of the three different types of BPs used in this project.
Figure 3.2: Photograph of the different types of BPs used in this project: (A) small, circular BPs with a diameter of 35 mm, (B) rectangular BPs measuring 5.5 cm × 8 cm, and (C) rectangular BPs measuring 6 cm × 12 cm.

3.3 Characterisation techniques

A large number of characterisation techniques were utilised to investigate both CNT dispersions and BP membranes. For each technique a brief overview of the conditions used is systematically described in the sections below.

3.3.1 UV-vis-NIR spectrophotometry

Absorption spectra of all CNT dispersions were obtained between 300 and 1000 nm using a double beam Cary 500 UV-vis-NIR spectrophotometer. The dispersions were first appropriately diluted with Milli-Q water to ensure that the measured absorbances were within the optimal range of the instrument, and placed into 1 cm pathlength quartz stoppered cuvettes. All spectra were collected at room temperature (~ 21°C) unless otherwise stipulated.

3.3.2 Microscopy

A Leica Z16 APO LED1000 optical microscope equipped with a digital camera was used to perform preliminary assessments of the effectiveness of different dispersants to
produce stable dispersions of CNTs. Images were obtained by drop casting a small volume of dispersion onto a glass slide after each period of sonication. The surface morphology of BPs was examined using a JEOL JSM-7500FA field emission scanning electron microscope (FESEM), located at the University of Wollongong electron microscopy facility. The operating voltage of the SEM was 5 kV. Samples were cut into small strips and mounted onto a conductive stub using carbon tape, or by wedging the sample between a screw mount on the stub itself. All materials were sufficiently conductive to enable images to be obtained without having to first coat them with a metallic or carbon layer. Images obtained by SEM were analysed using Image Pro Plus software to obtain quantitative information about the size of surface pores.

3.3.3 Thickness measurement

The thicknesses of BPs were measured using a Mitutoyo IP65 digital micrometer. Measurements were made at 10 separate points on each BP and averaged to provide a mean thickness.

3.3.4 Contact angle measurement

The hydrophobicity of a material is commonly measured by determining the contact angle of a water droplet on its surface. The contact angles of BPs were determined using the sessile drop method and a Data Physics SCA20 goniometer fitted with a digital camera. The contact angles of 2 µL Milli-Q water droplets (Figure 3.3) on the surfaces of the BPs were calculated using the accompanying Data Physics software (SCA20.1).
The mean contact angle was calculated using measurements performed on at least five water droplets.

![Image of water droplet and contact angle](image_url)

**Figure 3.3**: (A) Image of a water droplet on the surface of a BP. (B) Schematic illustration of the contact angle (θ) of a water droplet on the surface of a material.

### 3.3.5 Zeta potential analysis

The zeta potential (ZP) of the surfaces of different BPs was estimated using a SurPASS electrokinetic analyser (Anton Paar GmbH, Graz, Austria) to determine the membrane surface charge. The ZP of the BP surface was calculated from the measured streaming potential using the Fairbrother-Mastin process. Streaming potential measurements were conducted in aqueous 1 mM KCl solution. HCl and KOH solutions were employed to adjust the pH by means of automatic titration. For each measurement, the test solution was used to thoroughly flush the cell prior to pH adjustment. All streaming potential measurements were conducted at a room temperature of ~ 21°C, which was determined by the temperature probe of the system.
3.3.6 Mechanical testing

The mechanical properties of BP samples were determined using a Shimadzu EZ-S universal testing device and BP samples cut into small rectangular strips measuring approximately 15 mm × 4 mm and mounted into a small paper frame. The length of the sample between the top and bottom clamps was kept constant at 10 mm. The paper frame was cut between the clamps prior to testing, and the mounted samples were then stretched using a 50 N load cell until failure occurred. The samples were tested at ambient temperature (~ 21 °C) with a strain rate of 0.1 mm min⁻¹. All results were recorded via an attached personal computer using the Trapezium X software package provided with the instrument, and analysed using Microsoft Excel to yield the corresponding stress-strain curves. These stress-strain curves were used to determine the Young’s modulus, tensile strength, ductility and toughness of samples. The ductility was taken as the percentage elongation (% EL) of the sample at break, and is described by Equation 3.1:

\[ \text{Ductility} = \frac{l - l_0}{l_0} \times 100 \% \]  

Equation 3.1

where \( l \) is the distance at break and \( l_0 \) is the initial distance.³ The Young’s modulus of a buckypaper strip was determined as the slope of the linear part of the stress-strain diagram using Equation 3.2:

\[ E = \frac{\sigma}{\varepsilon} \]  

Equation 3.2

where \( E \) is the Young’s modulus of the material expressed in GPa, \( \sigma \) is the stress and \( \varepsilon \) is the strain.³ The tensile strength of the material is the stress (\( \sigma_{\text{max}} \)) at the maximum position on the stress–strain curve, while the toughness is calculated from the area underneath the stress-strain curve up to the point of fracture.
3.3.7 Electrical conductivity

The electrical conductivity of BP samples was evaluated using a standard two-point probe method. Buckypaper samples were cut into rectangular strips approximately 3 mm wide and 40 mm long. The BP strips were fixed onto a small piece of copper tape (3M) adhered to a glass microscope slide using high purity silver paint (SPI) to prepare low resistance contacts. Another glass microscope slide was clamped onto the slide containing the BP strip using bulldog clips to ensure the sample was secure, and a continuous connection during the testing procedure (Figure 3.4). Experiments were performed by applying a triangular waveform with voltage limits of -0.05 and 0.05 V to the sample using a waveform generator (Agilent 33220A). Both the current (I) and voltage (V) responses were measured using a multimeter (Agilent 34410A) connected within the simple circuit, and attached to a personal computer recording data points every 1.0 s. This enabled I-V plots to be constructed which could then be used to determine resistance for the length of sample used. Using these resistance values, the conductivity could then be calculated by accounting for the sample thickness, which was measured using a digital micrometre (IP65, Mitutoyo). Measurements were repeated for a minimum of five lengths for each BP strip.

Figure 3.4: Photograph of the configuration used to connect a BP strip to the multimeter and waveform generator used in the two-point probe conductivity method.
3.3.8 Microanalysis

Measurement of the percentages of different elements present in BPs and pristine CNTs was performed by the Microanalytical Unit of the Research School of Chemistry, The Australian National University. Elemental analyses were also performed on different BP samples by the Campbell Microanalytical laboratory, Department of Chemistry, University of Otago, New Zealand. Prior to analysis, BP samples were ground into a fine powder using a mortar and pestle. The percentages of C, H and N were determined using a Carlo Erber 1106 Automatic Analyser, and a procedure in which the sample underwent combustion, and the resulting gasses were separated and analysed by gas chromatography. The percentage of sulphur present was measured using a Dionex Ion Chromatography Analyser.

3.3.9 Thermogravimetric analysis

Thermogravimetric analyses (TGA) were carried out on a Shimadzu DTG-60 TGA analyser to determine the thermal stability of BP samples. The samples were scanned within the temperature range 25 – 550 °C at a ramp rate of 10 °C min\(^{-1}\) under a continuous flow of N\(_2\).

3.3.10 Nitrogen adsorption/desorption analysis

Adsorption-desorption isotherms were obtained at the Australian Nuclear Science and Technology Organisation (ANSTO) using a Micromeritics\textsuperscript{®} surface area analyser (ASAP 2010 or ASAP 2400) operating at 77 K to determine the surface area and pore-size distribution of BP samples. Prior to analysis, the pristine samples (SWNTs and
MWNTs) were degassed at 150 °C and the BPs were all degassed at 120 °C under vacuum. The resulting isotherms were analysed using the Horvath-Kawazoe (HK) and Barrett, Joyner and Halenda (BJH) methods to determine the distribution of small and large pores, respectively.\(^5\,^6\) In addition, multipoint Brunauer, Emmett, and Teller (BET) analysis of the isotherms was used to calculate the specific surface area of the BPs.\(^7\) Numerical integration of the pore size distribution curves resulting from analysis of nitrogen adsorption/desorption isotherms was performed using the BJH and HK methods in order to obtain the interbundle pore volumes for the BPs. The nanotube bundle diameter can be calculated using Equation 3.3:

\[
A_{\text{BET}} = \frac{4}{\rho_{\text{CNT}} \cdot D_{\text{bun}}}
\]

Equation 3.3

where \(A_{\text{BET}}, D_{\text{bun}}\) and \(\rho_{\text{CNT}}\) are the BET surface area, CNT bundle diameter, and nanotube bundle density (estimated as 1500 kg/m\(^3\)),\(^8\) respectively.

### 3.4 Permeability studies

The permeability of BPs towards water and different solutes was investigated using the procedures outlined in the following sections. All permeability experiments were performed in the Environmental Engineering Laboratories, School of Civil, Mining and Environmental Engineering at the University of Wollongong.

#### 3.4.1 Water permeability of BPs determined using a dead-end filtration experimental setup

The permeability of BPs towards water was measured using a custom-made dead-end filtration cell setup (active filtration area = 6.5 cm × 3.5 cm) (Figure 3.5). The
buckypaper was first placed on a piece of porous stainless steel in the filtration cell, which provided mechanical support to the membrane. Compressed air was used to induce a transmembrane pressure and obtain a flux of water across an individual BP. The volume of water passing across the membrane was monitored for 10 min using an analytical balance connected to a computer. A schematic illustration of the apparatus used to perform water transport experiments is shown in Figure 3.6. From the slope of the resulting plot of accumulated permeate volume against time the permeate flux ($J$) was determined.

![Figure 3.6](image_url)

Figure 3.5: Digital photographs of the custom-made filtration cell used to enclose BPs during water permeability measurements: (A) side view, and (B) top view after removing the upper half of the Perspex chamber.

Initially, a pressure of 1 psi (0.069) was applied and the permeate flux was recorded. The pressure applied to the BP was then incrementally increased and the process repeated, affording values of $J$ at several different pressures. This data was then used to determine the water permeability ($f$) for each BP using the Equation 1.3 (chapter 1).
3.4.2 Removal of BPA

The permeability of different types of BPs towards the endocrine disrupting compound BPA was examined using the same dead-end filtration cell. Experiments involving BPA were performed using four different BPs, and feed solutions containing between 600 and 650 μg L⁻¹ BPA in Milli-Q water. The pressures applied to MWNT/ Trix and MWNT/PTS BPs at the commencement of experiments were 0.57 and 0.60 bar, respectively. These pressures were selected as water permeability experiments showed that they would result in a constant flux of water across both membranes of 10 L m⁻² h⁻¹. For the MWNT–NH₂/Trix and MWNT–COOH/Trix BPs much lower applied pressures of 0.26 and 0.24 bar, respectively, were applied at the commencement of experiments in order to avoid membrane rupture. These were the pressures estimated from water transport experiments to result in a flux of water across both membranes of 2 L m⁻² h⁻¹. In most cases the permeate solution was collected sequentially in six
samples, of 20 mL volume each. As the MWNT–COOH/Trix buckypaper had a very low permeability, only six separate samples of 3 mL volume were collected.

The amounts of BPA present in samples of permeate were measured using a Shimadzu HPLC system (Kyoto, Japan), and compared to that present in the initial feed solution, to determine the percentage rejection of BPA by the buckypaper. The HPLC system was equipped with a Supelco Drug Discovery C-18 column (diameter 4.6 mm, length 150 mm, pore size 5 μm), and a UV–vis detector, set to 280 nm. The mobile phase consisted of Milli-Q water, and two eluents composed of either 80% acetonitrile (ACN) with 20% buffer solution, or 20% ACN with 80% buffer solution, respectively. The buffer was a 25 mM potassium dihydrogen orthophosphate solution. This mobile phase was delivered at 1 mL/min, and the sample injection volume was 50 μL. The area of the peak that corresponds to BPA in the chromatograms for the sample and the feed solution were then compared, allowing the percentage of BPA that had passed through the buckypaper to be calculated. The inverse of this value afforded the per cent removal of BPA, which shows how much BPA had been rejected by the BP.

3.4.3 Removal of a mixture of twelve TrOCs

Investigation into the permeability of MWNT/Trix, MWNT/PTS and MWNT/biopolymer BPs towards a mixture of twelve TrOCs was also examined. Experiments involving TrOCs were performed using six different BPs, and a set of 12 compounds that included pharmaceuticals, pesticides and personal care products (i.e. amitriptyline, trimethoprim, sulfamethoxazole, diclofenac, bezafibrate, caffeine, atrazine, primidone, carbamazepine, pentachlorophenol, linuoron and triclosan). These
TrOCs are frequently detected in secondary treated effluent and sewage-impacted water bodies at trace levels. A combined stock solution containing 1 g L\(^{-1}\) of each compound was prepared in pure methanol. The stock solution was kept at −18 °C in the dark and was used within one month of preparation. The stock solution was introduced into the Milli-Q feed solution to give a final concentration of each compound of approximately 50 µg L\(^{-1}\). The pressures applied to MWNT/Trix and MWNT/PTS BPs at the commencement of experiments were the same as those used in experiments involving BPA rejection. The pressures applied to MWNT/BSA, MWNT/LSZ, MWNT/CHT and MWNT/DNA buckypapers were 1.54, 1.10, 0.69 and 1.00 bar, respectively. These pressures were selected as water permeability experiments showed that they would result in a constant flux of water across all membranes of 5 L m\(^{-2}\) h\(^{-1}\). In all cases the permeate solutions were collected sequentially in six amounts, of 20 mL each. The TrOC rejection, \(R\) (%) for each solute, was calculated using \textbf{Equation 1.1} (chapter 1).

The concentrations of each TrOC present in the feed and permeate samples were determined using a Shimadzu Liquid Chromatography-mass spectrometry system (LC-MS 2020) equipped with an electrospray ionisation (ESI) interface. A Phenomenex Kinetex 2.6 µm C8 column (50 mm × 4.6 mm) was used as the chromatography column and was maintained at 26 °C inside a column oven (CTO-20A). The mobile phase was Milli-Q water containing 0.1% (v/v) formic acid and acetonitrile. The mobile phase flow rate was 0.5 mL min\(^{-1}\) and the sample injection volume was 10 µL. The analytes from the HPLC system were fed directly into a quadrupole mass spectrometer via the ESI source. ESI positive ionisation \([M + H]^+\) mode was used for analysis of caffeine, primidone, trimethoprim, sulfamethoxazole, carbamazepine, bezafibrate, atrazine, linuron and amitriptyline, while ESI negative ionisation \([M-H]^-\) mode was used for analysis.
of pentachlorophenol, diclofenac and triclosan. All mass spectra were acquired using a
detector voltage of 0.9 kV, desolvation line temperature of 250 °C, and heating block
temperature of 200 °C. High purity nitrogen gas was used as both the nebulising and
drying gas at a flow rate of 1.5 and 10 L min⁻¹, respectively. Standard solutions of the
analytes were prepared at 1, 10, 50, 100, 500 and 1000 ng mL⁻¹ concentration, and an
internal instrument calibration was carried out with carbamazepine-d10 as the internal
standard. The calibration curves for all the analytes had a correlation coefficient of 0.99
or higher.

3.4.4 Water permeability and salt rejection study of BPs using a cross-flow NF/RO
system

A laboratory scale cross-flow NF/RO system (Figure 3.7) was used to investigate the
water permeability and salt rejection properties of different BPs. The system consisted
of a custom-built cross-flow stainless steel cell with an effective membrane filtration
area of 40 cm² (4cm × 10cm) and a channel height of 2 mm. The feed solution was kept
in a stainless feed reservoir of 5 litres, and was fed to the BP membrane cell by a high
pressure pump (HydraCell, Wanner Engineering Inc., Minneapolis, MN, USA). The
permeate flow and cross-flow velocity were regulated by a bypass valve and a back-
pressure regulator (Swagelok, Solon, OH, USA). A digital flow meter (FlowCal, GJC
Instruments Ltd, Cheshire, UK) connected to a PC was used to monitor the permeate
flow, and the cross-flow was measured with a manual flow meter. The feed pressure as
indicated by a pressure gauge was also recorded during water permeability and salt
rejection experiments. Throughout the entire filtration experiment the temperature of the
feed solution was kept constant at 20 ± 1 °C using a temperature control unit (Neslab
RTE 7, Thermo Scientific Inc., Waltham, MA, USA) equipped with a stainless steel heat exchanger coil which was submerged directly into the feed reservoir.

**Figure 3.7:** Schematic illustration of the cross-flow filtration system used to perform water and solute permeability experiments.

At the commencement of the filtration experiment, the buckypaper membrane was subjected to Milli-Q water at high pressure for at least 1 h, until a stable permeate flux had been achieved. Unless otherwise stated, the cross-flow velocity was kept constant at 0.35 m s\(^{-1}\). Once a stable permeate flux had been achieved, the pressure was reduced and the permeate flux of pure water (Milli-Q) at different applied pressures was obtained, to enable the calculation of the water permeability of the buckypaper. Subsequently the Milli-Q water in the filtration system then received an aqueous solution containing 16 g L\(^{-1}\) of both NaCl and MgSO\(_4\) to make up a feed solution of 2 g
Throughout salt rejection experiments, the both permeate and retentate were re-circulated via the feed reservoir. The system was continuously operated for 1 h prior to the collection of the feed and permeates samples for analysis. At each sampling event, 50 mL of feed and permeate solutions were collected simultaneously. An Agilent Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES 710) was used to determine cation concentrations in the feed and permeate solutions.
3.5 References


Chapter 4
Preparation, Characterisation and Applications of BPs Composed of MWNTs and Low Molecular Weight Molecules

This chapter describes the preparation and characterisation of MWNT BP membranes containing a range of functional dispersant molecules with low molecular weight. The permeability of these membranes towards water as well as a range of trace organic contaminants is also discussed. The work presented in this chapter is based on the following published journal article:


Below are the contributions made by the authors to this publication:

Md. Harun-Or Rashid: Prepared all BPs and submitted samples for elemental analysis, as well as carried out contact angle analysis, N\textsubscript{2} adsorption/desorption analysis of MWNT/Trix BP, bisphenol A rejection studies and TrOCs rejection studies on all BPs. Also performed water permeability studies and mechanical property assessments on MWNT/Trix, MWNT/PTS, MWNT–NH\textsubscript{2}/Trix and MWNT–COOH/Trix BPs. Wrote first draft of the manuscript and was heavily involved in preparing all subsequent drafts.

Son Q. T. Pham: Prepared samples for SEM and N\textsubscript{2} adsorption desorption studies on MWNT–COOH/Trix, MWNT–NH\textsubscript{2}/Trix and MWNT/PTS BPs.
Like J. Sweetman: Trained Md. Harun-Or Rashid and Son Q. T. Pham how to prepare MWNT dispersions and BPs, as well as how to characterise the electrical and mechanical properties of BPs.

Leighton J. Alcock: Prepared BP samples and carried out mechanical properties measurements and analysis of N$_2$ adsorption/desorption measurements performed on MWNT/C6S and MWNT/TSP BPs.

Anthony Wise: Performed preliminary water permeability studies on MWNT/Trix, MWNT/C6S, MWNT/TSP, and MWNT/PTS BPs.

Long D. Nghiem: Provided facilities and expertise for performing water permeability studies, bisphenol A and TrOCs rejection experiments on all BPs.

Gerry Triani: Provided facilities and expertise for performing N$_2$ adsorption/desorption experiments on all BPs.

Marc in het Panhuis and Stephen F. Ralph: Provided overall project direction and guidance with respect to analysis of experimental results. Also contributed to the preparation of the latter and final version of the journal manuscript.
4.1 Introduction

To date only a few studies have described the filtration characteristics of the class of CNT membranes known as BPs. Early investigations into their permeability reported results obtained using composite materials consisting of the BPs still attached to their original PVDF support membranes.\textsuperscript{1,2} These composite materials were highly effective for removing bacteria and viruses from water supplies, while evidence has also emerged that BPs could be used for desalination or gas separation.\textsuperscript{3,4}

More recently, the preparation of free-standing BPs containing SWNTs was reported.\textsuperscript{5} No supporting membrane was present in these BPs, which were obtained by vacuum filtration of aqueous dispersions of SWNTs, which were prepared using either Triton X-100, or one of several low molecular mass ligands including a derivatised porphyrin and calixarene, to assist in formation of the dispersion. Microanalysis and Energy Dispersive X-ray spectroscopic examination of the BPs provided direct evidence for retention of the macrocyclic molecules within the structure of the membranes. Scanning electron microscopy and analysis of nitrogen adsorption/desorption isotherms showed that both the surface and internal morphologies of the BPs were strongly dependent on the macrocyclic molecules that had been incorporated into their structures during preparation. It was therefore not surprising that the permeability of the BPs towards water varied markedly.

In this chapter the preparation and properties of MWNT BPs are described, along with the results of an investigation into their permeability towards water. Each of the BPs was synthesised using a MWNT dispersion prepared using Triton X-100 or one of the
low molecular mass macrocyclic ligands used in the previous study involving SWNT BPs. This enabled a comparison to be made of the effect of incorporating different dispersants into MWNT BPs on their permeability towards water, as well as a comparison of the aqueous permeability of MWNT and SWNT BPs containing the same dispersants. A further aim of the work presented in this chapter was to explore for the first time the ability of BPs to remove TrOCs from an aqueous solution. Filtration experiments were conducted to determine the permeability of the MWNT BPs towards a single TrOC (BPA), as well as a mixture of 12 TrOCs. The presence of these TrOCs in the environment is of significant concern owing to their ability to disrupt normal functioning of the endocrine system.

4.2 Surface morphology of MWNT BPs

A sonication time of 30 min was previously reported to be suitable for preparing dispersions containing MWNTs and the low molecular mass dispersants Trix and ciprofloxacin (cipro). Consequently all dispersions used to make BPs in the current study were prepared using the same sonication time in order to facilitate comparison. Filtration of these dispersions gave uniform BPs that could be readily removed from their underlying support membranes. Figure 4.1 shows scanning electron micrographs of BPs composed of MWNT/C6S, MWNT/PTS, MWNT/TSP and MWNT–COOH/Trix. These were obtained to examine the effect of using different dispersants on the surface morphology and pore structure of the resulting materials.
Examination of the SEM images of different BPs revealed highly porous surface structures. These images have a number of similarities to each other, and to that of a MWNT/Trix BP reported previously. In each case a highly entangled mat of CNTs and CNT aggregates, with roughly comparable dimensions is apparent. This indicates that the surface morphologies of the BPs are very similar to each other, and suggests that the presence of different dispersants or types of MWNTs does not impact greatly on membrane surface features.
4.3 Membrane composition

All BPs were extensively washed after their preparation using vacuum filtration, to remove loosely bound dispersant molecules. However, it was anticipated that even after this washing procedure, some dispersant molecules would remain bound to the MWNTs as a result of effectively being trapped within the membranes. In order to confirm this hypothesis, elemental analysis was performed on the pristine MWNTs and BPs.

Evidence for retention of Trix or macrocyclic ligands in the BPs was provided by the microanalytical results shown in Table 4.1 The as-received MWNTs used to prepare the BPs consisted almost entirely of C, with the only other element present to a significant extent being H. There was no N present, and virtually no S as well. This was important to establish as these elements were expected to be present in many of the BPs if the latter retained significant amounts of macrocyclic dispersant.

Table 4.1: Microanalytical data of raw (non-dispersed) MWNTs and different MWNT BPs. The error associated with each value is ± 0.1 %.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw MWNTs</td>
<td>98.2  1.5  &lt; 0.1  0.2</td>
</tr>
<tr>
<td>MWNT/Trix</td>
<td>96.2  2.6  0.4  &lt; 0.1</td>
</tr>
<tr>
<td>MWNT/C6S</td>
<td>85.7  1.2  0.1  1.2</td>
</tr>
<tr>
<td>MWNT/PTS</td>
<td>84.8  2.7  2.2  2.0</td>
</tr>
<tr>
<td>MWNT/TSP</td>
<td>83.9  3.0  1.0  1.3</td>
</tr>
</tbody>
</table>

Comparison of the percentage of C present in BPs containing C6S, PTS and TSP, to the fraction of this element present in the raw MWNTs revealed a decrease of 14 – 15% in all cases. This was accompanied by an increase in the percentage of H present. In addition, these three BPs contained significant amounts of N and/or S. Both sets of
observations are consistent with small amounts of C6S, TSP and PTS being retained in the BP samples, even after they had been thoroughly washed after preparation. Addition of the elemental percentages in Table 4.1 for the MWNT/C6S, MWNT/PTS and MWNT/TSP BPs does not equal 100%. This is because these dispersants also contain a significant amount of O, which was not analysed for as part of this work.

The fraction of C present in a MWNT/Trix BP was slightly less than that in the MWNT starting material, while the fraction of H was slightly greater. In addition, the MWNT/Trix BP did not contain significant amounts of either S or N. Each of these results is consistent with a small amount of Trix being retained by the BP, as this dispersant does not contain either N or S. Overall the changes in elemental composition between the raw MWNTs and BPs shown in Table 4.1 are comparable to those seen previously with the analogous membranes prepared using SWNTs.5

4.4 Mechanical properties of MWNT BPs

Robust mechanical integrity is an important property BPs must exhibit if they are to be used for filtration applications. This is because the membrane must be able to survive the application of a wide range of pressures and flow rates for extended periods of time, and possibly high working temperatures as well. The mechanical properties of the different BPs were evaluated using the tensile test method described in section 3.3.6. A typical set of results is presented in Figure 4.2, with all BPs exhibiting stress/strain curves that were linear at low strain, but displayed significant curvature at higher values. These results suggest that the BPs fail ultimately owing to their inherently brittle nature. Reflecting this, all BPs failed when a strain between 0.2% and 1.2% was
applied. Using the data contained in the stress/strain curves, it was possible to derive the values of Young’s modulus (E), tensile strength (σ_{Break}), ductility (ε_{Break}), and toughness (T) presented in Table 4.2.

![Representative stress–strain curves for MWNT BPs.](image)

**Figure 4.2:** Representative stress–strain curves for MWNT BPs.

Inspection of Table 4.2 reveals that changing the dispersant used during preparation of the MWNT BPs affected the mechanical properties of the final material. For example, the Young’s modulus of the four types of BPs prepared using MWNTs ranged between 0.34 ± 0.15 and 1.2 ± 0.2 GPa, while the ductility of the same materials varied from 0.59 ± 0.23% to 1.3 ± 0.2%. In general, mechanical properties of the BPs prepared using MWNTs is either comparable to, or a factor of between two and five times smaller, than values reported previously for the corresponding BPs synthesised using SWNTs and the same dispersant molecules. This is illustrated by comparing the tensile strengths of the two classes of buckypapers. In the case of MWNT/PTS, the tensile strength was determined to be 13 ± 2 MPa, which is similar to the value reported previously for SWNT/PTS (15 ± 6 MPa). However, the tensile strengths for MWNT
BPs prepared using C6S, TSP and Trix dispersants (2.5 ± 1.2 to 5.6 ± 2.6 MPa) are all significantly lower than that for the corresponding membranes produced using SWNTs (13 ± 9 to 20 ± 10 MPa). Similar trends may be discerned after comparing the other mechanical properties reported here for MWNT BPs, with those in the literature for the corresponding materials synthesised using SWNTs. Based on this evidence the latter materials are the more robust of the two classes of BPs.

Table 4.2: Mechanical properties of MWNT BPs. Values shown are the average of at least 3 samples, with the errors reported determined from the standard deviation obtained from all measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Ductility (%)</th>
<th>Young’s modulus (GPa)</th>
<th>Toughness (Jg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>4.6 ± 1.5</td>
<td>1.4 ± 0.3</td>
<td>0.34 ± 0.15</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>MWNT/C6S</td>
<td>4.4 ± 1.3</td>
<td>0.59 ± 0.23</td>
<td>0.94 ± 0.13</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>MWNT/PTS</td>
<td>13.0 ± 2.0</td>
<td>0.9 ± 0.3</td>
<td>1.2 ± 0.2</td>
<td>0.6 ± 0.3</td>
</tr>
<tr>
<td>MWNT/TSP</td>
<td>2.5 ± 1.2</td>
<td>1.0 ± 0.5</td>
<td>0.34 ± 0.15</td>
<td>0.02 ± 0.005</td>
</tr>
<tr>
<td>MWNT–NH₂/Trix</td>
<td>1.6 ± 0.7</td>
<td>0.50 ± 0.20</td>
<td>0.4 ± 0.1</td>
<td>0.04 ± 0.02</td>
</tr>
<tr>
<td>MWNT–COOH/Trix</td>
<td>3.7 ± 0.8</td>
<td>0.30 ± 0.05</td>
<td>1.3 ± 0.4</td>
<td>0.04 ± 0.01</td>
</tr>
</tbody>
</table>

Although MWNT–COOH/Trix BPs exhibited the highest Young’s modulus, the mechanical properties of MWNT–COOH/Trix and MWNT–NH₂/Trix generally proved to be the poorest of all the materials examined. For example, MWNT–NH₂/Trix showed the lowest tensile strength (and MWNT–COOH/Trix the third lowest), and both BPs prepared using substituted MWNTs exhibited poorer values of ductility than the remaining materials. The lack of robustness of BPs prepared from substituted MWNTs resulted in measurements of their permeability to water having to be conducted over a very narrow range of applied pressures, compared to each of the other materials examined.
4.5 Electrical conductivity of MWNT BPs

Membranes that are electrically conductive may be advantageous for filtration applications, owing to the potential for modulating solute rejection by applying an electrical potential.\textsuperscript{9,10} For example, Madaeni \textit{et al.} showed that polypyrrole (conducting polymer) coated ultrafiltration membranes are able to reject BSA a greater extent than non-conducting membranes.\textsuperscript{11} In addition, some nanostructured materials have been shown to exhibit dynamically tuneable wettability in response to changes in an applied electrochemical potential.\textsuperscript{12} Recently Vecitis \textit{et al.} showed that by applying potentials of 2 and 3 V, an electrochemical MWNT membrane filter reduced the number of bacteria and viruses in the effluent to 0.\textsuperscript{10}

The electrical conductivity of MWNT BPs was obtained using a two-point probe method described in section 3.3.7. \textbf{Table 4.3} shows that the electrical conductivity of the MWNT BPs fall within the range $24 \pm 16$ to $58 \pm 11$ S cm$^{-1}$. This is a narrower range of values compared to those reported previously for the corresponding SWNT buckypapers.\textsuperscript{5} This suggests either that incorporation of the dispersants has a smaller effect on the electrical properties of membranes composed of MWNTs, or that smaller amounts of dispersant molecules were present in the latter materials. On some occasions, the conductivities of BPs prepared using the same dispersant, but different types of CNTs, varied significantly. For example, the conductivity of a SWNT/PTS BP was stated previously to be $220 \pm 60$ S cm$^{-1}$.\textsuperscript{5} while the value reported here for the analogous material prepared using MWNTs is $58 \pm 11$ S cm$^{-1}$. This is consistent with the results of an earlier investigation, which showed that the conductivity of BPs prepared using SWNTs and either the antibiotic ciprofloxacin, or the surfactant Trix,
were greater than that of the corresponding materials prepared using MWNTs and the same dispersant molecules.\textsuperscript{8}

Table 4.3: Electrical conductivities of MWNT BPs determined using the two-point probe method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrical conductivity (S cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>24 ± 16</td>
</tr>
<tr>
<td>MWNT/C6S</td>
<td>47 ± 7</td>
</tr>
<tr>
<td>MWNT/PTS</td>
<td>58 ± 11</td>
</tr>
<tr>
<td>MWNT/TSP</td>
<td>39 ± 8</td>
</tr>
<tr>
<td>MWNT─HN(_2)/Trix</td>
<td>25 ± 1</td>
</tr>
<tr>
<td>MWNT─COOH/Trix</td>
<td>26 ± 2</td>
</tr>
</tbody>
</table>

4.6 Contact angle of MWNT BPs

The wettability or hydrophobicity of a surface is a very important property of a membrane as it indicates whether or not the membrane will interact readily with a surrounding solution.\textsuperscript{13,14} In order to assess the viability of BP membranes for filtration applications, an understanding of their ability to interact with solvent molecules needs to be developed. One of the most popular methods for investigating these interactions is to determine the wettability of the membrane surface using its contact angle. The contact angle is defined as the angle between the tangential line to a liquid drop placed on the surface of the membrane.\textsuperscript{15} When water is the liquid used, contact angles less than 90° indicate that the membrane surface is hydrophilic, whereas high contact angles (\(> 90°\)) show that the membrane is hydrophobic in nature. Low contact angles are commonly preferred for membranes where water flow through a membrane is important. In contrast, contact angles greater than 90° are required in applications such
as membrane distillation where separation of solutions is desired, as this will prevent the solutions from entering membrane pores without the application of pressure.\textsuperscript{16} The contact angles of the MWNT BPs were determined using 2 μL water droplets delivered via a syringe, as shown in Figure 4.3.

![Figure 4.3: Images of 2 μL water droplets added to the surfaces of BPs: (A) MWNT–NH\textsubscript{2}/Trix and (B) MWNT–COOH/Trix.](image)

The contact angles of the MWNT BPs are reported in Table 4.4, and cover a relatively narrow range of values between 28 ± 1° and 55 ± 10°. This indicates that each membrane is hydrophilic in nature. These contact angles are similar to that reported in a similar study conducted by Whitten \textit{et al.} who obtained a water contact angle of 82° for SWNT/Trix buckypapers.\textsuperscript{17} In contrast, Dumée \textit{et al.} showed that MWNT BPs produced from organic solvents such as 2-propanol displayed a higher contact angle of 113.3°.\textsuperscript{14} The lower contact angles of the buckypapers in Table 4.4 are most likely due to the presence of hydrophilic functional groups (–COOH, –NH\textsubscript{2}) in the nanotubes themselves, as well as in the dispersant molecules on the BP surfaces. This is an important property for a material to exhibit if its intended primary use is to function as a filtration membrane for separation of molecules in aqueous solutions. In general the contact angles reported here are similar to those reported previously for analogous BPs prepared using SWNTs and the same dispersant molecules,\textsuperscript{5} suggesting that the choice
of CNT has little effect on the wettability of these materials. Low contact angles indicates that water will more readily flow into the pores of MWNT BPs, and lower pressures will be required to achieve transport through these membranes.

Table 4.4: Contact angles of 2 μL water droplets on MWNT BPs containing low molecular weight dispersants.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>53 ± 9</td>
</tr>
<tr>
<td>MWNT/C6S</td>
<td>49 ± 15</td>
</tr>
<tr>
<td>MWNT/PTS</td>
<td>49 ± 16</td>
</tr>
<tr>
<td>MWNT/TSP</td>
<td>44 ± 14</td>
</tr>
<tr>
<td>MWNT–NH₂/Trix</td>
<td>53 ± 2</td>
</tr>
<tr>
<td>MWNT–COOH/Trix</td>
<td>28 ± 1</td>
</tr>
</tbody>
</table>

4.7 Internal morphology of MWNT BPs

The SEM images illustrated in Figure 4.1 suggest that each of the BPs have similar surface morphologies, regardless of the type of carbon nanotube (MWNT or substituted MWNT) or dispersant they were prepared from. This was further supported by the results of a quantitative analysis of the pore openings of these materials, which are summarised in Table 4.5. Average surface pore diameters of BPs were obtained from the SEM images. Each of the BPs was found to have surface pores with average diameters > 50 nm. These values are significantly larger than those reported previously for the corresponding materials prepared using SWNTs and the same dispersants, which were shown by SEM to exhibit a greater variety of surface morphologies. The reported surface pore diameters are based only on measurements from SEM images and do not
necessarily reflect the internal pore size of the BPs, which have a greater impact on solute permeability and rejection.

Table 4.5: Average surface pore diameters ($D_{SEM}$) of BPs imaged by SEM. Pore diameters were determined by using image analysis software (Image Pro Plus) and micrographs taken at 70,000× magnification.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average surface pore diameter $D_{SEM}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>75 ± 18</td>
</tr>
<tr>
<td>MWNT/C6S</td>
<td>78 ± 26</td>
</tr>
<tr>
<td>MWNT/PTS</td>
<td>69 ± 21</td>
</tr>
<tr>
<td>MWNT/TSP</td>
<td>88 ± 23</td>
</tr>
<tr>
<td>MWNT–NH$_2$/Trix</td>
<td>83 ± 21</td>
</tr>
<tr>
<td>MWNT–COOH/Trix</td>
<td>55 ± 18</td>
</tr>
</tbody>
</table>

In order to investigate whether the internal morphologies of the materials also exhibited similar features to each other, nitrogen adsorption/desorption measurements were performed on the BPs. Figure 4.4 shows representative examples of the isotherms derived by performing these measurements. In each case the data obtained resulted in a type IV isotherm, with hysteresis being exhibited at higher relative pressures. The isotherms illustrated in Figure 4.4 are similar in overall appearance to those reported previously for BPs prepared using MWNTs or SWNTs, and dispersants similar to those used in the current study.\textsuperscript{5,8}
Figure 4.4: Nitrogen adsorption (blue) and desorption (red) isotherms for: (A) MWNT–COOH/Trix and (B) MWNT/PTS BPs. The insets show the pore size distributions for the BPs derived from BJH and HK analysis of the isotherms.
Analysis of the isotherms derived from nitrogen adsorption/desorption measurements for all BPs was performed using the BJH and HK methods. This enabled the distribution of large and small pores present within the materials to be calculated, along with other aspects of the internal morphology of the BPs presented in Table 4.6. In addition, the surface areas of the BPs shown in Table 4.6 were derived through analysis of the binding isotherms using the BET method. The insets in Figure 4.4 show the pore size distributions derived through application of the BJH and HK methods to the isotherms determined for these BPs. In both cases a large peak is present at ~ 7.5 Å (0.75 nm), which is attributed to the presence of interstitial pores between individual nanotubes within nanotube aggregates. In addition, a much broader peak is present between ~ 50 and 60 Å (5 – 6 nm) owing to the presence of larger pores present between aggregates of nanotubes. The pore distribution curves calculated for the other BPs examined as part of the current study showed similar features to those seen in Figure 4.4.

### Table 4.6: Specific surface area ($A_{\text{BET}}$), average internal pore diameter ($d_{\text{BET}}$), average nanotube bundle diameter ($D_{\text{bun}}$), and interbundle pore volume derived from data obtained from nitrogen adsorption-desorption isotherms for MWNT BPs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area $A_{\text{BET}}$ (m² g⁻¹)</th>
<th>Average internal pore diameter $d_{\text{BET}}$ (nm)</th>
<th>Average nanotube bundle diameter $D_{\text{bun}}$ (nm)</th>
<th>Interbundle pore volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>300 ± 1.0</td>
<td>24 ± 1</td>
<td>8.8 ± 0.2</td>
<td>91 ± 5</td>
</tr>
<tr>
<td>MWNT/C6S</td>
<td>250 ± 1.0</td>
<td>26 ± 3</td>
<td>11 ± 0.2</td>
<td>94 ± 6</td>
</tr>
<tr>
<td>MWNT/PTS</td>
<td>180 ± 0.1</td>
<td>20 ± 2</td>
<td>15 ± 0.1</td>
<td>96 ± 8</td>
</tr>
<tr>
<td>MWNT/TSP</td>
<td>240 ± 1.0</td>
<td>26 ± 3</td>
<td>11 ± 0.2</td>
<td>92 ± 5</td>
</tr>
<tr>
<td>MWNT–NH₂/Trix</td>
<td>260 ± 2.0</td>
<td>21 ± 2</td>
<td>10 ± 0.1</td>
<td>94 ± 5</td>
</tr>
<tr>
<td>MWNT–COOH/Trix</td>
<td>380 ± 2.0</td>
<td>10 ± 1</td>
<td>7.1 ± 0.1</td>
<td>87 ± 3</td>
</tr>
</tbody>
</table>
Inspection of the data presented in Table 4.6 shows that each of the internal pore characteristics of the BPs generally fall within a relatively narrow range of values. The average internal pore diameters of the membranes vary between 10 ± 1 and 26 ± 3 nm, while the average nanotube bundle diameters range between 7.1 ± 0.1 and 15 ± 0.1 nm. These values contrast with those obtained previously for BPs prepared using SWNTs and Trix, C6S, PTS, TSP or sulfated β-cyclodextrin (β-CD). With the exception of SWNT/PTS, the average internal pore diameter of these SWNT BPs was reported previously to vary from 2.0 ± 0.2 nm to 4.0 ± 0.4 nm. In contrast, the MWNT BPs examined as part of the current study have much larger internal pores separating aggregates of nanotubes with a larger average diameter. This accounts for why the interbundle pore volumes determined for the MWNT BP membranes (range 87 – 96%) are, on average, slightly greater than what were measured previously for the corresponding membranes composed of SWNTs (range 76 ± 5 to 93 ± 6%).

A further distinction between the two classes of BPs is revealed through examination of their surface areas. For the MWNT membranes studied here, the surface areas ranged from 180 ± 0.1 m² g⁻¹ for MWNT/PTS to 380 ± 2.0 m² g⁻¹ for MWNT–COOH/PTS. In contrast, the specific surface areas of most of the SWNT BPs studied previously varied from 360 ± 4 m² g⁻¹ to 790 ± 4 m² g⁻¹, showing that they typically had greater surface areas. Analysis of the pore structure information derived through analysis of nitrogen adsorption/desorption isotherms therefore reveals that there are some significant differences for membranes prepared using the two different classes of CNTs.
4.8 Permeability of MWNT BPs

Although membrane-based separations are now commonplace within the industrial and scientific communities, there is still considerable interest in the development of new materials for desalination and other membrane filtration applications. This stems from problems associated with currently available materials, such as membrane fouling, short service lifetimes and low solute selectivity. The results presented above showed that the MWNT BPs displayed satisfactory mechanical and electrical properties, which make them candidates as novel membrane materials. The results in following sections provide information on the permeability of the BPs towards water and selected organic solutes.

4.8.1 Water permeability studies

One of the primary considerations when assessing a potential filtration membrane is its permeability, especially towards water. The permeability of the BPs towards water was determined using a dead-end filtration cell. Experiments were commenced by increasing the pressure applied to the feed solution, until water could be seen entering the receiving cell. The volume of water entering the receiving cell was then monitored for approximately 10 min, before the applied pressure was increased and the process repeated (Figure 4.5). For each BP examined, transport of water commenced when the applied pressure was less than 1 bar (Table 4.7). There was little difference between the pressures required to initiate water transport across each of the BPs, or with those applied to induce the passage of water across similar membranes composed of SWNTs in an earlier study. Increasing the pressure applied to all BPs composed of MWNTs or substituted MWNTs resulted in the amount of water permeating across the membrane also increasing.
Figure 4.5: Effect of pressure on the volume of water permeating across a MWNT/PTS BP.

Table 4.7: Membrane permeability ($f$), water transport initiation pressure, rupture pressure and thicknesses of different MWNT BPs.$^a$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Membrane permeability ($f$) (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
<th>Transport initiation pressure (bar)</th>
<th>Rupture pressure (bar)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>24 ± 6</td>
<td>0.24 ± 0.03</td>
<td>1.1 ± 0.3</td>
<td>37 ± 3</td>
</tr>
<tr>
<td>MWNT/C6S</td>
<td>17 ± 4</td>
<td>0.36 ± 0.26</td>
<td>1.3 ± 0.1</td>
<td>48 ± 3</td>
</tr>
<tr>
<td>MWNT/PTS</td>
<td>23 ± 6</td>
<td>0.51 ± 0.23</td>
<td>1.2 ± 0.3</td>
<td>47 ± 1</td>
</tr>
<tr>
<td>MWNT/TSP</td>
<td>21 ± 3</td>
<td>0.40 ± 0.17</td>
<td>1.4 ± 0.3</td>
<td>57 ± 3</td>
</tr>
<tr>
<td>MWNT–NH$_2$/Trix</td>
<td>13 ± 2</td>
<td>0.22 ± 0.05</td>
<td>0.38 ± 0.04</td>
<td>49 ± 1</td>
</tr>
<tr>
<td>MWNT–COOH/Trix</td>
<td>17 ± 4</td>
<td>0.19 ± 0.01</td>
<td>0.26 ± 0.01</td>
<td>38 ± 1</td>
</tr>
</tbody>
</table>

$^a$ Values shown are the average and standard deviation from measurements made on at least two samples.

The permeate flux of each type of BP increased linearly as expected, when the applied pressure was increased, as shown in Figure 4.6 and Figure 4.7. The MWNT–NH$_2$/Trix and MWNT–COOH/Trix BPs could only sustain a small pressure (i.e. 0.38 and 0.26 bar, respectively) before they ruptured (Table 4.7), and the membranes failed. This may be attributed to the significantly poorer mechanical properties of these two BPs, as
noted in Section 4.4. The membrane permeabilities \( f \) were derived from the slopes of the plots in Figure 4.6 and Figure 4.7 using Equation 1.3 (chapter 1). The permeabilities of the BPs are presented in Table 4.7. Changing the identity of either the type of CNT (functionalised or non-functionalised) or dispersant present in the BP had little effect on membrane permeability. In contrast, SWNT BPs prepared using Trix, C6S, PTS and TSP as dispersants were found to exhibit a considerable range of membrane permeability from 83 ± 5 to 2400 ± 1300 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). Furthermore the permeability of the SWNT BPs was in all cases much greater than that of the corresponding membranes prepared using MWNTs examined in the current study. This result contrasts with that reported in a recent investigation by Wang et al. into the permeability of BPs prepared from SWNTs or MWNTs towards different fluids. In the latter investigation, BPs prepared from SWNTs were found to be less permeable by approximately two orders of magnitude. A number of factors may contribute to this fundamentally different result to what is reported here. For example, in the study reported by Wang et al., BPs were prepared from CNTs sourced from different suppliers, and were prepared in most instances by filtration of dispersions under a positive pressure, rather than by the vacuum filtration method we have employed. Clearly it will be important in future studies to determine the cause of this fundamental difference in permeability of what are very similar materials.
Figure 4.6: Effect of applied pressure on the permeate flux ($J$) of different MWNT BPs containing low molecular weight dispersants.

There are a number of possible factors that may contribute to the lower permeability of MWNT (and functionalised MWNT) BPs reported in this chapter, compared to those made from SWNTs studied previously, as well as the lack of sensitivity of the permeability of former group of materials to changes in the dispersant incorporated into their structure. One is variation in the thicknesses of BPs prepared from SWNTs on the one hand, and either MWNTs or functionalised MWNTs on the other. Comparison of the buckypaper thicknesses presented in Table 4.7, with those obtained previously for BPs composed of SWNTs, however, revealed no significant variations. This indicates that the lower permeability displayed by the MWNT BPs in the present study are not due to water having to permeate across materials with a greater overall thickness.
The most likely cause of the variations in permeability between SWNT and MWNT BPs is therefore differences in internal pore structure revealed by analysis of nitrogen adsorption/desorption isotherms. In particular, it was noted above that MWNT BPs have an internal structure consisting of pores with much larger average diameters, and therefore greater volumes than most of their SWNT counterparts. This internal structure is most likely forced upon MWNT BPs by the presence of what are generally much larger aggregates of nanotubes than those present in SWNT BPs. The presence of larger internal pores in MWNT BPs may result in a greater number of water molecules becoming trapped, instead of passing rapidly across the membrane as is found with the corresponding materials composed of SWNTs. Consistent with this idea is the observation of very fast rates of transport through the centre of individual nanotubes present in aligned CNT membranes. This has been attributed in part to the formation of ordered chains of water molecules held together by strong hydrogen bonds, which flow within the confined spaces of the individual nanotubes in a friction-free manner.\textsuperscript{23,24}
4.8.2 Rejection of bisphenol A

The results presented above demonstrate the permeability towards water of BPs composed of MWNTs or substituted MWNTs. Although the membrane permeabilities displayed were less than those determined previously for similar materials composed of SWNTs, the selectivity exhibited by a membrane towards solutes of interest can be an even more important property when assessing suitability for specific applications. It was therefore decided to investigate the ability of the BPs to reject a typical organic pollutant. Experiments were performed using MWNT/Trix, MWNT/PTS, MWNT–NH$_2$/Trix and MWNT–COOH/Trix BPs and feed solutions containing bisphenol A. The experiments were conducted using the same dead-end filtration apparatus used for performing permeability measurements (described in section 3.4.2). Figure 4.8 illustrates the results of these experiments.

In the case of MWNT/Trix, MWNT–NH$_2$/Trix and MWNT–COOH/Trix BPs the extent of BPA removal remained constant at approximately 90% throughout the experiment. Mass balance calculations performed using these BPs showed that there was significant retention of BPA by the membrane in all cases. This suggests that each of these BPs exhibits a significant ability to retain or reject BPA molecules. This is most likely due to adsorption of BPA molecules or their rejection by a size exclusion mechanism. In contrast to the above results, Figure 4.8d shows that the removal of BPA by MWNT/PTS BPs clearly decreased as the experiment progressed. Mass balance calculations performed with this BP showed that, within experimental error, all BPA eventually passed through this particular membrane. This suggests that MWNT/PTS buckypapers lack the ability to adsorb significant amounts of BPA that was exhibited by
each of the other three types of membranes examined. One possible explanation for this unexpected result centres on the lower surface area of MWNT/PTS BPs compared to each of the other membranes (Table 4.6), which may result in a smaller number of sites for analyte adsorption to occur. Another possible explanation centres on MWNT/PTS being the only one of the four BPs containing a dispersant that is likely to participate in significant levels of interaction with BPA molecules in the solvent.

**Figure 4.8:** Average bisphenol A removal obtained using different BP membranes: (a) MWNT/Trix, (b) MWNT–NH₂/Trix, MWNT–COOH/Trix and (d) MWNT/PTS. In each case the feed solution contained 180 mL of 685 μg L⁻¹ bisphenol A. The error bars represent the standard deviations obtained from experiments performed in triplicate for all BPs except MWNT–NH₂/Trix, for which duplicate experiments were performed.
4.8.3 Removal of a mixture of TrOCs

In order to further explore the potential of the BPs to reject organic compounds, a second set of experiments were performed using solutions containing a total of twelve TrOCs, and either a MWNT/Trix or MWNT/PTS BP (described in section 3.4.3). The organic molecules chosen for examination included pharmaceuticals, personal care products and pesticides all with a molecular weights less than 400 g mol\(^{-1}\). The TrOCs included compounds with a range of net charges at neutral pH, and different hydrophobicities (Table 4.8).

**Table 4.8: Physicochemical properties of selected TrOCs.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Category</th>
<th>Molecular weight (g mol(^{-1}))</th>
<th>Log (D) (^a) (pH 7)</th>
<th>(pK_a) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amitriptyline</td>
<td>Hydrophilic, charged</td>
<td>277</td>
<td>2.28</td>
<td>9.18</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td></td>
<td>290</td>
<td>0.27</td>
<td>7.04</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td></td>
<td>253</td>
<td>-0.96</td>
<td>5.18</td>
</tr>
<tr>
<td>Diclofenac</td>
<td></td>
<td>296</td>
<td>1.77</td>
<td>4.18</td>
</tr>
<tr>
<td>Bezafibrate</td>
<td></td>
<td>362</td>
<td>-0.93</td>
<td>3.29</td>
</tr>
<tr>
<td>Caffeine</td>
<td>Hydrophilic, neutral</td>
<td>194</td>
<td>-0.63</td>
<td>0.52</td>
</tr>
<tr>
<td>Atrazine</td>
<td></td>
<td>216</td>
<td>2.64</td>
<td>2.27</td>
</tr>
<tr>
<td>Primidone</td>
<td>Hydrophilic, neutral</td>
<td>218</td>
<td>0.83</td>
<td>12.26</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td></td>
<td>236</td>
<td>1.89</td>
<td>13.94</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td></td>
<td>266</td>
<td>2.85</td>
<td>4.68</td>
</tr>
<tr>
<td>Linuron</td>
<td>Hydrophobic, neutral</td>
<td>249</td>
<td>3.12</td>
<td>12.13</td>
</tr>
<tr>
<td>Triclosan</td>
<td></td>
<td>290</td>
<td>5.28</td>
<td>7.8</td>
</tr>
</tbody>
</table>

\(^a\) Values for \(pK_a\) and \(\log D\) were obtained from the SciFinder Scholar (ACS) database.

**Figure 4.9** shows how the percentage removal of each of the TrOCs varied as the total volume of permeate collected increased for the two buckypapers investigated. Inspection of the data shown in **Figure 4.9A**, which was obtained using a MWNT/Trix
Figure 4.9: Efficiency of removal of selected trace organic contaminants (TrOCs) using: (a) MWNT/Trix and (b) MWNT/PTS BPs. For each experiment the feed solution contained twelve different TrOCs each at a concentration of 50 μg L$^{-1}$. The total numbers of bed volumes of permeate that passed through each BP were: 1430 (MWNT/Trix); and 1110 (MWNT/PTS).
BP, shows that the extent of removal of most of the TrOCs was $\geq 90\%$. The one notable exception to this trend was primidone, which is a hydrophilic and neutral pharmaceutical. In contrast to the above results, Figure 4.9B shows that a MWNT/PTS BP was much less effective in removing many of the TrOCs from the solution. This showed that MWNT/PTS was the more permeable of the two BPs investigated towards these compounds.

Figure 4.10 shows the final percentage removals obtained at the end of the above experiments. In the case of the MWNT/Trix BP, the final percentage removal for eleven of the twelve TrOCs was $\geq 90\%$, while for MWNT/PTS only two of the organic compounds were rejected by the membrane this effectively. After the conclusion of the experiment, only four compounds were removed by the MWNT/PTS BP to an extent of 60\% or greater, while for the remaining eight compounds the final removal efficiencies were less than 40\%. The lower removal efficiency of MWNT/PTS is in accord with the results observed during experiments performed using BPA, and again may be attributable to the lower surface area of this material. However, it is not possible to readily discern a reason why some TrOCs were removed by the MWNT/PTS BP far more efficiently than others, based on differences in hydrophobicity, molecular weight and charge. Whilst these experiments therefore further highlight the ability of MWNT buckypapers to remove organic compounds from solution, and in some cases with a degree of specificity, further work is required to determine the origin of the latter property.
4.9 Conclusions

Uniform, free-standing BPs were successfully produced from aqueous dispersions containing MWNTs or substituted MWNTs, and either the surfactant Trix or one of several macrocyclic ligands. The morphology of all membranes was investigated by a
combination of SEM and nitrogen adsorption/desorption analysis. The BPs were permeable towards water, however, the flux across the membranes did not vary greatly. This is consistent with the results of scanning electron microscopic examination of the surfaces of the BPs, which showed very little variation in surface morphology. In addition, analysis of nitrogen adsorption/desorption binding isotherms derived using different MWNT BPs revealed strong similarities between their internal pore structures. For example, the average internal pore size of each buckypaper produced using unfunctionalised MWNTs ranged between $20 \pm 2$ and $26 \pm 3$ nm, and the average nanotube bundle diameters ranged from $7.1 \pm 0.1$ to $15 \pm 0.1$ nm. The specific surface areas of all the MWNT BPs studied here varied from $180 \pm 0.1$ to $380 \pm 2.0$ m$^2$ g$^{-1}$, showing that they typically had lower surface area than similar SWNT BPs.

The composition of the BPs was investigated by elemental analysis, which provided evidence that the dispersant molecules were retained in the membrane structure. The incorporation of these molecules was shown to influence the physical properties of the BPs, including their hydrophobicity (contact angle) and mechanical properties. The contact angles of the buckypapers revealed that each was hydrophilic in nature, which suggests that they may require a low onset pressure (liquid entry pressure) to induce transport of aqueous solutions across the membrane surfaces. Most BPs displayed similar mechanical properties, with the exception of MWNT/PTS, which displayed a higher Young’s modulus and tensile strength of $1.2 \pm 0.2$ GPa and $13 \pm 2$ MPa, respectively, compared to other MWNT BPs prepared in this study.
Permeability experiments performed using solutions containing only BPA, or a mixture of twelve TrOCs, demonstrated the ability of most of the MWNT BPs to reject a variety of organic compounds. MWNT/Trix, MWNT–NH$_2$/Trix and MWNT–COOH/Trix BPs proved to be effective at removing BPA from aqueous solutions, with the extent of BPA removal remaining constant at approximately 90% throughout the experiments. The BP that showed the least ability to perform this function was MWNT/PTS, perhaps as a result of its lower surface area limiting its ability to adsorb dissolved organic solutes. A MWNT/Trix BP was able to remove most of the twelve TrOCs examined to an extent of $\geq 90\%$. The results presented here highlight the ability of free-standing BPs to function as selective nanofiltration media. In order to fully realise this aim it is important to modify the BPs so as to improve their robustness and durability, whilst retaining the selective molecular recognition characteristics. The following two chapters will describe work performed in an attempt to realise these goals.
4.10 References


Chapter 5

Preparation, Characterisation and Nanofiltration Applications of Tough MWNT BPs Containing Biopolymers

This chapter discusses the preparation and characterisation of MWNT BPs containing a range of biopolymer dispersant molecules. The permeability of these membranes towards water as well as a mixture of twelve trace organic contaminants is also discussed, as is their ability to reject simple salts from aqueous solutions. Parts of this chapter describing the synthesis, properties and permeability of MWNT/biopolymer BPs has recently been submitted for publication:


Below are the contributions made by the authors to this submitted article:

Md. Harun-Or Rashid: Prepared all BPs and submitted samples for elemental and N₂ adsorption/desorption analyses, as well as carried out all characterizations of BPs. Also performed water permeability studies, TrOCs rejection studies and salt rejection studies of BPs. Wrote first draft of the manuscript and was heavily involved in preparing all subsequent drafts.

Nicholas Scales: Carried out N₂ adsorption/desorption experiments on all BPs.
Gerry Triani: Provided facilities and expertise for performing N₂ adsorption/desorption experiments on all BPs.

Long D. Nghiem: Provided facilities and expertise for performing water permeability studies, TrOCs and salt rejection experiments on all BPs.

Marc in het Panhuis and Stephen F. Ralph: Provided overall project direction and guidance with respect to analysis of experimental results. Also contributed to the preparation of the latter and final version of the journal manuscript.
5.1 Introduction

The potential of CNTs to remove TrOCs and other classes of contaminants from water supplies has been shown by a number of recent investigations. CNTs have been shown to have high adsorption capacities for phenols, heavy metals, and natural organic matter.\textsuperscript{1-4} In addition, several workers have suggested that CNTs may be more effective adsorbents than activated carbon for removing organic compounds, due to their larger specific surface areas, and the diverse range of contaminant/adsorbent interactions possible.\textsuperscript{5,6}

These investigations have also provided impetus for studies into the effectiveness of BPs for removal or recovery of dissolved pollutants from water supplies. In the previous chapter, the permeability of BPs prepared from dispersions containing MWNTs and low molecular weight dispersants was shown, along with their ability to reject a variety of TrOCs, including BPA. In general, MWNT BP membranes are quite brittle. To use BPs for filtration applications, it will be essential to improve their mechanical properties, such as by enhancing the strength of the connections between nanotube bundles. Recently, it has been shown that BPs prepared from aqueous dispersions of SWNTs, that also contained biopolymers, exhibited superior mechanical properties compared to analogous membranes made from dispersions containing low molecular mass dispersants.\textsuperscript{7} In view of these results, and the potential for the biopolymer molecules trapped within BPs to interact by a variety of mechanisms with dissolved solutes, it was decided to explore the potential of MWNT/biopolymer BPs for removing selected TrOCs and simple salts from aqueous solutions. Multi-walled carbon nanotubes were chosen for this initial investigation owing to their lower cost and greater ease of dispersion.
5.2 Preparation of MWNT/biopolymer dispersions

Formation of dispersions containing MWNTs and different biopolymer dispersants was monitored using absorption spectrophotometry and optical microscopy. It has been established that MWNTs can generally be more readily dispersed in solution than SWNTs. Consequently we pursued formation of MWNT dispersions using solutions containing relatively low concentrations of biopolymers, and by only briefly applying ultrasonic energy. The latter was an important consideration, as the length of sonication time must be sufficient to disperse the MWNTs effectively, but it should not be so long as to create defects in the nanotubes, shorten their lengths, or otherwise adversely affect their electronic properties. Similarly, it has also been shown previously that the decomposition of dispersant molecules such as carbohydrates and other polymeric species, can occur as a result of sustained periods of sonication. Absorption spectrophotometry is well suited for monitoring the effects of changes in sonication time or sample conditions on the extent of dispersion of CNTs. This is because it is a convenient method for assessing the extent of debundling of nanotubes in dispersions. Bundled CNTs exhibit minimal absorption in the region between 300 and 1000 nm. In contrast, absorbance throughout this region of the spectrum grows in response to increases in the amount of CNTs dispersed in solution.

Figure 5.1 shows a representative series of absorption spectra obtained by sonicating a sample containing MWNTs and LSZ for different periods of time. The absorbance increased in a regular fashion at all wavelengths as the sonication time was increased up to 7 min. During this period the nanotubes were debundled to an increasing extent, resulting in a dispersion containing a greater concentration of MWNTs. Increasing the sonication further to 10 min or longer resulted in minimal further changes to the
absorption spectrum. This indicated that there was little further debundling of the MWNTs, and that a sonication time of 10 min was sufficient to ensure production of an optimised MWNT/LSZ dispersion.

Figure 5.1: Effect of increasing sonication time on the absorption spectrum of a typical MWNT/LSZ dispersion. Each sample was measured after being diluted 100× using Milli-Q water (concentration of MWNTs = 0.001% (w/v) after dilution).

In order to identify a suitable sonication time for preparing the other types of dispersions, the absorbance at a single wavelength (660 nm) was monitored as a function of time for samples containing MWNTs and different biopolymers. This wavelength was chosen as it had been used previously in experiments designed to determine the optimum sonication time for producing dispersions containing SWNTs and biopolymers. In addition, this value was the wavelength of maximum absorbance corresponding to one of the van Hove singularities. Figure 5.2 shows the variation in UV absorbance at 660 nm for each of the MWNT/biopolymer dispersions produced as part of the current work, in response to increasing sonication time.
Figure 5.2: Effect of increasing sonication time on the absorbance at 660 nm of MWNT dispersions containing different biopolymers. All samples were measured after being diluted 100× using Milli-Q water (concentration of MWNTs = 0.001% (w/v) after dilution).

In each case absorbance had reached a plateau region after 10 min of sonication. This indicates that this period of time was sufficient to produce a highly dispersed sample of MWNTs suitable for preparing buckypapers. Increasing the sonication period resulted in no further significant changes to the absorbance at 660 nm. This contrasts with the behaviour observed previously for SWNT dispersions containing many of the same biopolymer dispersants, where absorbance was found to increase significantly with sonication time up to 24 min.7

The effect of increasing sonication time on the physical appearance of the MWNT/biopolymer dispersions was also examined using optical microscopy. Figure 5.3 shows some typical results obtained, using a MWNT/LSZ dispersion as an example. After just 1 min of sonication large clumps of MWNTs can still be clearly seen, however after 10 min the dispersion obtained was homogeneous, with no solid
aggregates of non-stabilized carbonaceous material apparent. This provides further evidence that at sonication times > 10 min the bundles of MWNTs have been completely separated.

![Figure 5.3: Optical microscope images of a MWNT/LSZ dispersion that had been sonicated for: (a) 1 min; (b) 10 min and (c) 15 min, taken immediately following sonication.](image)

### 5.3 Preparation of MWNT/biopolymer BPs

A wide range of BPs were successfully obtained from aqueous MWNT dispersions produced using chitosan, bovine serum albumin, lysozyme, DNA and gellan gum. To the best of our knowledge, the synthesis, characterisation and applications of MWNT BPs incorporating a variety of biopolymers has been hitherto unexplored. All BPs in this study were subjected to a simple washing procedure after preparation to remove loosely adsorbed dispersant molecules. This left behind free-standing and flexible BP membranes as shown in [Figure 5.4](image). In their dried state, the BPs were sufficiently robust to be handled and trimmed to any desired size and shape for characterisation studies. The following sections describe the systematic examination of the structure and properties of these BPs, which was conducted prior to evaluating their ability to act as selectively permeable membranes.
Figure 5.4: Free-standing and flexible MWNT/CHT BPs: (A) a circular BP with a diameter of 35 mm and (B) a rectangular BP measuring 6 cm × 12 cm.

5.4 Surface morphology of MWNT/biopolymer BPs

The effect on the surface morphology of the MWNT BPs of introducing different biopolymer dispersants was examined using SEM imaging. Micrographs of the various buckypapers at different magnifications are shown in Figure 5.5 and Figure 5.6. When viewed with the lower magnification of 10,000×, the SEM images showed that the surfaces of all BPs appeared to be relatively smooth (Figure 5.5). Higher magnification (70,000×) images (Figure 5.6) showed a highly entangled mass of nanotubes was present on the surface of each of the membranes, which was reminiscent of the morphology reported previously for MWNT/Trix BPs prepared by a similar method.18
Of the five membranes shown in Figure 5.6, the MWNT/LSZ membrane exhibited the tightest packing of nanotube fibres, and as a consequence appeared to have a lower proportion of larger pore openings on its surface. Overall, however, the surface morphology of the five MWNT BPs resembled each other very closely. In contrast, SEM studies showed significant differences between the surface morphology of BPs composed of SWNTs and the same biopolymer dispersants. This suggests either that there may have been limited retention of biopolymer molecules in the case of the MWNT BPs, or that they inherently differ very little in surface, and possibly internal morphology. Evidence in support of the latter explanation was provided by reports that BPs prepared from dispersions containing SWNTs and low molecular mass dispersants also exhibited a greater range of surface morphologies in SEM studies, than the corresponding membranes prepared using the same dispersants and MWNTs.
5.5 Microanalysis

Elemental analysis data (Table 5.1) were obtained for each of the BPs in order to establish whether the biopolymer molecules had been retained within their structures. Both BPs prepared using protein dispersants and, to a lesser extent, that prepared using DNA, showed significantly greater amounts of N than the raw (non-dispersed) MWNTs. This provides support for a significant degree of retention of these biopolymers in the BPs. Further evidence is provided by the observation that P was incorporated to a significant extent into the MWNT/DNA membrane, and S for both of the materials prepared using protein dispersants. Table 5.1 also shows that the MWNT/CHT BP contained 1.3% N, which is significantly greater than the amount present in the raw MWNTs (< 0.3%). This indicates that N was incorporated into the MWNT/CHT BP, as expected, owing to the presence of amine groups in chitosan.
Table 5.1: Elemental composition of raw (non-dispersed) MWNTs and different MWNT/biopolymer BPs. The error in each case is ± 0.1%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Raw MWNTs</td>
<td>97.8</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>81.2</td>
</tr>
<tr>
<td>MWNT/LSZ</td>
<td>85.3</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>84.8</td>
</tr>
<tr>
<td>MWNT/GG</td>
<td>61.7</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>82.9</td>
</tr>
</tbody>
</table>

The only dispersant used to make a BP which does not contain N, S or P was gellan gum. Therefore in order to determine if this biopolymer had been retained in the MWNT/GG BPs, it was necessary to look closely at the percentages of C and H in this membrane. For the MWNT/GG buckypaper, the amount of H present was greater than for any other membrane, and far in excess of that in the raw MWNTs. Furthermore the amount of C present was considerably less than for any of the other BPs or the raw MWNTs. Both of these results are consistent with retention of gellan gum molecules within the MWNT/GG BP.

The percentage composition of elements such as N, S and P within the current MWNT/biopolymer BPs is similar to that of these elements in membranes prepared using either MWNTs or SWNTs, and low molecular mass dispersants. Since these elements are not present in significant amounts in either the raw MWNTs used to prepare the BPs, or the solvent, these results provide strong support for the retention of biopolymer molecules within the BPs. This in turn suggests that the lack of variation in
their surface morphologies noted above is most likely an inherent characteristic of membranes prepared using MWNTs.

5.6 Mechanical properties of MWNT/biopolymer BPs

We have previously examined the effect of replacing the low molecular weight dispersant Triton X-100, by various biopolymers including several of those studied as part of the current investigation, on the mechanical properties of BPs prepared using SWNTs. It was found that the tensile strength of the materials depended on the molecular mass of the dispersant molecules, perhaps as a result of larger biopolymers being able to overlap and interact with greater numbers of nanotubes. Even more dramatic was the increase in ductility and toughness of the membranes prepared using SWNTs and either GG or CHT, compared to those made using SWNTs and Triton X-100, LSZ or BSA. In view of these results, it was anticipated that the mechanical properties of the MWNT/biopolymer BPs would also show improvements relative to those made using the same CNTs, and low molecular mass dispersants. Figure 5.7 shows representative stress-strain curves obtained for the MWNT/biopolymer BPs, while Table 5.2 collates the tensile strength, ductility, Young’s modulus and toughness derived from those curves, along with other selected physical properties.
Inspection of the data in Table 5.2 reveals some of the same trends observed in a previous study involving SWNT/biopolymer BPs. Most notably, incorporation of the polysaccharide dispersants CHT and GG again resulted in membranes that exhibited superior ductility and toughness to any of the other materials, including a MWNT/Trix BP. In addition, the ductility of each of the BPs containing biopolymers was greater than for a range of other membranes prepared using MWNTs and low molecular mass dispersants. It is also apparent from Table 5.2 that the tensile strengths of the MWNT/CHT and MWNT/GG BPs were significantly greater than that of most of the other membranes examined as part of the current study, with the exception of that incorporating BSA. In contrast to the above observations, there was little difference amongst the values derived for the Young’s modulus of the materials.
Table 5.2: Physical properties of MWNT/biopolymer BPs. All initial dispersions used to prepare BPs contained 0.1% (w/v) MWNTs. Values shown are the average of at least 3 samples, with the errors reported determined from the standard deviation obtained from all measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial concentration of dispersant (% w/v)</th>
<th>Tensile strength (MPa)</th>
<th>Ductility (%)</th>
<th>Young’s modulus (GPa)</th>
<th>Toughness (J g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>1.0</td>
<td>5 ± 2</td>
<td>1.3 ± 0.2</td>
<td>0.6 ± 0.3</td>
<td>0.10 ± 0.06</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>0.2</td>
<td>24 ± 3</td>
<td>3.2 ± 1.0</td>
<td>0.7 ± 0.3</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td>MWNT/LSZ</td>
<td>0.2</td>
<td>13 ± 3</td>
<td>2.9 ± 1.2</td>
<td>0.5 ± 0.2</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>0.05</td>
<td>28 ± 2</td>
<td>5.3 ± 2.7</td>
<td>0.9 ± 0.3</td>
<td>1.7 ± 0.3</td>
</tr>
<tr>
<td>MWNT/GG</td>
<td>0.05</td>
<td>26 ± 2</td>
<td>4.0 ± 0.6</td>
<td>0.6 ± 0.1</td>
<td>1.7 ± 0.4</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>0.05</td>
<td>14 ± 2</td>
<td>2.2 ± 0.7</td>
<td>0.4 ± 0.1</td>
<td>0.6 ± 0.2</td>
</tr>
</tbody>
</table>

The data in Table 5.2 confirmed our hypothesis that incorporation of the biopolymers into MWNT BPs would result in significant improvements to their mechanical properties, thus making them attractive candidates for water permeability and solute rejection experiments. In addition, the above observations also raised the question of whether further improvements to the mechanical properties could be obtained by preparing the BPs from dispersions containing higher concentrations of the biopolymers. In order to test this hypothesis, MWNT/biopolymer BPs were prepared using four different concentrations of each of the biopolymers, and their mechanical properties measured. The results of this investigation are presented in Table 5.3.
Table 5.3: Effect of the initial concentration of biopolymer used during preparation of MWNT/biopolymer dispersions, on the mechanical properties of BPs. All dispersions contained MWNTs with a concentration of 0.1% (w/v). Values shown are the average of at least 3 samples, with the errors reported determined from the standard deviation obtained from all measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial concentration of dispersant (% w/v)</th>
<th>Tensile Strength (MPa)</th>
<th>Ductility (%)</th>
<th>Young’s Modulus (GPa)</th>
<th>Toughness (J g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/BSA</td>
<td>0.2</td>
<td>24 ± 3</td>
<td>2.6 ± 1.0</td>
<td>0.7 ± 0.3</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>26 ± 2</td>
<td>3.7 ± 0.2</td>
<td>1.5 ± 0.1</td>
<td>0.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>28 ± 2</td>
<td>4.0 ± 0.9</td>
<td>1.7 ± 0.3</td>
<td>0.9 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>44 ± 3</td>
<td>5.9 ± 1.0</td>
<td>2.1 ± 0.1</td>
<td>1.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>34 ± 4</td>
<td>5.0 ± 0.4</td>
<td>1.8 ± 0.2</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>0.05</td>
<td>28 ± 2</td>
<td>5.3 ± 2.7</td>
<td>0.9 ± 0.3</td>
<td>1.7 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>33 ± 4</td>
<td>5.8 ± 1.5</td>
<td>1.1 ± 0.2</td>
<td>1.8 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>36 ± 3</td>
<td>6.3 ± 0.8</td>
<td>1.2 ± 0.1</td>
<td>1.9 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>58 ± 7</td>
<td>8.1 ± 1.2</td>
<td>2.1 ± 0.3</td>
<td>3.3 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>64 ± 8</td>
<td>10.8 ± 1.7</td>
<td>2.5 ± 0.1</td>
<td>4.1 ± 1.1</td>
</tr>
<tr>
<td>MWNT/GG</td>
<td>0.05</td>
<td>26 ± 2</td>
<td>4.0 ± 0.6</td>
<td>0.6 ± 0.1</td>
<td>1.7 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>30 ± 2</td>
<td>5.8 ± 0.5</td>
<td>1.0 ± 0.1</td>
<td>1.9 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>41 ± 5</td>
<td>6.3 ± 0.7</td>
<td>1.7 ± 0.2</td>
<td>3.2 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>43 ± 2</td>
<td>8.3 ± 1.1</td>
<td>2.1 ± 0.2</td>
<td>4.3 ± 1.8</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>0.05</td>
<td>14 ± 2</td>
<td>2.2 ± 0.7</td>
<td>0.4 ± 0.1</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>15 ± 4</td>
<td>3.4 ± 0.5</td>
<td>0.6 ± 0.1</td>
<td>0.9 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>20 ± 4</td>
<td>4.7 ± 0.7</td>
<td>0.9 ± 0.2</td>
<td>1.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>26 ± 5</td>
<td>5.3 ± 0.4</td>
<td>1.0 ± 0.3</td>
<td>1.5 ± 0.5</td>
</tr>
</tbody>
</table>

Increasing the concentration of gellan gum or DNA in the solutions used to prepare BPs, from 0.05% to 0.3% (w/v), resulted in significant improvements in all four mechanical properties, as did raising the concentration of chitosan from 0.05 to 0.4% (w/v). For example, in the case of MWNT/CHT BPs the tensile strength, ductility, Young’s modulus and toughness were each found to increase by more than 100%. These results suggest that even more robust BPs could have been prepared using solutions containing even higher concentrations of these dispersants. However, this was not pursued owing to the considerable difficulty associated with filtering the viscous dispersions used to produce the membranes. Furthermore examination of the mechanical properties of MWNT/BSA BPs obtained using solutions containing
increasing concentrations of BSA, suggested that for some materials there may be an optimum concentration of dispersant, and that use of higher concentrations may result in less robust materials. In the case of MWNT/BSA BPs, all mechanical properties showed significant improvements when the concentration of BSA in the dispersions used to produce the membranes was raised from 0.2 to 0.5% (w/v). Further raising the concentration of BSA to 0.6% (w/v), however, resulted in small, but noteworthy decreases in the mechanical properties.

The results presented in Table 5.3 therefore highlight the potential benefits of preparing BPs from solutions containing MWNTs as well as relatively high concentrations of biopolymer dispersant. A drawback associated with such a strategy is that the amount of time required to filter the dispersions to yield the BPs in some instances increased from a few hours to 3 – 4 days. As a consequence, the internal morphological properties and permeability characteristics of the membranes were investigated using materials prepared from dispersions containing the lowest concentrations of biopolymer reported in Table 5.3.

5.7 Mechanical stability of MWNT/biopolymer BPs

In order to further evaluate the strength and durability of the MWNT/biopolymer BPs, three of the membranes were selected for an investigation into the effect of time on their mechanical properties. One batch of these three BPs was stored at room temperature (c.a. 21 °C), while another batch was stored in Milli-Q water, also at c.a. 21 °C. Their mechanical properties were then measured at 30 day intervals to determine if any variation occurred. The results of this study are presented in Tables 5.4 and 5.5.
Table 5.4: Effect of time on the mechanical properties of selected BPs stored at room temperature (c.a. 21 °C). All initial dispersions used to prepare BPs contained 0.1% (w/v) MWNTs. The concentrations of all biopolymers in the initial dispersions used for preparing BPs were 0.3% (w/v).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duration of storage</th>
<th>Thickness (µm)</th>
<th>Tensile strength (MPa)</th>
<th>Ductility (%)</th>
<th>Young’s modulus (GPa)</th>
<th>Toughness (J g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/BSA</td>
<td>0 days</td>
<td>55 ± 7</td>
<td>23 ± 3</td>
<td>3.0 ± 0.3</td>
<td>1.7 ± 0.1</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>0 days</td>
<td>55 ± 2</td>
<td>20 ± 2</td>
<td>4.8 ± 0.4</td>
<td>0.9 ± 0.2</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>0 days</td>
<td>45 ± 4</td>
<td>59 ± 8</td>
<td>8.7 ± 0.5</td>
<td>2.1 ± 0.3</td>
<td>3.3 ± 0.6</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>30 days</td>
<td>65 ± 4</td>
<td>23 ± 3</td>
<td>3.2 ± 0.5</td>
<td>1.4 ± 0.1</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>30 days</td>
<td>57 ± 2</td>
<td>17 ± 1</td>
<td>4.8 ± 0.7</td>
<td>0.7 ± 0.1</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>30 days</td>
<td>41 ± 3</td>
<td>58 ± 12</td>
<td>6.8 ± 0.5</td>
<td>2.8 ± 0.7</td>
<td>2.7 ± 1.0</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>60 days</td>
<td>65 ± 1</td>
<td>29 ± 7</td>
<td>3.4 ± 0.8</td>
<td>1.5 ± 0.2</td>
<td>0.6 ± 0.3</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>60 days</td>
<td>58 ± 2</td>
<td>25 ± 4</td>
<td>4.3 ± 0.6</td>
<td>1.2 ± 0.1</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>60 days</td>
<td>43 ± 4</td>
<td>65 ± 4</td>
<td>5.2 ± 0.7</td>
<td>3.2 ± 0.5</td>
<td>2.2 ± 0.3</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>90 days</td>
<td>64 ± 3</td>
<td>29 ± 4</td>
<td>2.5 ± 0.2</td>
<td>1.8 ± 0.2</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>90 days</td>
<td>60 ± 2</td>
<td>24 ± 3</td>
<td>4.1 ± 0.3</td>
<td>1.0 ± 0.2</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>90 days</td>
<td>47 ± 2</td>
<td>65 ± 11</td>
<td>4.6 ± 0.7</td>
<td>2.8 ± 0.8</td>
<td>2.0 ± 0.3</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>120 days</td>
<td>61 ± 2</td>
<td>22 ± 2</td>
<td>3.2 ± 0.3</td>
<td>1.4 ± 0.1</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>120 days</td>
<td>57 ± 2</td>
<td>19 ± 4</td>
<td>4.9 ± 1.7</td>
<td>0.7 ± 0.1</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>120 days</td>
<td>41 ± 3</td>
<td>61 ± 8</td>
<td>7.5 ± 1.6</td>
<td>3.0 ± 0.4</td>
<td>3.1 ± 1.0</td>
</tr>
</tbody>
</table>

Both tables show that there were no significant changes detected to any of the mechanical properties of the MWNT/BSA, MWNT/DNA and MWNT/CHT BPs, under either set of storage conditions, over a period of at least 90 days. These results provide further support for the potential of MWNT/biopolymer BPs as durable filtration media. This view is further supported by the lack of any observable changes to the physical appearance of any of the BPs over the course of this study, and the absence of significant alterations to their measured thicknesses (Tables 5.4 and 5.5).
Table 5.5: Effect of time on the mechanical properties of selected BPs stored in Milli-Q water at room temperature (c.a. 21 °C). All initial dispersions used to prepare BPs contained 0.1% (w/v) MWNTs. The concentrations of all biopolymers in the initial dispersions used for preparing BPs were 0.3% (w/v).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stored in Milli-Q water</th>
<th>Thickness (µm)</th>
<th>Tensile strength (MPa)</th>
<th>Ductility (%)</th>
<th>Young's modulus (GPa)</th>
<th>Toughness (J g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/BSA</td>
<td>0 days</td>
<td>57 ± 5</td>
<td>25 ± 3</td>
<td>3.1 ± 0.6</td>
<td>1.4 ± 0.3</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>0 days</td>
<td>44 ± 2</td>
<td>38 ± 9</td>
<td>5.2 ± 0.4</td>
<td>1.5 ± 0.6</td>
<td>1.3 ± 0.4</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>0 days</td>
<td>43 ± 4</td>
<td>60 ± 8</td>
<td>4.8 ± 0.7</td>
<td>3.1 ± 0.6</td>
<td>1.8 ± 0.5</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>30 days</td>
<td>54 ± 5</td>
<td>28 ± 3</td>
<td>3.2 ± 0.5</td>
<td>1.5 ± 0.3</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>30 days</td>
<td>43 ± 2</td>
<td>39 ± 7</td>
<td>4.9 ± 0.6</td>
<td>1.8 ± 0.5</td>
<td>1.2 ± 0.3</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>30 days</td>
<td>44 ± 4</td>
<td>58 ± 12</td>
<td>4.5 ± 0.8</td>
<td>2.9 ± 0.5</td>
<td>1.7 ± 0.6</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>60 days</td>
<td>53 ± 3</td>
<td>29 ± 9</td>
<td>3.4 ± 1.3</td>
<td>1.6 ± 0.2</td>
<td>0.7 ± 0.5</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>60 days</td>
<td>44 ± 2</td>
<td>37 ± 5</td>
<td>5.3 ± 0.4</td>
<td>1.7 ± 0.2</td>
<td>1.2 ± 0.4</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>60 days</td>
<td>43 ± 5</td>
<td>56 ± 14</td>
<td>4.2 ± 1.9</td>
<td>2.6 ± 0.2</td>
<td>1.6 ± 1.2</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>90 days</td>
<td>53 ± 2</td>
<td>33 ± 3</td>
<td>3.0 ± 0.3</td>
<td>1.8 ± 0.2</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>90 days</td>
<td>42 ± 1</td>
<td>42 ± 5</td>
<td>4.0 ± 0.9</td>
<td>2.3 ± 0.2</td>
<td>1.0 ± 0.3</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>90 days</td>
<td>45 ± 4</td>
<td>60 ± 11</td>
<td>4.4 ± 1.0</td>
<td>3.1 ± 0.4</td>
<td>1.7 ± 0.8</td>
</tr>
</tbody>
</table>

5.8 Electrical conductivity of MWNT/biopolymer BPs

Most of the MWNT/biopolymer BPs exhibited low electrical conductivities, similar to that of MWNT/Trix. Table 5.6 shows that the electrical conductivity of the MWNT/biopolymer BPs varied between 24 ± 1 and 48 ± 5 S cm⁻¹. The low conductivity of these materials suggests that the large biopolymer molecules may have been wrapped around the MWNTs, effectively coating their surfaces. This would have created an electron tunnelling barrier at CNT junctions, resulting in increased electrical resistance. ⁷, ²¹
Table 5.6: Electrical conductivities of MWNT/biopolymer BPs determined using the two-point probe method. All initial dispersions used to prepare BPs contained 0.1% (w/v) MWNTs.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Initial concentration of dispersant (% w/v)</th>
<th>Electrical conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>1.0</td>
<td>31± 3</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>0.2</td>
<td>28 ± 2</td>
</tr>
<tr>
<td>MWNT/LSZ</td>
<td>0.2</td>
<td>24 ± 1</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>0.05</td>
<td>48 ± 5</td>
</tr>
<tr>
<td>MWNT/GG</td>
<td>0.05</td>
<td>26 ± 1</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>0.05</td>
<td>30 ± 2</td>
</tr>
</tbody>
</table>

5.9 Thermal stability of MWNT/biopolymer BPs

For many separation applications, it is essential that the membrane or adsorbant being employed possesses a high degree of thermal stability. Therefore, the effect of temperature on MWNT/biopolymer buckypapers was investigated using TGA by applying temperatures between 25 – 550 °C to all samples. Figure 5.8 compares the TGA trace obtained from raw MWNTs with that of the different BPs containing biopolymers. In all cases, a small loss of mass was observed when the BPs were heated to 100 °C, which can be attributed to the evaporation of residual water trapped inside the membranes. The TGA traces also showed that between 100 °C and 250 °C, the mass of all the BPs remained relatively constant. Above 250 °C there was then a decrease in mass which may be attributed to the decomposition of incorporated dispersant molecules. Overall the TGA traces of the BPs revealed that the membranes exhibited a significant degree of thermal stability, which is important for many membrane applications. This is indicated by the majority of the sample remaining intact until a temperature of ~ 500 °C was reached.
5.10 Wettability of MWNT/biopolymer BPs

The hydrophobicity of a membrane surface is an important characteristic of a material that is potentially going to be used as filtration media. It was hypothesised that interactions between the CNTs and hydrophilic biopolymers might enhance the hydrophilicity of the BPs. In order to investigate this, the contact angles of the
MWNT/biopolymer BPs were determined by contact angle analysis, using 2 μL water droplets delivered via a syringe, as described in section 3.3.4. Figure 5.9 shows representative images of droplets deposited onto the surface two different BPs, while Table 5.7 collates the results obtained. The contact angles of the MWNT/biopolymer BPs ranged between 29 ± 2° and 57 ± 6°, indicating that they could all be considered as having hydrophilic surfaces. All MWNT/biopolymer BPs, with perhaps the exception of MWNT/BSA, were more hydrophilic than MWNT/Trix, which gave a contact angle of 53 ± 9°. Furthermore, the contact angles for the MWNT/biopolymer BPs were significantly lower than those reported previously for SWNT/biopolymer BPs which varied between 67 ± 6° and 76 ± 4.7

**Figure 5.9:** Images of 2 μL water droplets added to the surface of BPs: (A) MWNT/BSA and (B) MWNT/LSZ.
Table 5.7: Contact angles of 2 μL water droplets on MWNT/biopolymer BPs. All initial dispersions used to prepare the BPs contained 0.1% (w/v) MWNTs.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Initial concentration of dispersant (% w/v)</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>1.0</td>
<td>53 ± 9</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>0.2</td>
<td>57 ± 6</td>
</tr>
<tr>
<td>MWNT/LSZ</td>
<td>0.2</td>
<td>32 ± 3</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>0.05</td>
<td>32 ± 4</td>
</tr>
<tr>
<td>MWNT/GG</td>
<td>0.05</td>
<td>39 ± 5</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>0.05</td>
<td>29 ± 2</td>
</tr>
</tbody>
</table>

5.11 Zeta potential analysis

The zeta potential of a membrane is a quantitative measure of the electrical potential of its surface. By measuring the effect of pH on the zeta potential of a membrane, the overall acidity or basicity of its surface can be determined. In addition, the isoelectric point (IEP), which is the pH value at which the zeta potential is equal to zero, can be determined. This is an important parameter to determine because the overall charge of the membrane surface is different depending on whether the solution the membrane is in contact with has a pH above or below the IEP. The effect of pH on the zeta potential of selected MWNT/biopolymer BPs is shown in Figure 5.10, while the IEPs determined for the membranes from this data is presented in Table 5.8. The IEPs of the MWNT/BSA, MWNT/DNA and MWNT/CHT BPs were determined to be 6.9 ± 0.3, 7.5 ± 0.2 and 8.6 ± 0.4, respectively. When immersed in solutions with pH values less than these IEPs, the membranes exhibited positive surface charges. In contrast, when the surrounding pH was raised above the IEP, the overall surface charge of the membranes acquired a negative value. Of the BPs investigated, only MWNT/GG BP exhibited a negative surface charge throughout the entire pH range investigated. This
was an interesting result, as several studies have reported that negative membrane zeta potentials could lead to higher salt rejection capabilities, owing to enhanced electrostatic interactions between the negatively charged membrane surface and negatively charged solutes.\textsuperscript{22,23} As the MWNT/GG BP did not show a positive zeta potential at any pH studied, it was not possible to determine a value for the IEP of this membrane.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.10}
\caption{Effect of pH on the zeta potential of selected MWNT/biopolymer BPs in aqueous 1 mM KCl solution.}
\end{figure}

\begin{table}[h]
\centering
\caption{Isoelectric point obtained from zeta potential analysis of selected MWNT/biopolymer BPs.}
\begin{tabular}{ll}
\hline
Sample & Isoelectric point (pH) \\
\hline
MWNT/BSA & 6.9 ± 0.3 \\
MWNT/CHT & 8.6 ± 0.4 \\
MWNT/DNA & 7.5 ± 0.2 \\
\hline
\end{tabular}
\end{table}
5.12 Surface pore and internal pore structure of MWNT/biopolymer BPs

Average surface pore diameters \( (D_{SEM}) \) of BPs were obtained from the SEM images shown in Figure 5.6, are summarised in Table 5.9. The average surface pore diameters of the MNWT/biopolymer BPs varied between 33 ± 9 and 54 ± 12 nm. All therefore appear to have significantly smaller surface pore diameters than MWNT/Trix membranes \( (D_{SEM} = 80 ± 20 \text{ nm}) \). This was a somewhat surprising result, as SEM suggested that there was little difference between the surfaces of the latter BP on the one hand, and those containing the biopolymers. Previous studies of BPs containing MWNTs and low molecular weight dispersants showed these possessed surface pore diameter similar to that of MWNT/Trix \( (80 ± 20 \text{ nm}) \), and greater than those of the MWNT/biopolymer BPs reported here.\(^{18,20}\) For example, the average surface pore diameters of MWNT/C6S, MWNT/PTS and MWNT/TSP BPs were found to be 78 ± 26, 69 ± 21, and 88 ± 23 nm, respectively. These values were comparable to the value above for a MWNT/Trix membrane, but greater than those determined for the BPs containing MWNTs and biopolymers, all of which had surface pore diameters less than 54 nm.

Table 5.9: Average surface pore diameters \( (D_{SEM}) \) of BPs imaged by SEM. Pore diameters were determined by using image analysis software (Image Pro Plus) and SEM micrographs taken at 70K magnification.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Average surface pore diameter ( D_{SEM} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix(^a)</td>
<td>80 ± 20</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>51 ± 13</td>
</tr>
<tr>
<td>MWNT/LSZ</td>
<td>33 ± 9</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>54 ± 12</td>
</tr>
<tr>
<td>MWNT/GG</td>
<td>48 ± 11</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>52 ± 10</td>
</tr>
</tbody>
</table>

\(^a\) From reference 20.
Nitrogen adsorption/desorption measurements were performed on each of the MWNT/biopolymer BPs, resulting in Type IV isotherms, such as those presented in Figure 5.11 for MWNT/CHT and MWNT/LSZ. Each of the isotherms was similar in overall appearance to those obtained previously for BPs prepared using MWNTs and low molecular weight dispersants. For example, the isotherms illustrated in Figure 5.11 all exhibit a significant degree of adsorption and desorption at all relative pressures, as well as hysteresis at higher relative pressures. All isotherms were analysed using the BJH, and HK methods, to yield the surface and internal morphological properties compiled in Table 5.10. In addition, the insets in Figure 5.11 show the distribution of pore sizes for the MWNT/CHT and MWNT/LSZ BPs derived through analysis of the isotherms using the BJH and HK approaches. The average internal pore diameters of the MWNT/biopolymer BPs were derived from the adsorption/desorption data using the BET method, and are presented in Table 5.10, along with the average internal pore diameter for a MWNT/Trix BP.

MWNT BPs containing biopolymers were found to generally have lower surface areas than previously studied membranes prepared using MWNTs and low molecular mass dispersants. All five MWNT/biopolymer BPs had surface areas which were less than 200 m² g⁻¹, while the majority of MWNT BPs studied previously, which contained low molecular mass dispersants, exhibited surface areas significantly greater than this value. For example, the surface areas of MWNT/Trix, MWNT/C6S and MWNT/TSP BPs were previously determined to be 300, 250 and 240 m² g⁻¹, respectively.
Figure 5.11: Nitrogen adsorption (blue line) and desorption (red line) isotherms for: (A) MWNT/CHT and (B) MWNT/LSZ BPs. The insets show the pore size distributions for the BPs derived from BJH and HK analysis of the isotherms.
The data presented in Table 5.10 also suggests that some differences may exist between the internal pore structures of the MWNT/biopolymer BPs, and those examined previously, which were prepared from the same type of CNTs and low molecular weight dispersants such as C6S, PTS and TSP. Incorporation of the latter dispersants was found to typically result in BPs with average nanotube bundle diameters < 11 nm, and interbundle pore volumes > 90%.\textsuperscript{18,20} For example, MWNT/C6S and MWNT/TSP BPs were reported to have interbundle pore volumes of 94 ± 6% and 92 ± 5%, respectively.\textsuperscript{20} In contrast, all of the BPs investigated as part of the current study exhibited average nanotube bundle diameters > 13.0 ± 0.1 nm and interbundle pore volumes < 90%.

\textbf{Table 5.10:} Surface morphological and internal pore properties of different MWNT BPs. All initial dispersions used for preparing BPs contained 0.1% (w/v) MWNTs. These initial dispersions also contained one of the following dispersants: Trix 1.0% (w/v); CHT, GG or DNA 0.05% (w/v), LSZ or BSA 0.2% (w/v).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area $A_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>Average internal pore diameter $d_{\text{BET}}$ (nm)</th>
<th>Average nanotube bundle diameter $D_{\text{bun}}$ (nm)</th>
<th>Interbundle Pore volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw MWNTs</td>
<td>290 ± 2</td>
<td>29 ± 3</td>
<td>9.2 ± 0.1</td>
<td>96 ± 3</td>
</tr>
<tr>
<td>MWNT/Trix</td>
<td>251 ± 2</td>
<td>17 ± 2</td>
<td>10.6 ± 0.1</td>
<td>92 ± 4</td>
</tr>
<tr>
<td>MWNT/BSA</td>
<td>136 ± 1</td>
<td>19 ± 1</td>
<td>19.6 ± 0.2</td>
<td>86 ± 5</td>
</tr>
<tr>
<td>MWNT/LSZ</td>
<td>161 ± 1</td>
<td>16 ± 1</td>
<td>16.5 ± 0.2</td>
<td>82 ± 4</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>196 ± 1</td>
<td>23 ± 3</td>
<td>13.6 ± 0.2</td>
<td>83 ± 5</td>
</tr>
<tr>
<td>MWNT/GG</td>
<td>163 ± 1</td>
<td>20 ± 2</td>
<td>16.3 ± 0.2</td>
<td>86 ± 5</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>200 ± 2</td>
<td>23 ± 3</td>
<td>13.3 ± 0.1</td>
<td>83 ± 5</td>
</tr>
</tbody>
</table>

Examination of the surface and internal morphologies of the MWNT BPs containing biopolymers therefore revealed some consistent differences from those of membranes.
previously examined which contained this class of CNTs. These differences, combined with the contrasting range of intermolecular interactions afforded by the presence of the biopolymers in the MWNT/biopolymer BPs, were hoped might lead to novel water and solute permeability characteristics. These properties were therefore explored by performing experiments using two different classes of membrane filtration equipment.

5.13 Permeability studies

5.13.1 Permeability of MWNT/biopolymer BPs towards water

In an initial set of experiments, a dead-end filtration cell was used to compare the permeabilities towards water of the biopolymer-containing MWNT BPs to each other, and to that of a MWNT/Trix BP. Experiments were initiated by raising the pressure applied to the feed solution until water commenced passing across the membranes into the receiving solution. Once water transport had commenced, the volume of water in the receiving solution was measured as a function of time for 10 min, and then the pressure increased incrementally and the process repeated. This yielded a series of linear permeability plots for the MWNT/biopolymer BPs (Figure 5.12). Each of the BPs investigated proved to be permeable towards water at only relatively low pressures (< 1 bar). Furthermore, the water transport behaviour of the BPs resulted in permeability plots that were very similar in overall appearance to each other. The pressure applied to the BPs was increased, and the process repeated, until membrane rupture occurred.
Figure 5.12: Representative water permeability plots for selected BPs: (A) MWNT/CHT; (B) MWNT/BSA; (C) MWNT/DNA and (D) MWNT/GG.

The permeate fluxes ($J$) for the membranes were derived from the slopes of plots of volume of water as a function of time. Figure 5.13 shows that the permeate flux of each membrane increased in a linear fashion as a function of applied pressure. From these plots, a pressure-independent membrane flux ($f$) or permeability was then calculated, using Equation 1.3. The values of membrane flux determined for each of the MWNT/biopolymer BPs using this procedure are presented in Table 5.11, and show a degree of dependence on BP thickness. For example, the MWNT/CHT BP, which was found to exhibit the highest degree of water permeability, had the smallest thickness. Despite this general observation, a linear correlation between water permeability and membrane thickness was not apparent for the limited range of data available.
Figure 5.13: Effect of applied pressure on the permeate flux ($J$) of MWNT/biopolymer BPs. All dispersions contained MWNTs with a concentration of 0.1% (w/v).

Table 5.11: Membrane permeability ($f$), water transport initiation pressure, rupture pressure and thickness of MWNT/biopolymer BPs.* All initial dispersions used for preparing BPs contained 0.1% (w/v) MWNTs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial concentration of dispersant (% w/v)</th>
<th>Membrane permeability ($f$) (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
<th>Liquid entry pressure (bar)</th>
<th>Rupture pressure (bar)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/BSA</td>
<td>0.2</td>
<td>10 ± 4</td>
<td>0.40 ± 0.10</td>
<td>3.4 ± 0.1</td>
<td>59 ± 7</td>
</tr>
<tr>
<td>MWNT/LSZ</td>
<td>0.2</td>
<td>14 ± 3</td>
<td>0.60 ± 0.15</td>
<td>2.7 ± 0.3</td>
<td>58 ± 3</td>
</tr>
<tr>
<td>MWNT/CHT</td>
<td>0.05</td>
<td>22 ± 4</td>
<td>0.30 ± 0.05</td>
<td>3.7 ± 0.2</td>
<td>41 ± 3</td>
</tr>
<tr>
<td>MWNT/GG</td>
<td>0.05</td>
<td>19 ± 3</td>
<td>0.25 ± 0.05</td>
<td>2.0 ± 0.6</td>
<td>63 ± 5</td>
</tr>
<tr>
<td>MWNT/DNA</td>
<td>0.05</td>
<td>13 ± 2</td>
<td>0.50 ± 0.15</td>
<td>2.5 ± 0.5</td>
<td>44 ± 4</td>
</tr>
</tbody>
</table>

* Values shown are the average and standard deviation from measurements made on at least three samples.

The five MWNT/biopolymer BPs investigated as part of the current study had similar thicknesses to those of membranes previously prepared using MWNTs and low molecular weight dispersants (such as C6S, TSP and PTS). As a consequence, it was
not surprising that their liquid entry pressures (i.e. the smallest applied pressure required for water transport) were also similar. **Table 5.11** shows that the liquid entry pressure for the MWNT/biopolymer BPs ranged from 0.25 ± 0.05 to 0.6 ± 0.15 bar. These values are comparable to those for other BPs prepared using MWNTs or substituted MWNTs, and low molecular weight dispersants (such as C6S, TSP and PTS), which were typically 0.51 bar or less.\(^{20}\) In contrast, the MWNT/biopolymer BPs in the current study exhibited significantly higher rupture pressures than MWNT membranes containing low molecular weight dispersants, such as C6S, TSP and PTS previously reported. All BPs in the current study exhibited rupture pressures of more than 2.0 bar, with the MWNT/CHT and MWNT/BSA BPs proving to be especially robust (rupture pressures of 3.7 ± 0.2 and 3.4 ± 0.1 bar, respectively). In contrast, the rupture pressures of MWNT BPs prepared using low molecular weight dispersants, such as C6S, TSP and PTS, was reported to be less than 1.4 bar.\(^{20}\) Buckypapers prepared from SWNTs and the same low molecular weight dispersants were also been shown to be susceptible to failure in water transport experiments, with membrane rupture pressures of less than 1.4 bar.\(^{19}\) These observations are consistent with the improved mechanical properties of the MWNT/biopolymer BPs (**Table 5.3**).

The water permeabilities of the five MWNT/biopolymer BPs were in the range 10 to 22 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). These values are comparable to those of BPs composed of MWNTs and low molecular mass dispersants (e.g. C6S, TSP, PTS), which varied from 17 ± 4 to 24 ± 6 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\).\(^{20}\) These results indicate that incorporation of biopolymers into MWNT BPs resulted in marked improvements in mechanical properties, without compromising their water permeability. In particular, MWNT/CHT BPs were deemed to be the most
suitable for further investigation, as their rupture pressure and membrane flux were both superior to that of the other MWNT/biopolymer BPs investigated here.

5.13.2 Removal of TrOCs

Having established that each of the BPs in Table 5.11 allowed the transport of water at relatively low applied pressures, a series of experiments was then conducted to determine if the presence of the biopolymers in these materials affected their permeability towards a mixture of twelve TrOCs, including pharmaceuticals, pesticides, caffeine and personal care products. Each of the TrOCs were relatively small molecules with molecular weights < 400 g mol$^{-1}$. The experimental protocol for these experiments was described in section 3.4.3 (chapter 3). Figure 5.14 shows how the percentage removal of each of the TrOCs varied as the total volume of permeate collected increased for the four BPs investigated, while Figure 5.15 shows the final percentage removals obtained at the end of the experiments.
Figure 5.14: Effect of time on the removal of trace organic contaminants using different BPs: (a) MWNT/CHT; (b) MWNT/BSA; (c) MWNT/DNA and (d) MWNT/LSZ. For each experiment the feed solution contained twelve TrOCs each at a concentration of 50 µg L⁻¹. The error bars represent the standard deviations obtained from experiments performed in quadruplicate for all BPs except MWNT/LSZ, for which triplicate experiments were performed.

The permeability of the BPs towards the mixture of twelve TrOCs varied significantly. The MWNT/CHT BP achieved the highest degree of TrOC rejection, with the final percentage removal values for nine of the twelve TrOCs being > 95% (Figure 5.15). In contrast, the MWNT/LSZ BP could only achieve over 95% removal for two TrOCs. The MWNT/LSZ BP also exhibited removals of less than 40% for trimethoprim, carbamazepine and atrazine. None of the other BPs exhibited such a low degree of
rejection for any of the twelve TrOCs investigated here. These results demonstrate that these BPs are capable of solute-selective rejection.

Overall, the permeability of the BPs towards the mixture of TrOCs varied according to the following order: MWNT/CHT < MWNT/DNA ~ MWNT/BSA < MWNT/LSZ. The two BPs containing protein dispersants (i.e. BSA and LSZ) were the most permeable towards the TrOCs. This may be rationalised by proposing that the greater range of functional groups present in these biopolymers (e.g. carboxylic acid, hydroxyl, thiol, phenol, guanidine, amine) may have facilitated interactions that lead to the transport of the organic compounds across the BPs. In contrast, chitosan only contains hydroxyl and amine groups, and DNA a range of aromatic nitrogen and amine nitrogen atoms, as well
as phosphates and hydroxyls. This may have limited the range of interactions that can take place between MWNT/GG or MWNT/DNA BPs and TrOCs bearing hydrophilic groups. Such interactions may be required to draw the organic compounds to the surface of the BPs, in order to facilitate their transfer via the internal pores. In good agreement with this hypothesis, MWNT/Trix membranes were previously shown to exhibit a much higher degree of rejection of the same mixture of TrOCs compared to MWNT/PTS membranes.\textsuperscript{20} This may be attributed to ether oxygen atoms being the only heteroatoms in the Trix dispersant present in MWNT/Trix membranes, whereas the PTS present in MWNT/PTS BPs contains both imine and sulfonic acid groups. It might be envisaged that, for example, dipole-dipole interactions between polar or charged functional groups present on the biopolymer dispersants within the BP, and the organic solutes, might initially result in more organic compounds being drawn to the surface of the BP. This is an important first step in the transport mechanism for all solutes. The more molecules that approach and interact with a membrane surface, the more likely they will be transported across that membrane. In addition, the presence of such interactions throughout the interior of the membrane may facilitate subsequent passage of the organic compound across the BP.

5.13.3 Desalination using MWNT/biopolymer BPs

Nanofiltration and desalination of water samples are currently amongst the most important applications of membrane technology. To date there have been, to the best of our knowledge, no published studies which have described the ability of free-standing BPs to filter solutions containing simple inorganic salts. Therefore we decided to investigate the permeability of selected BPs towards water and simple salts, using a
cross-flow filtration system that operates under higher applied pressures than the dead-end filtration system used for the experiments described above. The two BPs chosen for this study were MWNT/CHT membranes prepared using solutions containing 0.2 and 0.3% (w/v) chitosan. These were selected in part because MWNT/CHT membranes showed excellent mechanical properties, and the highest rupture pressures in experiments performed with the dead-end filtration cell. In addition, the filtration process used to produce MWNT/CHT membranes was significantly shorter than for other BPs of comparable robustness.

**Figure 5.16** presents the results of water transport experiments performed with the two BPs. From the slopes of the two graphs, the membrane flux of the MWNT/CHT (0.2% (w/v) BP was determined to be $29 \pm 6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, while for the MWNT/CHT (0.3% (w/v) membrane a significantly lower value of $11 \pm 1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ was obtained. These results show that there is therefore a trade-off between the greater mechanical strength afforded by the presence of additional dispersant molecules, and outright membrane permeability. It is also noteworthy that the aqueous permeability of the BP prepared from a solution containing 0.2% (w/v) CHT was higher in experiments performed using the cross-flow filtration cell, than when the dead-end filtration cell was used.
Figure 5.16: Effect of applied pressure on the permeate flux \((J)\) of different MWNT/CHT free-standing BPs operating in a cross-flow NF/RO filtration system. Solid lines are linear fits to the data. All BPs were prepared from initial dispersions containing 0.1\% (w/v) MWNTs. A schematic illustration of the filtration system can be found in Figure 3.7.

The same two types of BPs were then used in solute rejection experiments performed using a feed solution containing TrOCs, as well as 2 g L\(^{-1}\) NaCl and MgSO\(_4\). Figure 5.17 shows the effect of applied pressure on the extent of rejection of NaCl and MgSO\(_4\) by both BPs. In the case of the BP prepared from a solution containing MWNTs and 0.2\% (w/v) chitosan, the extent of salt rejection could be monitored until the applied pressure reached \(ca. 10\) bar, at which point membrane rupture occurred. In contrast, membrane rupture did not occur until an applied pressure of \(ca. 18\) bar was reached for the BP prepared from a dispersion of MWNTs and 0.3\% (w/v) chitosan, reflecting the greater mechanical integrity of this membrane.
Figure 5.17: Effect of applied pressure on the extent of salt rejection by MWNT/CHT BPs prepared from initial dispersions containing 0.1% (w/v) MWNTs and either 0.2% (w/v) CHT (closed symbols) or 0.3% (w/v) CHT (open symbols).

With both types of BPs the extent of rejection of NaCl and MgSO₄ was found to decrease significantly as the applied pressure was increased. In addition, the extent of rejection of MgSO₄ was found to be slightly greater than that of NaCl with both BPs. This is most likely due to stronger electrostatic interactions between divalent cations and anions, and polar groups on the surfaces of the BPs, or a consequence of the greater difficulty with which the larger sulfate anions can traverse the internal pore structures of the two membranes. Figure 5.17 also shows that the salt rejection capability of the BP prepared from the solution containing more chitosan was greater at all applied pressures. This may be because this membrane contained more polar and charged groups able to interact with and retard the progress of the charged electrolytes.
5.14 Conclusions

Fabrication of BPs from dispersions prepared using MWNTs and biopolymers resulted in membranes that were mechanically more robust than those reported previously, which had been prepared using dispersants of much lower molecular weight. This effect had been noted previously with analogous materials prepared using dispersions containing SWNTs, and can be attributed to the greater effectiveness with which the large biopolymer molecules can adsorb onto the surfaces of the nanotubes and thereby bind them together. Increasing the concentration of biopolymer in the dispersion used to fabricate the BPs typically resulted in significant improvements to their mechanical properties. Furthermore the presence of the biopolymers also resulted in a significantly different internal pore structure for the MWNT/biopolymer membranes, compared to those composed of the same type of nanotubes and low molecular mass dispersants. Perhaps the most important point of contrast was the larger nanotube bundle diameters for the former membranes revealed by analysis of the results of nitrogen adsorption/desorption measurements. The presence of significantly larger clumps of nanotubes within the internal structure of the MWNT/biopolymer BPs is likely to have been a major contributor to their smaller interbundle pore volumes. Furthermore their effects are likely to have also been felt at the surface of the BPs, where the materials prepared using biopolymer dispersants exhibited lower surface areas and surface pore diameters.

The results presented here further demonstrate that incorporation of biopolymer dispersants strengthens BPs, thereby making them potentially viable for water filtration and solute separation applications. Whilst permeability experiments performed using
MWNT/biopolymer BPs showed that they did not allow the passage of water molecules as readily as MWNT membranes containing low molecular mass dispersants, they still exhibited a notable ability to reject a variety of dissolved organic solutes. Furthermore we demonstrated for the first time that these materials are capable of rejecting the passage of inorganic solutes. Comparison of the results presented here for MWNT/biopolymer BPs, with those obtained previously for BPs composed of MWNTs and low molecular mass dispersants, indicates that the permeability and solute rejection properties of the latter materials are largely retained by the new class of BPs reported here. In future work we intend to explore whether these properties are also exhibited by BPs produced using SWNTs and biopolymer dispersants, and if the greater permeability previously noted for membranes composed of this class of CNTs, are retained in the presence of these high molecular mass dispersants.
5.15 References


(6) Pan, B.; Xing, B. *Environmental Science & Technology* **2008**, *42*, 9005.


Chapter 6

Preparation, Characterisation and Water Permeability of SWNT BPs Containing Biopolymers

This chapter discusses the characterisation of BPs prepared using SWNTs and biopolymer dispersant molecules for membrane filtration applications. These biopolymer dispersant molecules were also used to prepare the MWNT/biopolymer BPs described in chapter 5. In addition, the results of water permeability experiments performed using a dead-end filtration cell and the SWNT/biopolymer BPs are presented, and compared to those reported in chapter 5 that were obtained from a similar set of MWNT/biopolymer BPs. The results presented here for the SWNT/biopolymer BPs provide the basis for future studies to further explore the solute rejection characteristics of these materials.
6.1 Introduction

For BPs to be useful as membrane filtration materials, they should possess a range of properties including high porosity, large specific surface area, good chemical and thermal stability, and mechanical integrity. In chapter 5, it was observed that incorporation of biopolymers into MWNT BPs resulted in significant improvements to their mechanical properties and thermal stabilities, thus making them more attractive for water filtration and solute rejection applications. The potential of the MWNT/biopolymer BPs as filtration media was further reinforced by measurement of their water permeabilities. The permeabilities of these BPs ranged from 10 to 22 L m⁻² h⁻¹ bar⁻¹, which were comparable to those of BPs composed of MWNTs and low molecular weight dispersants, which were described and discussed in chapter 4.¹ Therefore incorporation of the biopolymers into MWNT BPs resulted in significant improvements in mechanical properties, without compromising their permeability characteristics.

In a previous study, Sweetman et al. reported that SWNT BPs containing macrocyclic ligands and low molecular weight dispersants sometimes exhibited dramatically higher water permeabilities than those shown by other SWNT BPs.² A drawback of the SWNT BPs prepared by Sweetman et al., which were prepared using SWNTs obtained from Unidym, was their brittle nature. For example, the tensile strengths of SWNT BPs prepared using macrocyclic ligands or Trix varied between 6 ± 3 and 20 ± 10 MPa.² In contrast, as described in chapter 5 the MWNT/biopolymer BPs prepared from this study exhibited much greater tensile strengths of between 13 ± 3 and 64 ± 8 MPa. In this chapter, SWNT BPs were prepared using the same biopolymer dispersants used to make
the MWNT/biopolymer BPs described in the previous chapter, in order to systematically characterised to investigate whether incorporation of the biopolymers into SWNT BPs would yield materials with improved mechanical properties, as well as potentially useful water and solute permeability characteristics. This chapter presents the results of these experiments.

### 6.2 Preparation of SWNT dispersions containing biopolymers

Sonication using an ultrasonic horn is a common method used to facilitate the dispersion of SWNTs into solution. The length of sonication required to effectively disperse SWNTs into biopolymer solutions was optimised using UV-vis-NIR spectroscopy and optical microscopy. It has been established that longer periods of sonication are usually required to disperse SWNTs into solution, than what is necessary to solubilise MWNTs.\(^3\) However, it is important to ensure sonication is kept as brief as possible, because prolonged exposure to ultrasonic energy may lead to structural defects and shortening of SWNTs, thereby adversely affecting their electronic properties.\(^4\)\(^-\)\(^6\) Optimisation experiments were performed using the same concentrations of nanotubes and dispersant molecules, as those used in the analogous experiments described in chapter 5 which used MWNTs. Therefore the only difference between the experiments described here and in the previous chapter, was that in this chapter all experiments were performed using SWNTs purchased from NanoIntegris Technologies (batch no. HR27004).

**Figure 6.1** shows the effect of sonication time on the absorption spectrum of a sample containing 0.1% (w/v) SWNTs and 0.05% (w/v) CHT. There is a general trend of
increasing absorbance at all wavelengths with longer sonication times. This shows that a larger number of SWNTs were being dispersed, as the dispersant molecules absorb minimally at the majority of wavelengths studied. In addition, with increasing sonication time a number of features called van Hove singularities became more prominent in the spectra, with each attributable to debundled SWNTs with a specific diameter and chiral vector. Therefore the absorbance at any given wavelength is proportional to the amount of SWNTs dispersed in solution. The presence of the Van Hove singularities is a direct consequence of the structure of SWNTs. Since the latter are effectively one-dimensional nanowires, with diameters measured in nanometres and lengths measurable in micrometres, the electronic state continuum of normal carbon transforms into a series of discrete energy levels. It is then possible for specific wavelengths of light to excite electrons from one energy level to the next, resulting in the van Hove singularities. As the sonication time was increased from 1 to 50 min, the intensities of the van Hove singularities increased, and they became sharper and better resolved, indicating that the SWNTs were becoming increasingly better dispersed.
Figure 6.1: Effect of increasing sonication time on the absorption spectrum of a SWNT/CHT dispersion. Each sample was measured after being diluted 100x using Milli-Q water (concentration of SWNTs = 0.001% (w/v) after dilution).

The absorbance of the SWNT/CHT solution was found to increase in a regular fashion at all wavelengths, as the sonication time was increased up to 15 min. Increasing the sonication further to 20 min or longer resulted in minimal further changes to the absorption spectrum. This indicated that little further debundling of the SWNTs occurred, and that a sonication time of 20 min was sufficient to ensure production of an optimised SWNT/CHT dispersion. In order to identify an optimum procedure for preparing the other types of SWNT/biopolymer dispersions, the absorbance of the solutions at 660 nm, which corresponds to one of the van Hove singularities, was plotted as a function of sonication time (Figure 6.2). The choice to use absorbance at 660 nm was made in order to be consistent with a previous study which had also
investigated the optimum sonication time for producing dispersions containing SWNTs and the same biopolymers.$^{10}$

**Figure 6.2:** Effect of increasing sonication time on the absorbance at 660 nm of SWNT dispersions containing different biopolymers. All samples were measured after being diluted 100× using Milli-Q water (concentration of SWNTs = 0.001% (w/v) after dilution).

**Figure 6.2** shows that small increments of sonication time initially had a major effect on the absorbance at 660 nm of all SWNT/biopolymer dispersions, but after 20 min further sonication had only a minimal impact. In each case absorbance had either reached or was nearing a plateau region after 20 min of sonication. Therefore 20 min was selected as the ideal amount of sonication time to produce dispersions for making SWNT/biopolymer BPs. In each case this amount of sonication was sufficient to produce solutions which gave well resolved van Hove singularities in absorption spectra, indicating that the SWNTs were well dispersed. In an earlier investigation of SWNT/biopolymer dispersions, containing many of the same biopolymer dispersants,
but SWNTs from a different supplier (Unidym), a sonication time of 24 min was found to be optimal.\textsuperscript{10}

To further verify that the SWNTs were well-dispersed after 20 min of sonication in the current study, the SWNT/biopolymer dispersions were examined using optical microscopy. The optical micrograph of a SWNT/CHT dispersion (Figure 6.3) revealed that after 5 min of sonication large aggregates of SWNTs were still observable. However, after 20 min sonication the dispersion obtained was homogeneous, with no sign of any nanotube aggregates. Similar results were obtained with each of the other SWNT/biopolymer dispersions.

![Figure 6.3: Optical microscope images of a SWNT/CHT dispersion that had been sonicated for: (a) 5 min; (b) 15 min and (c) 20 min.](image)

**6.3 Preparation of SWNT/biopolymer BPs**

The same preparation conditions were followed to prepare SWNT/biopolymer and SWNT/Trix BPs, as those used to synthesise the analogous MWNT membranes. This enabled the effect of changing the type of CNTs employed to prepare the BPs on the properties of the resulting materials to be explored. In the dried state, the free-standing SWNT/biopolymer BPs were found to be sufficiently robust to enable them to be handled and trimmed to the desired size and shape for further characterisation studies.
The following sections first describe the systematic examination of the structure and properties of the SWNT/biopolymer BPs, and then present a preliminary evaluation of their ability to act as membrane filters.

### 6.4 Surface morphology of SWNT/biopolymer BPs

The surface morphology of the SWNT/biopolymer BPs was examined using SEM imaging. SEM images were initially obtained using a magnification of 10,000× (Figure 6.4) in order to investigate their broad surface features. These revealed that the surfaces of the SWNT/biopolymer BPs appeared to be generally rougher than those of the MWNT/biopolymer BPs described in the previous chapter. This effect can only be attributed to the presence of the SWNTs in the BPs, instead of MWNTs.

![Figure 6.4: SEM images of SWNT/biopolymer BPs imaged at 10,000× magnification: (A) SWNT/BSA; (B) SWNT/LSZ; (C) SWNT/CHT; (D) SWNT/GG and (E) SWNT/DNA.](image)

Figure 6.5 shows SEM images of the SWNT/biopolymer BPs obtained at 70,000× magnification, and reveals that significant variations in surface morphology between the
membranes were present, although large bundles of SWNTs were apparent on all their surfaces. Overall the SEM images in Figure 6.5 show some similarities to those of the surfaces of BPs composed of SWNTs (sourced from Unidym) and the same biopolymer dispersants, which were investigated by Boge et al.\textsuperscript{10}

The SEM images of the SWNT/LSZ and SWNT/CHT BPs illustrated in Figures 6.5B and C, both show evidence of a significant number of pore openings on their surfaces. The SWNT/GG BP (Figure 6.5 D) showed fewer pores on its surface, which instead had a greater percentage of its total surface area covered in nanotube aggregates. More dramatic differences were apparent in the SEM images of the surfaces of the SWNT BPs prepared using BSA and DNA (Figures 6.5A and D). These showed large aggregates of SWNTs were present on the surfaces of these membranes, which had only small numbers of pore openings.

![Figure 6.5](image_url)

**Figure 6.5**: SEM images of SWNT/biopolymer BPs imaged at 70,000× magnification: (A) SWNT/BSA; (B) SWNT/LSZ; (C) SWNT/CHT; (D) SWNT/GG and (E) SWNT/DNA.
6.5 Elemental analysis

Microanalytical data were obtained for the raw SWNTs used for preparing the SWNT/biopolymer BPs, as well as the BPs themselves, in order to establish whether any biopolymer molecules had been retained within the membranes. The elemental analysis results obtained are shown in Table 6.1. The raw SWNTs used to prepare the BPs contained a much higher percentage of carbon than any of the BPs, which is evidence of incorporation of other elements into the latter materials. More definitive evidence was obtained by comparing the amounts of N, S and P present in the BPs, with that in the raw SWNTs. The latter were found to have, as expected, only very minor amounts of these three elements.

Table 6.1: Microanalytical data for raw (non-dispersed) SWNTs and different SWNT/biopolymer BPs. The error in each case is ± 0.1%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Raw SWNTs</td>
<td>68.1</td>
</tr>
<tr>
<td>SWNT/BSA</td>
<td>54.3</td>
</tr>
<tr>
<td>SWNT/LSZ</td>
<td>55.5</td>
</tr>
<tr>
<td>SWNT/CHT</td>
<td>48.9</td>
</tr>
<tr>
<td>SWNT/GG</td>
<td>50.6</td>
</tr>
<tr>
<td>SWNT/DNA</td>
<td>48.1</td>
</tr>
</tbody>
</table>

In contrast, SWNT BPs prepared using BSA, CHT, LSZ or DNA contained significant amounts of N, providing support for a significant degree of retention of the above biopolymers in these membranes. Further evidence was provided by the observation that the SWNT/DNA BP consisted of 3.1% P, while the amounts of S present in the
SWNT/BSA and SWNT/LSZ BPs were also much greater than the amount present in the raw SWNTs.

Gellan gum was the only dispersant used to prepare a SWNT/biopolymer BP which does not contain N, S or P. Therefore it was not possible to use the presence of elevated levels of one or more of these elements as evidence that GG had been retained to a significant extent in the SWNT/GG BPs. The most important evidence supporting incorporation of the biopolymer was therefore the much lower amount of C present in the SWNT/GG BP compared to the SWNT starting material.

The percentages of N, S and P within the SWNT/biopolymer BPs are comparable to those of these elements in BPs prepared using either MWNTs or SWNTs, and low molecular mass dispersants.\textsuperscript{1,2} Since these elements are not present in significant amounts in either the raw SWNTs used to prepare the BPs described in this chapter, or the solvent, the results presented in Table 6.1 provide support for the retention of biopolymer molecules within the BPs.

6.6 Mechanical properties of SWNT/biopolymer BPs

Investigations of the mechanical properties of the SWNT/biopolymer BPs were performed using the tensile test method outlined in section 3.3.6. Figure 6.6 shows representative stress-strain curves which reflect the mechanical properties of the SWNT BPs. For all SWNT BPs fractures were observed at strains of approximately 1 – 6%. The tensile strength, ductility, Young’s modulus and toughness of the
SWNT/biopolymer BPs prepared as a part of the current study were derived from the stress-strain curve, and are summarised in Table 6.2.

Figure 6.6: Representative tensile stress-strain curves for different SWNT BPs. The initial concentration of SWNTs in dispersions used to prepare the BPs was 0.1% (w/v).

The mechanical properties presented in Table 6.2 are comparable to those of the MWNT/biopolymers BPs investigated in previous chapter, as well as with those of SWNT/biopolymer BPs reported previously by Boge et al.\textsuperscript{10} For example, the SWNT/CHT and SWNT/GG BPs prepared for this study exhibited tensile strengths of $81 \pm 14$ and $45 \pm 8$ MPa, respectively, which are similar to the values of $64 \pm 8$ and $43 \pm 2$ MPa reported for the corresponding MWNT BPs in the previous chapter. Furthermore, the above values for the SWNT/CHT and SWNT/GG BPs are much higher than those
obtained previously for SWNT BPs prepared using low molecular weight dispersants (tensile strengths varied between 6 to 20 nm).\textsuperscript{2} The SWNT/CHT BPs exhibited highest tensile strength ($81 \pm 14$ MPa) amongst all the BPs investigated as part of the current study, as well as those reported in previous studies involving SWNTs and either biopolymer or low molecular weight dispersants.\textsuperscript{2,11} The tensile strengths of each of the SWNT/biopolymer BPs are also comparable to those of the MWNT/biopolymer BPs discussed in the previous chapter (Table 5.2). In addition, the SWNT/biopolymer BPs showed Young’s modulus between $1.6 \pm 0.2$ and $3.3 \pm 1.1$ GPa (Table 6.2), which were greater than those exhibited by the analogous MWNT/biopolymer BPs ($0.4 \pm 0.1$ to $0.9 \pm 0.3$ GPa), prepared using the same concentration (w/v) of biopolymer dispersants. The data in Table 6.2 therefore confirmed that incorporation of the biopolymer dispersants again resulted in membranes that exhibited superior mechanical properties to that of similar materials investigated previously.\textsuperscript{1,2}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial concentration of dispersant (% w/v)</th>
<th>Tensile strength (MPa)</th>
<th>Ductility (%)</th>
<th>Young’s modulus (GPa)</th>
<th>Toughness (J g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>1.0</td>
<td>12 ± 2</td>
<td>2.2 ± 0.3</td>
<td>1.0 ± 0.3</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td>SWNT/BSA</td>
<td>0.2</td>
<td>27 ± 4</td>
<td>2.0 ± 0.5</td>
<td>3.1 ± 0.4</td>
<td>0.26 ± 0.05</td>
</tr>
<tr>
<td>SWNT/LSZ</td>
<td>0.2</td>
<td>21 ± 3</td>
<td>1.1 ± 0.2</td>
<td>2.5 ± 0.4</td>
<td>0.10 ± 0.03</td>
</tr>
<tr>
<td>SWNT/CHT</td>
<td>0.05</td>
<td>81 ± 14</td>
<td>6.2 ± 1.0</td>
<td>3.3 ± 1.1</td>
<td>3.6 ± 1.1</td>
</tr>
<tr>
<td>SWNT/GG</td>
<td>0.05</td>
<td>45 ± 8</td>
<td>3.5 ± 0.5</td>
<td>3.1 ± 0.3</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>SWNT/DNA</td>
<td>0.05</td>
<td>13 ± 2</td>
<td>2.2 ± 0.2</td>
<td>1.6 ± 0.2</td>
<td>0.10 ± 0.04</td>
</tr>
</tbody>
</table>

Table 6.2: Physical properties of SWNT BPs. All initial dispersions used to prepare BPs contained 0.1% (w/v) SWNTs. Values shown are the average of at least 3 samples, with the errors reported determined from the standard deviation obtained from all measurements.
6.7 Electrical conductivity of SWNT/biopolymer BPs

The electrical conductivity of the SWNT/biopolymer BPs was investigated using the two-point probe method outlined in section 3.3.7. **Table 6.3** shows that the electrical conductivity of the SWNT/biopolymer BPs varied within the range 11 ± 2 to 75 ± 6 S cm\(^{-1}\), while the SWNT/Trix BPs prepared using SWNTs from the same supplier exhibited an electrical conductivity of 46 ± 3 S cm\(^{-1}\). The latter value is lower than that of 85 ± 2 S cm\(^{-1}\) reported earlier for SWNT/Trix BPs which were prepared using SWNTs obtained from Unidym instead of Nanointegris.\(^{2,10}\) In contrast, the conductivities obtained for the SWNT/CHT and SWNT/GG BPs prepared as part of the current project (75 ± 6 and 68 ± 4 S cm\(^{-1}\), respectively), were much higher compared to values reported for these materials prepared previously using different SWNTs (46.5 ± 2.6 and 3.9 ± 0.4 S cm\(^{-1}\), respectively).\(^{11}\) The higher electrical conductivity of SWNT/CHT and SWNT/GG BPs may be due to the use of much lower concentrations of biopolymer dispersants (only 0.05% (w/v)) during their preparation compared to 1.0% (w/v) for SWNT/Trix. It would therefore be expected that higher amounts of Trix dispersant molecules would have been incorporated into SWNT/Trix BPs, than biopolymer dispersants were into the corresponding SWNT/biopolymer BPs. The presence of higher levels of Trix may have resulted in more effective coating of the outside of the SWNTs, thereby creating a tunnelling barrier at CNT junctions and decreasing the conductivity of SWNT/Trix relative to the biopolymer BPs.
Table 6.3: Electrical conductivities of SWNT BPs determined using the two-point probe method. All initial dispersions used to prepare the BPs contained 0.1% (w/v) SWNTs.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Initial concentration of dispersant (% w/v)</th>
<th>Electrical conductivity measured in this study (S cm(^{-1}))</th>
<th>Electrical conductivity reported in the literature (S cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>1.0</td>
<td>46 ± 3</td>
<td>85 ± 2(^{a})</td>
</tr>
<tr>
<td>SWNT/BSA</td>
<td>0.2</td>
<td>11 ± 2</td>
<td>12 ± 3(^{b})</td>
</tr>
<tr>
<td>SWNT/LSZ</td>
<td>0.2</td>
<td>18 ± 2</td>
<td>52 ± 3(^{b})</td>
</tr>
<tr>
<td>SWNT/CHT</td>
<td>0.05</td>
<td>75 ± 6</td>
<td>46 ± 3(^{b})</td>
</tr>
<tr>
<td>SWNT/GG</td>
<td>0.05</td>
<td>68 ± 4</td>
<td>4 ± 1(^{b})</td>
</tr>
<tr>
<td>SWNT/DNA</td>
<td>0.05</td>
<td>26 ± 2</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^{a}\) From reference 11. \(^{b}\) Data obtained from reference 2.

Table 6.3 shows that BPs prepared from dispersions containing 0.05% (w/v) biopolymer dispersants (i.e. SWNT/CHT, SWNT/GG and SWNT/DNA BPs) exhibited greater electrical conductivities than the BPs obtained from dispersions containing 0.2% (w/v) biopolymer (SWNT/BSA and SWNT/LSZ). Similar trends were also observed for MWNT/CHT BPs, with the conductivity of the MWNT/CHT BPs prepared from a dispersion containing 0.05% (w/v) CHT greater than that of the other MWNT BPs prepared from dispersions containing 0.2% (w/v) dispersant (Table 5.6).

### 6.8 Thermal stability of SWNT/biopolymer BPs

The thermal stability of the SWNT/biopolymer BPs was investigated using TGA by applying temperatures between 25 – 550 °C to all samples. Figure 6.7 shows the TGA data obtained for the SWNT starting material and each of the SWNT/biopolymer BPs. All BP samples showed a small mass loss (< 12%) when heated to 100 °C, which was not exhibited by the raw SWNTs. This decrease in mass can be attributed to the evaporation of residual water molecules trapped within the BPs. No significant weight
losses were then observed between 100 °C and 250 °C, revealing that the SWNT/biopolymer BPs were thermally stable up to 250 °C. At higher temperatures all BPs showed evidence of significant mass loss attributable to the decomposition of the biopolymers, and then the SWNTs themselves.\textsuperscript{12}

\textbf{Figure 6.7}: TGA traces for SWNT starting material and SWNT/biopolymer BPs: (A) raw SWNTs; (B) SWNT/BSA; (C) SWNT/LSZ; (D) SWNT/CHT; (E) SWNT/GG and (F) SWNT/DNA.
6.9 Wettability of SWNT/biopolymer BPs

A well-known method for determining the wettability of membrane surfaces is contact angle measurement. The results of contact angle measurements performed on the different SWNT BPs are shown in Table 6.4. The water contact angles for the SWNT/biopolymer BPs varied between 63 ± 7° and 88 ± 3°, indicating that their surfaces were in general, hydrophobic in nature. Incorporation of the carbohydrate dispersants CHT and GG, afforded BPs that had contact angles approximately 20° lower than those containing protein molecules or DNA. This indicates that the former BPs were significantly more hydrophilic, and therefore potentially more suitable for use in aqueous filtration systems. The contact angles shown in Table 6.4 for the SWNT/biopolymer BPs prepared as part of the current study, are comparable to those reported previously for the same materials, prepared using SWNTs provided by a different supplier (Unidym). The contact angles for the latter SWNT/biopolymer BPs varied between 67 ± 6° and 76 ± 4°.10

Table 6.4: Contact angles of 2 μL water droplets on SWNT/biopolymer BPs.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Initial concentration of dispersant (% w/v)</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/BSA</td>
<td>0.2</td>
<td>83 ± 3</td>
</tr>
<tr>
<td>SWNT/LSZ</td>
<td>0.2</td>
<td>88 ± 3</td>
</tr>
<tr>
<td>SWNT/CHT</td>
<td>0.05</td>
<td>65 ± 8</td>
</tr>
<tr>
<td>SWNT/GG</td>
<td>0.05</td>
<td>63 ± 7</td>
</tr>
<tr>
<td>SWNT/DNA</td>
<td>0.05</td>
<td>86 ± 5</td>
</tr>
</tbody>
</table>
6.10 Surface pore and internal pore structure of SWNT/biopolymer BPs

The average surface pore diameters ($D_{SEM}$) of the SWNT/biopolymer BPs were obtained by analysis of SEM images, and are summarised in Table 6.5. The average surface pore diameters varied between $10 \pm 4$ and $22 \pm 7$ nm, while the $D_{SEM}$ for a SWNT/Trix BP prepared using the same SWNTs was $21 \pm 8$ nm. The latter value is comparable to that obtained previously for a SWNT/Trix BP prepared using SWNTs obtained from Unidym, which was $23 \pm 7$ nm. In contrast, the $D_{SEM}$ values of the SWNT/biopolymer BPs reported here are smaller than those reported in chapter 5 for the analogues set of MWNT/biopolymer BPs, which were between $33 \pm 9$ and $54 \pm 12$ nm. The variation in $D_{SEM}$ values between BPs containing the same biopolymers, and either SWNTs or MWNTs, is attributable to the larger diameters of the MWNTs, which results in less efficient packing of nanotube bundles, leading to larger membrane pores.

Table 6.5: Average surface pore diameters ($D_{SEM}$) of SWNT BPs determined by analysis of SEM images. Pore diameters were determined by using image analysis software (Image Pro Plus) and SEM micrographs taken at 70K magnification.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Average surface pore diameter $D_{SEM}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>$21 \pm 8$</td>
</tr>
<tr>
<td>SWNT/BSA</td>
<td>$13 \pm 4$</td>
</tr>
<tr>
<td>SWNT/LSZ</td>
<td>$22 \pm 7$</td>
</tr>
<tr>
<td>SWNT/CHT</td>
<td>$17 \pm 5$</td>
</tr>
<tr>
<td>SWNT/GG</td>
<td>$19 \pm 7$</td>
</tr>
<tr>
<td>SWNT/DNA</td>
<td>$10 \pm 4$</td>
</tr>
</tbody>
</table>

In order to characterise the internal pore structure of the SWNT/biopolymer BPs, nitrogen adsorption/desorption measurements were performed. Prior to analysis, the BPs were degassed under vacuum at 120 °C to remove any loosely adsorbed dispersant
molecules, as TGA confirmed that each of the membranes was stable at this temperature. Analysis of the results obtained from nitrogen adsorption/desorption measurements revealed that SWNT BPs containing LSZ, CHT and GG exhibited general Type IV isotherms, with hysteresis at higher relative pressures. Representative isotherms obtained for SWNT/CHT and SWNT/LSZ BPs are shown in **Figure 6.8**. The observation of hysteresis in the isotherms for the above materials is an indication that the rate with which nitrogen filled the pores of the BPs was different to the rate with which gas molecules were subsequently lost. In contrast with the above results, no reliable N$_2$ adsorption/desorption isotherms could be obtained for the cases of SWNT/BSA and SWNT/DNA BPs impeding further analyses of their specific surface area and internal pore diameters. The results obtained with other SWNT/biopolymer BPs confirmed the presence of a large proportion of mesopores (6 – 8 nm) and micropores (1 – 2 nm) in these materials. These values are comparable to those determined previously for BPs prepared using SWNTs sourced from Unidym, and macrocyclic ligands or other low molecular weight dispersants.

![Figure 6.8: Nitrogen adsorption (blue line) and desorption (red line) isotherms for BPs: (A) SWNT/CHT and (B) SWNT/LSZ.](image-url)
Each of the nitrogen adsorption/desorption isotherms was analysed using the BJH and HK methods to calculate the distribution of small pores (< 2 nm) and larger pores (> 2 nm), respectively, within the SWNT/biopolymer BPs. Combining the two sets of results yielded pore size distribution curves such as those shown for SWNT/CHT and SWNT/LSZ BPs in Figure 6.9. The small peaks at 0.9 nm in Figure 6.9A and at 0.8 nm in Figure 6.9B are attributed to the interstitial pores present in the SWNT/CHT and SWNT/LSZ BPs, respectively. A broad distribution of peaks corresponding to internal pores with diameters between 1 and 10 nm was also found to be present for the SWNT/CHT BP, while for the SWNT/LSZ BP similar pores with diameters varying between 2 and 6 nm were also detected. Both of these larger sets of membrane pores most likely correspond to those pores whose openings were observable via SEM.

![Graphs](image_url)

**Figure 6.9:** Pore size distribution of BPs derived using data obtained from nitrogen adsorption/desorption isotherms, by applying the HK method (red line) and BJH method (blue line): SWNT/CHT and (B) SWNT/LSZ.

Numerical integration of pore size distribution curves was performed in order to derive the interbundle pore volumes for the BPs. These data are presented in Table 6.6 and show that the sizes of the internal membrane pores varied widely between SWNT/biopolymer BPs. The interbundle pore volumes for the SWNT/LSZ and...
SWNT/CHT BPs were determined to be 67 ± 3 and 73 ± 4 %, respectively. These values are comparable to those obtained for the analogues BPs prepared using MWNTs and the same biopolymers (82 ± 4 and 83 ± 5% for MWNT/LSZ and MWNT/CHT BPs, respectively). In addition, the interbundle pore volumes for the SWNT/LSZ and SWNT/CHT BPs were similar to those of other SWNT BPs investigated previously. In contrast, the interbundle pore volume for the SWNT/GG BP prepared as part of the current work (26 ± 2%) was significantly smaller than that of the other two SWNT/biopolymer BPs referred to above. This appears to be a result of the much larger average nanotube bundle diameter for the SWNT/GG BP, of 177.7 ± 50 nm.

For example, SWNT/C6S and SWNT/PTS BPs have been reported to have interbundle pore volumes of 76 ± 5% and 78 ± 5%, respectively. Furthermore the interbundle pore volumes of SWNT/Trix BPs (88 ± 3%) prepared as part of the current study are comparable to those obtained for the analogous membranes prepared using SWNTs or MWNTs. In contrast, the interbundle pore volume for the SWNT/GG BP prepared as part of the current work (26 ± 2%) was significantly smaller than that of the other two SWNT/biopolymer BPs referred to above. This appears to be a result of the much larger average nanotube bundle diameter for the SWNT/GG BP, of 177.7 ± 50 nm.

Table 6.6: Surface and internal pore characteristics of raw SWNTs and SWNT BPs. All initial dispersions used for preparing BPs contained 0.1% (w/v) SWNTs. These initial dispersions also contained one of the following dispersants: Trix 1.0% (w/v); CHT, GG or DNA 0.05% (w/v); LSZ or BSA 0.2% (w/v).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area $A_{BET}$ (m²g⁻¹)</th>
<th>Average internal pore diameter $d_{BET}$ (nm)</th>
<th>Average nanotube bundle diameter $D_{bun}$ (nm)</th>
<th>Interbundle Pore volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw SWNTs</td>
<td>395 ± 5</td>
<td>14 ± 2.0</td>
<td>6.7 ± 0.3</td>
<td>97 ± 5</td>
</tr>
<tr>
<td>SWNT/Trix</td>
<td>33 ± 1</td>
<td>8 ± 1</td>
<td>80.8 ± 2</td>
<td>88 ± 3</td>
</tr>
<tr>
<td>SWNT/LSZ</td>
<td>40 ± 2</td>
<td>6 ± 0.5</td>
<td>67.9 ± 1.5</td>
<td>67 ± 3</td>
</tr>
<tr>
<td>SWNT/CHT</td>
<td>48 ± 3</td>
<td>7 ± 0.8</td>
<td>55.2 ± 3.5</td>
<td>73 ± 4</td>
</tr>
<tr>
<td>SWNT/GG</td>
<td>15 ± 1</td>
<td>2 ± 0.2</td>
<td>177.7 ± 50</td>
<td>26 ± 2</td>
</tr>
<tr>
<td>SWNT/BSA⁹</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SWNT/DNA⁹</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
</tbody>
</table>

⁹ No values were obtained.
The specific surface areas of the SWNT/biopolymer and SWNT/Trix BPs were calculated by the BET method, and found to vary between $1 \pm 0.1$ and $48 \pm 3 \, \text{m}^2 \, \text{g}^{-1}$. These values are lower than those derived for previously studied membranes prepared using SWNTs from a different supplier (Unidym) and low molecular weight ligands such as β-CD, C6S and TSP, which were reported to have surface areas of $690 \pm 4$, $580 \pm 3$ and $360 \pm 4 \, \text{m}^2 \, \text{g}^{-1}$, respectively.\(^2\) In addition, SWNT BPs prepared using Trix surfactant exhibited a surface area of $33 \, \text{m}^2 \, \text{g}^{-1}$, which is much lower compared with the corresponding membrane investigated previously.\(^2\) However, the specific surface areas of the SWNT/LSZ and SWNT/CHT BPs ($40 \pm 2$ and $48 \pm 3 \, \text{m}^2 \, \text{g}^{-1}$, respectively) prepared as part of the current project are comparable to that of SWNT/PTS BPs investigated previously, which were composed of SWNTs obtained from Unidym, and displayed a surface area of $30 \pm 1 \, \text{m}^2 \, \text{g}^{-1}$.\(^2\)

6.11 Water permeability of SWNT/biopolymer BPs

The water permeability of the SWNT/biopolymer BPs was measured using the same dead-end filtration cell setup used previously in experiments involving MWNT BPs prepared using either biopolymers or low molecular weight dispersants. Representative water permeability plots obtained for the SWNT/biopolymer BPs are shown in Figure 6.10.
Figure 6.10: Representative water permeability plots for selected SWNT/biopolymer BPs: (A) SWNT/CHT; (B) SWNT/LSZ; (C) SWNT/BSA and (D) SWNT/GG.

All the SWNT/biopolymer BPs investigated in the current study were found to become permeable towards water at pressures greater than 1 bar, which is a higher pressure than what was required to initiate water transport with either the MWNT/biopolymer BPs or SWNT BPs containing low molecular weight, macrocyclic ligand dispersants, discussed earlier in this thesis.\(^2\) The pressure required to initiate transport of water across the SWNT/biopolymer BPs varied between 1.0 ± 0.2 and 2.0 ± 0.5 bar in response to changes in the identity of the incorporated dispersant. The highest pressure required to initiate transport of water across a SWNT/biopolymer BP was observed for SWNT/BSA. This observation, together with the smaller volumes of water that eventually passed across this membrane with time compared to any other BP, provides
strong support that its permeability towards water was much lower compared to that of the other SWNT membranes investigated as part of this project.

The permeate fluxes \( (J) \) for the SWNT/biopolymer BPs were derived from the slopes of the plots of volume of water as a function of time shown in Figure 6.10. When the permeate fluxes of each membrane were then plotted as a function of applied pressure (Figure 6.11), the resulting graphs showed linear relationships. The slopes of these plots (Figure 6.11) were then used to calculate the pressure-independent membrane flux \( (j) \) or permeability of each BP by applying Equation 1.3. The values of membrane flux determined for each of the SWNT BPs, along with their membrane rupture pressures are presented in Table 6.7. The five SWNT/biopolymer BPs investigated as part of the current study varied in thickness between 26 ± 2 and 56 ± 6 µm. These values are comparable to those of membranes previously prepared using SWNTs obtained from Unidym, and low molecular weight macrocyclic ligand dispersants.² The SWNT/CHT BPs were found to exhibit the highest degree of water permeability \( (6 ± 1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}) \) of the SWNT/biopolymer BPs investigated here, as well as the smallest thickness \( (26 ± 2 \text{ µm}) \). In contrast, the SWNT/BSA and SWNT/DNA BPs exhibited the lowest water permeabilities, perhaps in part due to their greater thicknesses, of 55 ± 4 and 56 ± 6 µm, respectively.
Figure 6.11: Effect of applied pressure on the permeate flux \( (J) \) of SWNT BPs containing different dispersants: (A) BPs containing BSA, LSZ, GG, DNA and Trix; and (B) SWNT/CHT. All dispersions contained SWNTs with a concentration of 0.1\% (w/v).

Table 6.7: Membrane permeability \( (f) \), water transport initiation pressure, rupture pressure and thickness of SWNT BPs.\(^*\) All initial dispersions used for preparing BPs contained 0.1\% (w/v) SWNTs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial concentration of dispersant (% w/v)</th>
<th>Membrane permeability ( (f) ) (L m(^{-2}) h(^{-1}) bar(^{-1}))</th>
<th>Liquid entry pressure (bar)</th>
<th>Rupture pressure (bar)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>1.0</td>
<td>1.1 ± 0.2</td>
<td>0.8 ± 0.1</td>
<td>1.6 ± 0.2</td>
<td>28 ± 3</td>
</tr>
<tr>
<td>SWNT/BSA</td>
<td>0.2</td>
<td>0.9 ± 0.2</td>
<td>2.0 ± 0.5</td>
<td>4.0 ± 0.3</td>
<td>55 ± 4</td>
</tr>
<tr>
<td>SWNT/LSZ</td>
<td>0.2</td>
<td>1.8 ± 0.3</td>
<td>1.0 ± 0.2</td>
<td>3.6 ± 0.5</td>
<td>50 ± 4</td>
</tr>
<tr>
<td>SWNT/CHT</td>
<td>0.05</td>
<td>6.0 ± 1.0</td>
<td>1.5 ± 0.5</td>
<td>4.4 ± 0.5</td>
<td>26 ± 2</td>
</tr>
<tr>
<td>SWNT/GG</td>
<td>0.05</td>
<td>1.5 ± 0.2</td>
<td>1.4 ± 0.3</td>
<td>3.2 ± 0.3</td>
<td>37 ± 2</td>
</tr>
<tr>
<td>SWNT/DNA</td>
<td>0.05</td>
<td>1.0 ± 0.2</td>
<td>1.8 ± 0.3</td>
<td>3.2 ± 0.2</td>
<td>56 ± 6</td>
</tr>
</tbody>
</table>

\(^*\) Values shown are the average and standard deviation from measurements made on at least three samples.

Of all the SWNT BPs examined, only SWNT/Trix BP exhibited a liquid entry pressure of less than 1 bar. These results suggest that the SWNT/biopolymer BPs prepared as part of the current work may in general be less permeable towards water than the other classes of BPs previously examined in this thesis. This was indeed found to be the case, with the water permeabilities of the SWNT/biopolymer BPs and also SWNT/Trix falling within the range 0.9 to 6 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). These values are much lower compared to permeabilities of 160, 800 and 2400 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) for SWNT/β-CD, SWNT/C6S and
SWNT/PTS, respectively, all of which contained low molecular weight dispersants. In addition, the SWNT/Trix BPs prepared as a part of the current study exhibited a water permeability of $1.1 \pm 0.2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, whereas in a previous investigation where SWNT/Trix BPs were prepared using SWNTs obtained from Unidym, a permeability of $83 \pm 5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ was reported. However, the permeabilities exhibited by SWNT/biopolymer BPs are still comparable with the water permeability values ($1.4 – 12 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) of commercial NF membranes (Table 1.1).

The above results highlight that changing the identity of dispersant molecules incorporated into the BPs in the current study had little effect on membrane permeability, and that the SWNT BPs were generally far less permeable than what has been reported for apparently identical SWNT/biopolymer BPs prepared previously. The most likely explanation for both observations is differences in the SWNTs used to prepare the BPs. For the current investigation, the SWNTs were purchased from NanoIntegris Technologies (70+% C purity; batch no. HR27004), whereas for the previous study by Sweetman et al., SWNTs were obtained from Unidym™ (85+% C purity). The results of SEM studies suggested that the use of the former CNTs appeared to have resulted in the production of denser BPs than those prepared previously. This may have contributed to the much lower water permeabilities exhibited by the SWNT/biopolymer BPs prepared as part of this thesis. In addition, the high contact angles exhibited by the SWNT/biopolymer BPs ($63 \pm 7 – 88 \pm 3^\circ$) suggests another reason for their low water permeability.
Whilst the lack of permeability exhibited by the SWNT/biopolymer BPs in the current study was an impediment to further studies into their solute rejection properties, they did exhibit significantly higher rupture pressures than SWNT membranes containing low molecular weight macrocyclic ligands, reported previously. All SWNT/biopolymer BPs in the current study exhibited rupture pressures of more than 3.0 bar, with the SWNT/CHT and SWNT/BSA BPs proving to be especially robust (rupture pressures of 4.4 ± 0.5 and 4.0 ± 0.3 bar, respectively). These values are comparable to those of MWNT BPs prepared using same biopolymer dispersant molecules (Table 5.11). In contrast, the rupture pressures of SWNT BPs prepared using low molecular weight macrocyclic ligands, such as C6S, TSP and PTS, was reported to be less than 1.4 bar. In addition, MWNTs BPs prepared from the above low molecular weight dispersants were also been shown to be susceptible to failure in water transport experiments, with membrane rupture pressures of less than 1.4 bar. These observations are consistent with the improved mechanical properties displayed by the biopolymer-containing SWNT membranes (Table 6.2).

6.12 Conclusions

This chapter reported the successful preparation of free-standing SWNT BPs from aqueous dispersions containing SWNTs and one of several biopolymer dispersant molecules. The elemental composition of the SWNT/biopolymer BPs was investigated by microanalysis, which provided evidence that the dispersant molecules were retained within the membranes. The incorporation of these biopolymer molecules was shown to favourably influence the mechanical properties of the SWNT BPs and their wettability, as reflected in the results of contact angle analysis.
The surface and internal morphology of all SWNT/biopolymer BPs was investigated by SEM and through analysis of nitrogen adsorption/desorption isotherms. The surface pore diameters of the SWNT/biopolymer BPs varied between 10 ± 4 and 22 ± 7 nm, which are similar to those obtained previously for SWNT BPs prepared using low molecular weight dispersants and SWNTs from a different supplier (Unidym). Of the BPs examined, SWNT/CHT was shown to possess the largest surface pores compared to the other SWNT BPs investigated here. In addition, analysis of nitrogen adsorption/desorption isotherms derived using different SWNT/biopolymer BPs revealed strong similarities between their internal pore structures. For example, the average internal pore diameter of each SWNT/biopolymer BP ranged between 1 ± 0.1 and 7 ± 0.8 nm. The interbundle pore volumes determined for the SWNT/biopolymer BPs varied between 26 ± 2 and 73 ± 4%, and are smaller than what was measured previously for the corresponding SWNT membranes prepared using low molecular weight dispersants (range 76 ± 5 to 93 ± 6%). The specific surface areas of all SWNT/biopolymer BPs reported here varied from 1 ± 0.1 to 48 ± 3 m² g⁻¹, showing that they had a low surface area compared to other SWNT BPs prepared using low molecular weight dispersants and SWNTs sourced from Unidym instead of Nanointegris.

The results presented here further demonstrate that incorporation of biopolymer dispersants strengthens BPs, thereby making them potentially viable for water filtration and solute separation applications. Unfortunately water permeability experiments performed using the SWNT/biopolymer BPs showed they did not allow the passage of water molecules as readily as SWNT BPs containing low molecular mass dispersants. In
addition, the permeabilities determined for these materials were lower than those reported previously for the same group of SWNT/biopolymer BPs, prepared using CNTs from a different supplier. This was a surprising result, which at this stage appears may be due to the change in source of the SWNTs. It will therefore be of interest to further explore this issue, by preparing a range of BPs using the same dispersant molecules, and SWNTs from various suppliers and with a range of purities and physical properties. Once the reasons for the lack of permeability exhibited by the SWNT/biopolymer BPs in the current study are understood, it should be possible to prepare additional BPs of this class suitable for further exploration of their TrOC and salt rejection capabilities.
6.13 References


Chapter 7

Conclusions and Future Directions

This chapter summarises findings and results obtained from this project. In addition, a brief discussion of future work to further develop and explore key properties of BP membranes is included.
7.1 Conclusions

The overall goal of this study was to develop novel carbon nanotube BPs which could be used for water purification applications. Chapters 4 – 6 described the synthesis and characterisation of BPs prepared using dispersions containing MWNTs, substituted MWNTs or SWNTs, as well as a variety of dispersing agents including the surfactant Trix, various macrocyclic ligands, or biopolymers. While biopolymer molecules and Trix have been shown previously to form stable dispersions of SWNTs, this was the first occasion that macrocyclic ligands have been successfully used to form dispersions of MWNTs, which could then be used to prepare BPs. This was a promising result, as it offered a convenient route for preparing BPs that retained the macrocyclic ligands, and with them a potentially wider range of selective molecular recognition characteristics than what is afforded by BPs prepared with the assistance of conventional surfactant dispersants.

Uniform, free-standing BPs were successfully produced from each of the above aqueous dispersions, and were shown by the results of elemental analysis measurements to incorporate dispersant molecules within their structures. Tensile test measurements performed on the BPs showed that those prepared from dispersions containing MWNTs and biopolymers were mechanically more robust than those made from dispersions containing the same type of CNTs and low molecular weight dispersant molecules. Similar results have been obtained previously in studies involving BPs prepared from SWNTs, and either small molecules or biopolymers, and were attributed to the greater effectiveness with which the larger biopolymer molecules can adsorb onto the surfaces of the nanotubes and thereby bind them together. Obtaining the same outcome in experiments performed with MWNTs was an important finding, as the ultimate success
of a new class of materials for filtration applications rests just as much upon their ability to withstand moderate to high pressures, as it does upon their permeability characteristics and other properties.

Contact angle measurements revealed that all MWNT BPs prepared using biopolymers or low molecular weight dispersants possessed hydrophilic surfaces, with contact angles ranging from 28 ± 2 to 57 ± 5°. In contrast, SWNT/biopolymer BPs possessed less hydrophilic surfaces (63 ± 7 to 88 ± 3°). The electrical conductivities of the MWNT BPs prepared as a part of this project varied between 24 ± 16 and 58 ± 11 S cm⁻¹, while for the SWNT/biopolymer BPs the range was 11 ± 2 to 75 ± 6 S cm⁻¹. SWNT/GG BPs exhibited one of the highest electrical conductivities of all the materials investigated (68 ± 4 S cm⁻¹). This was an unexpected result, as previous studies of SWNT/biopolymer BPs had shown that there was a general trend of decreasing electrical conductivity, with increasing molecular weight of the dispersant used. As GG being was one of the largest biopolymers examined in this previous work (mol. wt. = 250 000 Da), SWNT/GG BPs exhibited the lowest conductivity (3.9 S cm⁻¹).¹² This was thought to be a result of the greater ability of large biopolymer dispersants to coat individual nanotubes or nanotube bundles, thereby creating a barrier to electron movement. These observations suggest that changes to the type of SWNTs employed to fabricate BPs can have a significant effect on the properties of the final material. Notwithstanding this, the electrical conductivity exhibited by the BPs prepared throughout this project may provide opportunities for modifying their solvent and/or solute permeability characteristics, through the application of uniform or pulsed electrical potentials. This is discussed further in section 7.2.
Analysis of the nitrogen adsorption/desorption binding isotherms for MWNT BPs prepared using Trix or one of a group of low molecular weight macrocyclic ligands, revealed strong similarities between their internal pore structures. For example, the internal pore diameters and nanotube bundle diameters both fell within relatively narrow ranges (20 – 26 nm and 7 – 15 nm, respectively). Furthermore, the interbundle pore volumes present in these materials were found to vary between only 87 – 96%. The lack of variation between the internal pore structures of this particular class of BPs correlated with the very similar levels of permeability towards water exhibited by these membranes (13 ± 2 to 24 ± 6 L m⁻² h⁻¹ bar⁻¹). These measurements were performed using a dead-end filtration apparatus, and revealed that the permeability of this group of BPs were much less than that of a related group of membranes which had been prepared from dispersions containing SWNTs and the same low molecular weight dispersant molecules.³,⁴ The permeability of the latter varied from 83 ± 5 to 2400 ± 1300 L m⁻² h⁻¹ bar⁻¹, suggesting that changing the type of CNTs used to prepare BPs, but keeping the dispersant molecules constant, can sometimes result in dramatic changes in water transport rates.³ Analysis of nitrogen adsorption/desorption isotherms for the SWNT BPs reported in the literature, showed that most contained much smaller bundles of nanotubes (diameters 3.4 ± 0.1 to 7.4 ± 0.1 nm) and smaller internal pores (diameters 2.0 ± 0.2 to 4.0 ± 0.4 nm) than the analogous MWNT BPs reported here for the first time, however the interbundle pore volumes of the former materials were still > 80%. Interestingly, the most permeable of these literature membranes proved to be SWNT/PTS, which had much larger nanotube bundles (diameter 90 ± 3 nm), resulting in considerably larger pores (average internal diameter 27 ± 3 nm), and a lower interbundle pore volume of 78 ± 5%.
The internal nanotube bundle diameters and internal pore diameters of the MWNT/biopolymer BPs reported here were within relatively narrow ranges. On average, however, the nanotube bundles of this class of membranes were slightly larger (13.3 ± 0.1 to 19.6 ± 0.2 nm) than those present in the BPs containing MWNTs and low molecular mass dispersants. This may account for why the internal pores of the MWNT/biopolymer BPs were perhaps slightly smaller (diameters ranged from 16 ± 1 to 23 ± 3 nm) than those present in the latter membranes, and their interbundle pore volumes were also perhaps on average smaller (all < 90%). Overall, however, the internal pore structures of both classes of MWNT BPs was similar. It was therefore not surprising that the permeabilities exhibited by the membranes containing biopolymers (10 – 22 L m⁻² h⁻¹ bar⁻¹) were also similar, and that relatively low applied pressures (< 1 bar) could be used to initiate transport of water across both types of membranes. These results also demonstrated that incorporation of biopolymers into MWNT BPs proved advantageous in terms of strengthening the membranes, but in general had only minor effects on their permeability towards water.

The permeability towards water of the SWNT/biopolymer BPs proved to be much lower (1 – 6 L m⁻² h⁻¹ bar⁻¹) than for either of the two classes of MWNT membranes examined as part of this project. Furthermore the former materials also required much higher applied pressures (1 – 2 bar) in order to initiate water transport. These results were also surprising, in view of the very high degree of water permeability reported previously for some BPs containing SWNTs, such as SWNT/PTS (2400 ± 1300 L m⁻² h⁻¹ bar⁻¹).³ It was also noteworthy that the SWNT/Trix BPs prepared during the current project exhibited a water permeability of 1.1 ± 0.2 L m⁻² h⁻¹ bar⁻¹, whereas in a previous
investigation involving this type of membrane, but prepared using SWNTs obtained from different supplier, a much higher value of $83 \pm 5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ was reported.\textsuperscript{3} This is a very large difference in permeability between what was initially assumed to be membranes with very similar surface and internal structures, which must be due to the change in the source of SWNTs used to prepare the initial dispersions for preparing the BPs.

Whilst the lack of significant water permeability exhibited by the SWNT/biopolymer BPs was disappointing, it is perhaps consistent with their very different internal pore structure and surface morphology, in contrast to either class of MWNT membranes. The internal pore diameters of the SWNT/biopolymer BPs varied between only 1 and 7 nm, most likely as a consequence of the very large nanotube bundles (diameters 55 – 4848 nm) present. These large clumps of nanotubes resulted in interbundle pore volumes ranging from 26 – 73\% for SWNT/GG, SWNT/LSZ and SWNT/CHT BPs. In addition, it did not prove possible to measure the interbundle pore volumes of the SWNT/BSA and SWNT/DNA BPs, owing to their extremely low surface areas and insignificant adsorption of nitrogen during the porosimetry analysis. Another major point of contrast between both classes of MWNT BPs on the one hand, and the SWNT/biopolymer BPs on the other, was that the surface areas of the former membranes were found to vary between $136 \pm 1$ and $380 \pm 2 \text{ m}^2 \text{ g}^{-1}$, while each of the five SWNT/biopolymer BPs studied had surface areas less than $48 \text{ m}^2 \text{ g}^{-1}$.

Permeability experiments performed using solutions containing only BPA, or a mixture of twelve TrOCs, demonstrated the ability of most of the MWNT BPs to reject a variety
of organic compounds. In the case of MWNT/Trix, MWNT–NH$_2$/Trix and MWNT–COOH/Trix BPs, the extent of BPA removal was more than 90%, when solutions containing only this solute were examined. Further evidence supporting the ability of the BPs to act as non-selective barriers to solutes was provided by experiments involving MWNT/Trix BPs, which showed more than 80% removal efficiency for 11 out of the 12 TrOCs present in a mixture.

The permeability of MWNT/biopolymer BPs towards dissolved TrOCs and inorganic salts was also investigated through filtration experiments, with MWNT/CHT BPs showing TrOC removal efficiencies > 95% for 9 of the mixture of 12 TrOCs (each at a concentration of 50 µg L$^{-1}$), and 30 – 55% and 40 – 70% for NaCl and MgSO$_4$, from solutions containing 2 g L$^{-1}$ NaCl and MgSO$_4$. The latter results further showcase the potential of BPs for nanofiltration and desalination applications. Some of the BPs examined showed a degree of selectivity in their permeability towards the mixture of 12 TrOCs. For example, MWNT/LSZ BPs showed relatively low solute rejection (less than 40%) towards some solutes (e.g. trimethoprim, carbamazepine and atrazine) but high rejection (over 95%) towards others (e.g. triclosan and bezafibrate). These results suggest that the presence of the dispersant molecules could be used to tailor the overall permeability characteristics of a BP, justifying further exploration of this class of materials.
7.2 Future directions

The results presented in this study have further demonstrated the potential of BPs as selectively permeable membrane filters. At the same time a number of questions arose during the conduct of this research, which provides scope for further fundamental and applied investigations into these materials. For example, whilst some MWNT BPs exhibited a high degree of performance with respect to blanket removal of all TrOCs present in an aqueous solution, few of the materials displayed a high degree of selectivity in their permeability characteristics, by showing a low degree of rejection towards one or two specific analytes at the same time as they prevented the passage of all others. This may be the result of relatively low extents of dispersant incorporation into the BPs and/or slow leaching of the dispersant molecules when the membrane is exposed to water. New methods are therefore required to ensure there is a higher degree of retention of the dispersant molecules in the first place, and that they are retained upon usage. One method of achieving these twin goals would be to prepare CNT membranes from dispersions of SWNTs or MWNTs that have macrocyclic ligands or other molecules covalently attached.

This thesis has also demonstrated for the first time that free standing BPs are capable of rejecting the passage of simple inorganic salts in a high pressure cross-flow NF/RO system. The potential use of these BP membranes for desalination of seawater requires further investigation including determining ways to further enhance both their strength and permeability to solvent and solutes. Among the five SWNT/biopolymer BPs investigated as a part of the current project, SWNT/CHT was shown to be the most robust (tensile strengths = 81± 14 MPa), exhibited the highest electrical conductivity
(75 ± 6 S cm⁻¹) and water permeability (6 ± 1 L m⁻² h⁻¹ bar⁻¹), and is therefore perhaps the prime candidate for further study. In view of the difference in permeability exhibited by SWNT/Trix BPs prepared for this project, and those reported previously, it will also be important to look in more detail at the effects of using CNTs from different suppliers to prepare BPs, on the physical properties and permeability characteristics of these materials.

Future work should also seek to take advantage of the electrical conductivity of BPs, by examining the effects of applying various types of electrical potentials on their solute adsorption rates and capacities. Furthermore the possibility of degrading adsorbed contaminants through electrochemical reactions mediated by the BPs should also be explored. For example, in a prior investigation it was shown that in the absence of electrochemical stimulation, that a monolayer of dye molecules adsorbed onto the surface of a PTFE-supported MWNT filter when the latter was exposed to a influent solution.⁵ In contrast, when the experiment was repeated under the same conditions, but with an electrochemical potential of 2 V applied to the membrane, more than 98% of the dye molecules were oxidised when they passed across the porous MWNT filter.⁵ In another previous study, an electrochemically active MWNT filter was shown to reduce the number of culturable bacteria and viruses in a permeate solution to 0, as well as inactivate > 75% of the sieved bacteria, and > 99.6% of the adsorbed viruses, when applied potentials of 2 and 3 V were used for 30 s.⁶ These results highlight how combining the ability to electrochemically degrade pollutant molecules, with the selective permeability and adsorption characteristics of BPs, may enable the latter to become a versatile and effective method for removing pollutants from water supplies.
The electrical conductivity inherent in BPs also offers opportunities for the development of novel strategies to overcome membrane biofouling, which continues to be one of the most intensive and critical areas of membrane research. For example, it was shown that application of small, applied electrical potentials on electrically conductive polypyrrole membrane surfaces can prevent the growth and proliferation of biofilms. In another prior investigation, electrically conductive MWNT/PA NF membranes were shown to have biofilm-preventing capabilities when an external electric potential was applied. Thus electrically conductive BPs also offer great potential for solving the biofouling challenge, thereby generating enormous economic benefits for a host of industries that employ membrane filtration processes.

7.3 Final statement

This thesis has demonstrated that free-standing CNT BPs produced from aqueous dispersions also containing low molecular weight dispersants or biopolymers offer considerable potential for a variety of separation applications, involving removal of dissolved organic or inorganic solutes. It is anticipated that further investigations will result in additional improvements to the properties of these materials, as well as how they may be best applied to the rapidly expanding range of membrane technology applications.
7.4 References


