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Synthesis, properties, water and solute permeability of MWNT buckypapers

Md. Harun-Or Rashid
University of Wollongong, mhor972@uowmail.edu.au

Son Q. T Pham
University of Wollongong, qtsp419@uowmail.edu.au

Luke J. Sweetman
University of Wollongong, lsweetma@uow.edu.au

Leighton J. Alcock
University of Wollongong, lja847@uowmail.edu.au

Anthony Wise
University of Wollongong, aw497@uowmail.edu.au

See next page for additional authors

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Abstract

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Keywords

Carbon nanotubes, buckypapers, water permeability, trace organic contaminants, bisphenol A, GeoQuest

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Authors

Md. Harun-Or Rashid, Son Q. T Pham, Luke J. Sweetman, Leighton J. Alcock, Anthony Wise, Long D. Nghiem, Gerry Triani, Marc in het Panhuis, and Stephen F. Ralph

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Synthesis, properties, water and solute permeability of MWNT buckypapers

Md. Harun-Or Rashid [a], S. Q. T. Pham [a], L. J. Sweetman [a], L. J. Alcock [a], A. Wise [a], L. D. Nghiem [b], G. Triani [c], M. in het Panhuis [a,d], S. F. Ralph [a*]

[a] Soft Materials Group, School of Chemistry, University of Wollongong, Wollongong, Australia. Email: sralph@uow.edu.au

[b] Strategic Water Infrastructure Laboratory, School of Civil, Mining and Environmental Engineering, University of Wollongong, Australia. Email: longn@uow.edu.au

[c] Institute of Materials Engineering, Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia. Email: gerry.triani@ansto.gov.au

[d] Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, AIIM Facility, University of Wollongong, Wollongong, Australia. Email: panhuis@uow.edu.au

* Author to whom correspondence should be addressed

ABSTRACT

High power tip sonication was used to prepare dispersions containing multi-walled carbon nanotubes (MWNTs), or multi-walled carbon nanotubes functionalised with carboxylic acid groups (MWNT-COOH) or amine groups (MWNT-NH_2). The dispersion of carbon nanotubes was facilitated by the presence of a surfactant (Triton X-100) or various macrocyclic ligands (derivatised porphyrin, phthalocyanine or calixarene) in the solution. Vacuum filtration of the dispersions afforded self-supporting membranes known as buckypapers. Microanalysis provided evidence for retention of the surfactant or macrocyclic ligands in the buckypapers, which were also characterised by measurement of their electrical conductivities (24 ± 16 to 58 ± 11 S/cm), contact angles (28 ± 1 to 55 ± 10 °) and mechanical properties (tensile strengths varied between 1.6 ± 0.7 and 13 ± 2 MPa). The surface and internal morphologies of the buckypapers were similar to each other, which correlates with the lack of variation observed in their permeability's towards water. The ability of selected buckypapers to remove trace organic contaminants (TrOCs) was also examined. A buckypaper prepared using Triton X-100 as the dispersant showed more than 80% removal efficiency for 11 out of the 12 TrOCs investigated in this study. On the other hand, a buckypaper prepared from MWNTs and phthalocyaninetetrasulfonic acid exhibited lower removal efficiencies for these TrOCs, possibly due to their smaller specific surface area.

Keywords: carbon nanotubes; buckypapers; water permeability; trace organic contaminants; bisphenol A

1. Introduction

There is considerable interest in the development of new materials for desalination and other membrane filtration applications [1]. This stems from problems associated with currently available materials, such as membrane fouling, short service lifetimes and low solute selectivity. Carbon nanotubes (CNTs) have attracted growing attention as a new material for preparing membranes that may overcome these problems. Interest in CNTs has been spurred by theoretical studies performed using molecular dynamics simulations, which revealed that they are exceptionally permeable towards gases and liquids [2, 3]. Furthermore, experiments performed with membranes composed of aligned CNTs have demonstrated their capacity to selectively filter solutes on the basis of differences in their sizes. Such behaviour was exhibited by aligned membranes composed of multi-walled carbon nanotubes (MWNTs), which transmission electron microscopy revealed had diameters measuring 6.5 nm [3]. The membranes were shown to allow the passage of gold nanoparticles with diameters of 2 or 5 nm, and $[Ru(bipy)_3]^{2+}$ molecules which are even smaller, but not gold nanoparticles with diameters > 10 nm. Other studies have also shown that membranes composed of aligned CNTs can perform a variety of filtration tasks, including separating the components of a hydrocarbon mixture, and removal of microorganisms such as *E. coli* from aqueous solution [4].

While the above results demonstrate that membranes composed of aligned CNTs show great promise as membrane materials, they are costly and difficult to produce on a scale that is sufficiently large for commercial applications. For example, the preparation of aligned CNT membranes may involve chemical vapour deposition or ion milling, which cannot readily be adapted for mass production of large membranes. Furthermore, hazardous chemicals such as hydrofluoric acid may also be required to

remove the substrate an aligned array of CNTs is deposited on. It is for these reasons that we, and others, have commenced exploring the potential of another class of CNT membranes known as buckypapers for filtration applications.

Buckypapers can be fabricated from dispersions of CNTs prepared by applying ultrasonic energy to samples containing commercial nanotubes and a suitable dispersant molecule. The high energy imparted through the use of an ultrasonic horn enables large bundles of nanotubes to be physically separated, with the resultant individual tubes stabilised through non-covalent interactions with dispersant molecules [5,6]. Filtration of these dispersions onto a support membrane, using either vacuum or positive pressure, then results in formation of the buckypaper [7], which consists of a tangled bed of nanotubes with a range of pore sizes that are larger than those present in aligned CNT membranes.

To date only a few studies have described the filtration characteristics of buckypapers. Early investigations into the permeability of buckypapers reported results obtained using composite materials consisting of the buckypapers still attached to their original polyvinylidene (PVDF) support membranes [8, 9]. These composite materials have been proven to be highly effective for removing bacteria and viruses from water supplies. Evidence has also emerged that buckuypapers could be used for desalination [10] or gas separation [11]. Recent research suggests that it may be possible to control the porosity of buckypapers by changing the average length of the MWNTs used in their preparation [12].

Recently, we reported the preparation of buckypapers composed entirely of single-walled carbon nanotubes (SWNTs) [13]. No supporting membrane was present in these buckypapers, which were obtained by vacuum filtration of aqueous dispersions of SWNTs, which were prepared using either Triton X-100, or one of

several macrocyclic ligands including a derivatised porphyrin and calixarene, to assist in formation of the dispersion. Microanalysis and Energy Dispersive X-ray spectroscopic examination of the buckypapers provided direct evidence for retention of the macrocyclic molecules within the structure of the membrane. Scanning electron microscopy and analysis of nitrogen adsorption/desorption isotherms showed that both the surface and internal morphologies of the buckypapers were strongly dependent on the macrocyclic molecules that had been incorporated into its structure during preparation. It was therefore not surprising that the permeability of the buckypapers towards water varied markedly.

Here we describe the preparation and properties of MWNT buckypapers, and the results of an investigation into their permeability towards water. Each of the buckypapers was synthesised using a MWNT dispersion prepared using Triton X-100 or one of the macrocyclic ligands used in our previous study involving SWNT buckypapers [13]. This enabled us to complete our first objective of examining the effect of incorporating different dispersants into MWNT buckypapers on their permeability towards water, as well as compare the aqueous permeability of MWNT and SWNT buckypapers prepared under identical conditions. Our second aim was to explore for the first time the ability of buckyapers to remove trace organic contaminants (TrOCs) from an aqueous solution. Filtration experiments were conducted to determine the permeability of the MWNT buckypapers towards a single TrOC (bisphenol A (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 [14, 15]. As a consequence there have been a number of studies that have investigated the use of different membrane systems to remove TrOCs from water supplies [16-20]. There has also been interest in

using carbon nanotubes in electrochemical sensors for detecting BPA [21, 22] or in devices used for its quantitative analysis [23]. Furthermore the ability of CNTs to remove BPA by adsorption has been explored [24-26]. Despite this, to the best of our knowledge, this is the first study which has examined the potential of free-standing buckypaper membranes to remove TrOCs from an aqueous solution.

2. Materials and methods

2.1 Reagents

All MWNTs used in this study were produced by Nanocyl S.A. (Belgium) using a chemical vapour deposition process. The range of nantoubes studied included multi-walled carbon nanotubes (MWNTs; batch nos. 091010 & 1000825), amine-functionalised MWNTs (MWNT-NH_2; batch no. LMWS-P-NH_2) and carboxylic acid-functionalised MWNTs (MWNT-COOH; batch no. MEL110513). The average diameter of each of the above types of nanotubes are 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. Triton X-100 (Trix; Sigma-Aldrich), 4-sulfonic calix[6]arene hydrate (C6S; Alfa Aesar), meso-tetra(4-sulfonatophenyl)porphyrin dihydrogenchloride (TSP; Frontier Scientific) and phthalocyaninetetrasulfonic acid (PTS; Frontier Scientific) were used as dispersants. Analytical grade BPA, amitriptyline, trimethoprim, sulfamethoxazole, diclofenac, bezafibrate, caffeine, atrazine, primidone, carbamazepine, pentachlorophenol, linuoron and triclosan from Sigma-Aldrich were used as model trace organic contaminants (TrOCs).

2.2 Preparation of MWNT dispersions

All dispersions were prepared in Milli-Q water (resistivity 18 MΩ cm) using sufficient MWNTs to give a final concentration of 0.1% (w/v). 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 a typical experiment, 15 mg of MWNTs were dispersed in 15 mL of dispersant solution by using a Branson 450 (400 W, Ultrasonics Corp.) digital sonicator horn with a probe diameter of 10 mm to apply ultrasonic energy for 30 min. The conditions used were power output = 16 W, pulse duration = 0.5 s and pulse delay = 0.5 s. The sample vial was kept inside an ice/water bath (at ~ 6 °C) throughout the sonication process to minimize increases in temperature.

2.3 Preparation of buckypapers

Small, circular buckypapers 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, β-CD or C6S, or 0.1% (w/v) PTS or TSP), and then placed in an ultrasonic bath (Unisonics, 50 Hz, 150 W) for 3 min. This process resulted in homogeneous dispersions (80 mL) containing 0.038 % (w/v) of MWNTs. Milli-Q water was added to give a total volume of 250 mL, and the resulting dispersion 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 tops of the filtration units to minimize evaporative losses during the filtration process.

A similar process was used to prepare larger, rectangular buckypapers. Initially six dispersions were prepared as described in section 2.2, and then added to 50 mL of dispersant solution. The resulting mixture was subjected to further treatment in an ultrasonic bath (Unisonics, 50 Hz, 150 W) for 3 min. The resulting homogeneous dispersions (140 mL) contained 0.064 % (w/v) of MWNTs, and were diluted to a total volume of 1 L with Milli-Q water. These final dispersions were filtered across a piece of commercial PVDF membrane (0.22 μm pore size; Millipore) housed in a custom-made filtration unit with a sintered glass frit measuring 5.5 cm x 8.0 cm. After the filtration process was completed, both types of buckypapers 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 procedure was adapted from our previous study involving SWNT buckypapers [13], and was found to be sufficient to remove any 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. This indicates that the washing procedure was successful in removing loosely adhering dispersant molecules. After washing, the damp buckypaper was allowed to dry overnight after being placed between absorbent paper sheets. The dry buckypaper was then carefully peeled away from the underlying commercial membrane filter.

2.4 Characterisation techniques

Measurement of the percentage of different elements present in buckypapers was performed by the Microanalytical Unit of the Research School of Chemistry, The Australian National University. 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. Scanning electron microscopic examination of the surface morphology of buckypapers was performed using a JEOL JSM-7500FA FESEM. All images were analysed using an image analysis package (Leica Application Suite) to provide quantitative information about the diameter of surface pores and thickness of each buckypaper. Energy Dispersive X-Ray (EDX) spectroscopy was performed in conjunction with imaging using the SEM to provide information on the identity of elements present on the surface of buckypaper samples. The contact angles, electrical conductivities and mechanical properties of buckypapers were measured using equipment and methods reported previously [13, 27].

A Micromeritics® surface area analyser (ASAP 2020) was used to obtain nitrogen adsorption/desorption isotherms for all buckypapers at 77 K. Prior to analysis, samples were placed under vacuum at 200 °C to remove any residual trapped gases. Analysis of the resulting isotherms using the Horvath-Kawazoe (HK) and Barrett, Joyner and Halenda (BJH) methods afforded the distribution of small and large pores, respectively [28,29]. In addition, the isotherms were analysed using the multipoint Brunauer, Emmett, and Teller (BET) method to calculate the specific surface areas of the buckypapers [30].

2.5 Permeability studies

A custom-made dead-end filtration cell setup was used to measure the permeability of the buckypapers towards water. Compressed air was used to induce a transmembrane pressure and obtain a water flux across an individual buckypaper. The buckypaper was placed on porous stainless steel, which provided mechanical support to the membrane. The volume of water passing across the membrane was monitored

for 10 min using an analytical balance connected to a personal computer. From the slope of the resulting plot of accumulated permeate volume against time the permeate flux (J) was determined. Initially, a pressure of 1 psi (0.069 bar) was applied and the permeate flux (J) was recorded. The pressure applied to the buckypaper was then incrementally increased and the process repeated, affording values of J at several different pressures. This data was then used to calculate the water permeability (f) for each buckypaper.

The permeability of different types of buckypapers towards BPA or a mixture of twelve TrOCs was examined using the same dead-end filtration cell. Experiments involving BPA were performed using four different buckypapers, and feed solutions containing between 600 and 650 μg/L BPA in Milli-Q water. The pressures applied to MWNT/Trix and MWNT/PTS buckypapers 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^2hr^1. For the MWNT-NH_2/Trix and MWNT-COOH/Trix buckypapers much lower applied pressures of 0.26 and 0.24 bar, respectively had to be 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^2hr^1. In most cases the permeate solution was collected sequentially in six samples, of 20 mL each. The thickness of each buckypaper obtained from SEM analysis (Section 2.4) was used to calculate the equivalent bed volume (BV). The total volume of permeate (120 mL) that was collected from MWNT/Trix, MWNT-NH_2/Trix and MWNT/PTS buckypapers equates to 1430, 1080 and 1110 BV, respectively. As the MWNT-

COOH/Trix buckypaper had a very low permeability, only six separate samples of 3 mL volume were collected, which is equivalent to 210 BV.

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 5μm), 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 afforded the percent removal of BPA, which shows how much BPA had been rejected by the buckypapers.

Investigations into the permeability of MWNT/Trix and MWNT/PTS buckypapers towards the mixture of TrOCs, used an aqueous solution of the latter that was prepared from a stock solution containing 1 g/L of each compound (i.e. amitriptyline, trimethoprim, sulfamethoxazole, diclofenac, bezafibrate, caffeine, atrazine, primidone, carbamazepine, pentachlorophenol, linuoron and triclosan) in pure methanol. The TrOC stock solution was introduced into the Milli-Q feed solution to give a final concentration of each compound of approximately 50 μg/L. The pressures applied to MWNT/Trix and MWNT/PTS buckypapers at the commencement of experiments were the same as those used in experiments involving

BPA, and the permeate solutions were collected sequentially in six amounts, of 20 mL each. The concentrations of each TrOC present in the feed and permeate samples were determined using a Shimadzu LC-MS system (LC-MS 2020) equipped with an electrospray ionization (ESI) interface. A Phenomenex Kinetex 2.6 μm C8 column (50 mm x 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 buffered with 0.1% (v/v) formic acid and acetonitrile. Details of the gradient elution protocol used are provided elsewhere [31]. The mobile phase flow rate was 0.5 mL/min and the sample injection volume was 10 μL. The analytes from the HPLC system were fed directly into a quadrupole mass spectrometer via an ESI source. ESI positive ionization $[M+H]^+$ mode was adopted for caffeine, primidone, trimethoprim, sulfamethoxazole, carbamazepine, bezafibrate, atrazine, linuron and amitriptyline, while ESI negative ionization $[M-H]^-$ mode was used for pentachlorophenol, diclofenac and triclosan. All mass spectra were acquired in selective ion monitoring mode with the detector voltage of 0.9 kV, desolvation line temperature of 250 ºC, and heating block temperature of 200 ºC. High purity nitrogen was used as both the nebulizing and drying gas at a flow rate of 1.5 and 10 L/min, respectively. Standard solutions of the analytes were prepared at 1, 10, 50, 100, 500 and 1000 ng/mL, and an internal instrument calibration was carried out with carbamazepine-d_{10} as the internal standard. The calibration curves for all the analytes had a correlation coefficient of 0.99 or higher.

3. Results and discussion

3.1 Composition and surface morphology of buckypapers

We previously reported that a sonication time of 30 min was suitable for preparing MWNT/Trix and MWNT/cipro (cipro = ciprofloxacin) dispersions [32]. Consequently all dispersions used to make buckypapers in the current study were prepared using the same sonication time in order to facilitate comparison of their physical properties. Filtration of these dispersions gave uniform buckypapers that could be readily removed from their underlying support membranes. Figure 1 shows scanning electron micrographs of buckypapers composed of MWNT/C6S, MWNT/PTS, MWNT/TSP and MWNT-COOH/Trix. These images have a number of similarities to each other, and to that of a MWNT/Trix reported previously [32]. 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 buckypapers 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.

Evidence for retention of Trix or macrocyclic ligands in the buckypapers is provided by the microanalytical results shown in Table 1. The as-received MWNTs used to prepare the buckypapers consisted almost entirely of carbon, with the only other element present to a significant extent being hydrogen. There was no nitrogen present, and virtually no sulfur as well. This was important to establish as these elements were expected to be present in many of the buckypapers if the latter retained significant amounts of macrocyclic dispersant.

Comparison of the percentage of carbon present in buckypapers 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 fraction of hydrogen present. In addition, these three buckypapers contained significant amounts of nitrogen and/or sulfur. Both sets of observations are consistent with small amounts of C6S, TSP and PTS being retained in the buckypaper samples, even after they had been thoroughly washed after preparation. Addition of the elemental percentages in Table 1 for the MWNT/C6S, MWNT/PTS and MWNT/TSP buckypapers does not equal 100%. This is because these dispersants also contain a significant amount of oxygen, which was not analysed for as part of this work.

The fraction of carbon present in a MWNT/Trix buckypaper was slightly less than that in the MWNT starting material, while the fraction of hydrogen was slightly greater. In addition, the MWNT/Trix buckypaper did not contain significant amounts of either sulfur or nitrogen. Each of these results is consistent with a small amount of Trix being retained by the buckypaper, as this dispersant does not contain either nitrogen or sulfur. Overall the changes in elemental composition between the raw MWNTs and buckypapers shown in Table 1 are comparable to those seen previously with the analogous membranes prepared using SWNTs [13].

3.2 Physical properties of buckypapers

The mechanical properties of the different buckypapers were evaluated using the tensile test method. Further interest in performing this investigation stemmed from our inability to reproducibly prepare SWNT buckypapers containing many of the same dispersants, as a result of their inconsistent and sometimes poor mechanical properties. A typical set of results is presented in Figure 2, with all buckypapers exhibiting stress/strain curves that were linear at low strain, but displayed significant curvature at higher values. These results suggest that the buckypapers fail ultimately

owing to their inherently brittle nature. Reflecting this, all buckypapers failed when an applied strain between 0.2 and 1.2% was applied. Using the data contained in the stress/strain curves we were able to derive the values of Young's modulus, tensile strength and ductility presented in Table 2.

Inspection of Table 2 reveals that changing the dispersant used during preparation of the MWNT buckypapers affected the mechanical properties of the final material. For example, the Young's modulus of the four types of buckypapers prepared using MWNTs ranged between only 0.34 ± 0.15 and 1.2 ± 0.2 GPa, while the ductility of the same materials varied from just 0.59 ± 0.23 to 1.3 ± 0.2%. In general, the mechanical properties of each of the buckypapers prepared using MWNTs is either comparable to, or a factor of between two and five times smaller, than values reported previously for the corresponding buckypapers synthesised using SWNTs and the same dispersant molecules [13]. 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) [32]. However, the tensile strengths for MWNT buckypapers 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) [13]. Similar trends may be discerned after comparing the other mechanical properties reported here for MWNT buckypapers, with those in the literature for the corresponding materials synthesised using SWNTs [13]. Based on this evidence the latter materials are the more robust of the two classes of buckypapers.

Although MWNT-COOH/Trix buckypapers exhibited the highest Young's modulus, the mechanical properties of MWNT-COOH/Trix and MWNT-NH_2/Trix

generally proved to be the poorest of all the materials examined. For example, MWNT-NH_2/Trix showed the lowest tensile strength (and MWNT-COOH/Trix the third lowest), and both buckypapers prepared using substituted MWNTs exhibited poorer values of ductility than the remaining materials. The lack of robustness in these materials 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.

Table 2 shows that the electrical conductivity of the MWNT buckypapers fall within the range 24 ± 16 to 58 ± 11 S/cm. This is a narrower range of values compared to those reported previously for the corresponding SWNT buckypapers [13]. 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 buckypapers prepared using the same dispersant, but different types of CNTs, varied significantly. For example, the conductivity of a SWNT/PTS buckypaper was stated previously to be 220 ± 60 S/cm [13], while the value reported here for the analogous material prepared using MWNTs is 58 ± 11 S/cm. This is consistent with the results of an earlier investigation, which showed that the conductivity of buckypapers 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 [32].

The contact angles of the buckypapers reported in Table 2 cover a relatively narrow range of values that indicate each membrane is hydrophilic in nature. 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 buckypapers prepared using SWNTs and the same dispersant molecules [13], suggesting that the choice of CNT has little effect on the wettability of these materials.

3.3 Internal morphology

The SEM images illustrated in Figure 1 suggest that each of the buckypapers have similar surface morphologies, regardless of the type of carbon nanotube (MWNT or substituted MWNT) or dispersant they were prepared from. This is further supported by the results of a quantitative analysis of the pore openings of these materials, which are summarised in Table 2. Each of the buckypapers 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 [13].

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 buckypapers. Fig. 3 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 Fig. 3 are similar in overall appearance to those reported previously for buckypapers prepared using MWNTs or SWNTs, and dispersants similar to those used in the current study [13, 32].

Analysis of the isotherms derived from nitrogen adsorption/desorption measurments for all buckypapers was performed using the Barrett, Joyner and

Halenda (BJH) [29] and Horvath-Kawazoe (HK) methods [28]. This enabled the distribution of large and small pores, respectively present within the materials to be calculated, along with other aspects of the internal morphology of the buckypapers presented in Table 3. In addition, the surface areas of the buckypapers shown in Table 3 were derived through analysis of the binding isotherms using the Brunnauer, Emmett and Teller (BET) method [30]. The insets in Fig. 3 show the pore size distributions derived through application of the BJH and HK methods to the isotherms determined for these buckypapers. In both cases a large peak is present at ~ 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 ~ 5 and 6 nm owing to the presence of larger pores present between aggregates of nanotubes. The pore distribution curves calculated for the other buckypapers examined as part of the current study showed similar features to those seen in Fig. 3.

Inspection of the data presented in Table 3 shows that each of the internal pore characteristics of the buckypapers 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 buckypapers prepared using SWNTs and Trix, C6S, PTS, TSP or sulfated β-cyclodextrin (β-CD) [13]. With the exception of SWNT/PTS, the average internal pore diameter of these SWNT buckypapers was reported previously to vary from 2.0 ± 0.2 nm to 4.0 ± 0.4 nm [13]. In contrast, the MWNT buckypapers 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 buckypapers (range 87 – 96%) are, on average,

slightly greater than what was measured previously for the corresponding membranes composed of SWNTs (range 76 ± 5 to 93 ± 6%). A further distinction between the two classes of buckypapers is revealed through examination of their surface areas. For the MWNT membranes studied here, the surface area ranged from 180 ± 0.1 m^2/g for MWNT/ PTS to 380 ± 2.0 m^2/g for MWNT-COOH/ PTS. In contrast, the specific surface areas of most of the SWNT buckypapers studied previously varied from 360 ± 4 m^2/g to 790 ± 4 m^2/g, showing that they typically had greater surface area. Analysis of the pore structure information derived through analysis of nitrogen adsorption/desorption isotherms therefore reveals that there are usually some significant differences for membranes prepared using the two different classes of CNTs.

3.4 Water permeability studies

The permeability of the buckypapers 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 to enter the receiving cell was then monitored for approximately 10 min, before the applied pressure was increased and the process repeated. For each buckypaper examined, transport of water commenced when the applied pressure was less than 1 bar (Table 4). There was little difference between the pressures required to initiate water transport across each of the buckypapers, or with those applied to induce the passage of water across similar membranes composed of SWNTs in an earlier study [13]. Increasing the pressure applied to all buckypapers composed of MWNTs or substituted MWNTs resulted in the amount of water permeating across the membrane also increasing.

The permeate flux of each type of buckypaper increased linearly as expected when the applied pressure was increased (Fig. 4). The MWNT-NH_2/Trix and MWNT-COOH/Trix buckypapers could only sustain a small pressure (i.e. 0.38 and 0.26 bar, respectively) before they ruptured (Table 4), and the membranes failed. This may be attributed to the significantly poorer mechanical properties of these two buckypapers, as noted in Section 3.2. The membrane permeability's (*f*) were derived from the slopes of the plots in Fig. 4 using $f = \frac{J}{A\Delta P}$ where *A* is the effective area of the membrane exposed to water, and ΔP is the pressure difference applied across the membrane. The permeabilites of the buckypapers are presented in Table 4. Changing the identity of either the type of CNT (functionalised or non-functionalised) or dispersant present in the buckypaper had little effect on membrane permeability. In contrast, SWNT buckypapers prepared using Trix, C6S, PTS and TSP as dispersants were found to exhibit a considerable range of membrane permeability [13]. Furthermore the permeability of the SWNT buckypapers 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 into the permeability of buckypapers prepared from SWNTs or MWNTs towards different fluids [33]. In the latter investigation buckypapers 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 we are reporting here. For example, in the study reported by Wang et al. [33], buckypapers 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.

There are a number of possible factors that may contribute to the lower permeability of MWNT (and functionalised MWNT) buckypapers we have prepared, compared to those made from SWNTs we studied previously, as well as the lack of sensitivity of the former group of materials to changes in the dispersant incorporated into their structure. One is variation in the thicknesses of buckypapers 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 with those obtained previously for buckypapers composed of SWNTs [13], however, reveals no significant variations. This indicates that the lower permeability displayed by the MWNT buckypapers 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 buckypapers is therefore differences in internal pore structure revealed by analysis of nitrogen adsorption/desorption isotherms. In particular, it was noted above that MWNT buckypapers 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 buckypapers by the presence of what are generally much larger aggregates of nanotubes than those present in SWNT buckypapers [13]. The presence of larger internal pores in MWNT buckypapers 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

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 [34, 35].

3.5 Rejection of trace organic contaminants

The results presented above demonstrate the permeability towards water of membranes composed of MWNTs or substituted MWNTs. Although each of the membranes exhibited a permeability that was less than that 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 buckypapers to reject typical organic contaminants. Experiments were initially performed using MWNT/Trix, MWNT/PTS, MWNT-NH_2/Trix and MWNT-COOH/Trix buckypapers and feed solutions containing BPA. The experiments were conducted using the same dead-end filtration apparatus used for performing permeability measurements. Fig. 5 shows the results of these experiments.

In the case of MWNT/Trix, MWNT-NH_2/Trix and MWNT-COOH/Trix buckypapers the extent of BPA removal remained constant at approximately 90% throughout the experiment. Mass balance calculations performed using these buckypapers showed that there was significant retention of BPA by the membrane in all cases. This suggests that each of these buckypapers exhibits a significant ability to retain BPA molecules, most likely by an adsorption mechanism. In contrast, Fig. 5d shows that the removal of BPA by MWNT/PTS buckypapers clearly decreased as the experiment progressed. Mass balance calculations performed with this buckypaper 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 buckypapers compared to each of the other membranes (Table 3), which may result in a smaller number of sites for analyte adsorption to occur.

In order to further explore the potential of the buckypapers to reject organic compounds, a second set of experiments was performed using solutions containing a total of twelve TrOCs, and either a MWNT/Trix or MWNT/PTS buckypaper. The organic molecules chosen for examination included pharmaceuticals, personal care products and pesticides. Their molecular weights are less than 400 g/mol. These TrOCs included compounds with a range of net charges at neutral pH, and different hydrophobicities (Table 5). Figure 6 illustrates the results of these rejection experiments.

Inspection of the data shown in Figure 6a, which was obtained using a MWNT/Trix buckypaper, shows that the extent of removal of most of the TrOCs was $\geq$ 90%. The one notable exception to this trend was observed with primidone, which is a hydrophilic and neutral pharmaceutical. In contrast to the above results, Figure 6b shows that a MWNT/PTS buckypaper was much less effective at removing TrOCs from solution. After the conclusion of the experiment, only four compounds were removed 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 buckypaper 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. Conclusion

Uniform, free-standing buckypaper membranes were successfully produced from aqueous dispersions containing MWNTs or substituted MWNTs, and either the surfactant Trix or one of several macrocyclic ligands. The buckypapers 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 buckypapers containing MWNTs or functionalised MWNTs, and different dispersants, which showed very little variation in surface morphology. In addition, analysis of nitrogen adsorption/desorption binding isotherms derived using different MWNT buckypapers 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 ± 2 and 26 ± 3 nm.

Permeability experiments performed using solutions containing only BPA, or a mixture of TrOCs, demonstrated the ability of most of the MWNT buckypapers to reject a variety of organic compounds. The buckypaper 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. We are currently exploring methods for producing new buckypapers that combine the ability to selectivity

remove TrOCs exhibited by the materials reported here, with superior mechanical properties.

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Table 1 Microanalytical data for MWNT buckypapers and MWNT starting material. The error associated with each value is ± 0.1%.

	Elemental composition (%)			
Sample	C	H	N	S
As-prepared MWNTs	98.2	1.5	0.0	0.2
MWNT/Trix	96.2	2.6	0.4	0.0
MWNT/C6S	85.7	1.2	0.1	1.2
MWNT/PTS	84.8	2.7	2.2	2.0
MWNT/TSP	83.9	3.0	1.0	1.3

Table 2 Physical properties of buckypapers. Values shown are the average of at least 3 samples, with the errors reported determined from the standard deviation obtained from all measurements.

Sample	Young's modulus (GPa)	Tensile strength (MPa)	Ductility (%)	Electrical conductivity (S/cm)	Contact angle (˚)
MWNT/Trix [b]	0.6 ± 0.3	6 ± 3	1.3 ± 0.2	24 ± 16	55 ± 10
MWNT/C6S	0.94 ± 0.13	4.4 ± 1.3	0.59 ± 0.23	47 ± 7	49 ± 15
MWNT/PTS	1.2 ± 0.2	13 ± 2	0.9 ± 0.3	58 ± 11	49 ± 16
MWNT/TSP	0.34 ± 0.15	2.5 ± 1.2	1.0 ± 0.5	39 ± 8	44 ± 14
MWNT-NH_2/Trix	0.4 ± 0.1	1.6 ± 0.7	0.50 ± 0.20	25 ± 1	53 ± 2
MWNT-COOH/Trix	1.3 ± 0.4	3.7 ± 0.8	0.30 ± 0.05	26 ± 2	28 ± 1

[b] Data for MWNT/Trix taken from reference 31.

Table 3 Surface morphological and internal pore properties of buckypapers.

Sample	Average surface pore diameter D_{SEM} (nm)[a]	Specific surface area A_{BET} (m^2/g)	Average internal pore diameter d_{BET} (nm)	Average nanotube bundle diameter D_{bun} (nm)	Interbundle pore volume (%)
MWNT/Trix [b]	80 ± 20	300 ± 1.0	24 ± 1	8.8 ± 0.2	91 ± 5
MWNT/C6S	78 ± 26	250 ± 1.0	26 ± 3	11 ± 0.2	94 ± 6
MWNT/PTS	69 ± 21	180 ± 0.1	20 ± 2	15 ± 0.1	96 ± 8
MWNT/TSP	88 ± 23	240 ± 1.0	26 ± 3	11 ± 0.2	92 ± 5
MWNT-NH_2/Trix	83 ± 21	260 ± 2.0	21 ± 2	10 ± 0.1	94 ± 5
MWNT-COOH/Trix	55 ± 18	380 ± 2.0	10 ± 1	7.1 ± 0.1	87 ± 3

[a] Average surface pore diameter determined by scanning electron microscopy. All other parameters determined through analysis of results obtained from nitrogen adsorption/desorption isotherms. [b] Data for MWNT/Trix taken from reference 31.

Table 4 Membrane permeability (*f*), water transport initiation pressure, rupture pressure and thicknesses of different buckypapers.[a]

Sample	Membrane flux (*f*) ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	Transport initiation pressure (bar)	Rupture pressure (bar)	Thickness (μm)
MWNT/Trix	24 ± 6	0.24 ± 0.03	1.1 ± 0.3	37 ± 3
MWNT/C6S	17 ± 4	0.36 ± 0.26	1.3 ± 0.1	48 ± 3
MWNT/PTS	23 ±6	0.51 ± 0.23	1.2 ± 0.3	47 ± 1
MWNT/TSP	21 ± 3	0.40 ± 0.17	1.4 ± 0.3	57 ± 3
MWNT-NH_2/Trix	13 ± 2	0.22 ± 0.05	0.38 ± 0.04	49 ± 1
MWNT-COOH/Trix	17 ± 4	0.19 ± 0.01	0.26 ± 0.01	38 ± 1

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

Table 5 Physicochemical properties of selected trace organic contaminants (TrOCs)

Compound	Category	Mol. Weight (g/mol)	Log D[a] (pH 7)	pK_a[a]
Aminotriptylene	Hydrophilic, charged	277	2.28	9.18
Trimethoprim		290	0.27	7.04
Sulfamethoxazole		253	-0.96	5.18
Diclofenac		296	1.77	4.18
Bezafibrate		362	-0.93	3.29
Caffeine	Hydrophilic, neutral	194	-0.63	0.52
Atrazine		216	2.64	2.27
Primidone		218	0.83	12.26
Carbamazepine		236	1.89	13.94
Pentachlorophenol		266	2.85	4.68
Linuron	Hydrophobic, neutral	249	3.12	12.13
Triclosan		290	5.28	7.8

[a] Values for p*K*a and log *D* were obtained from the SciFinder Scholar (ACS) database.

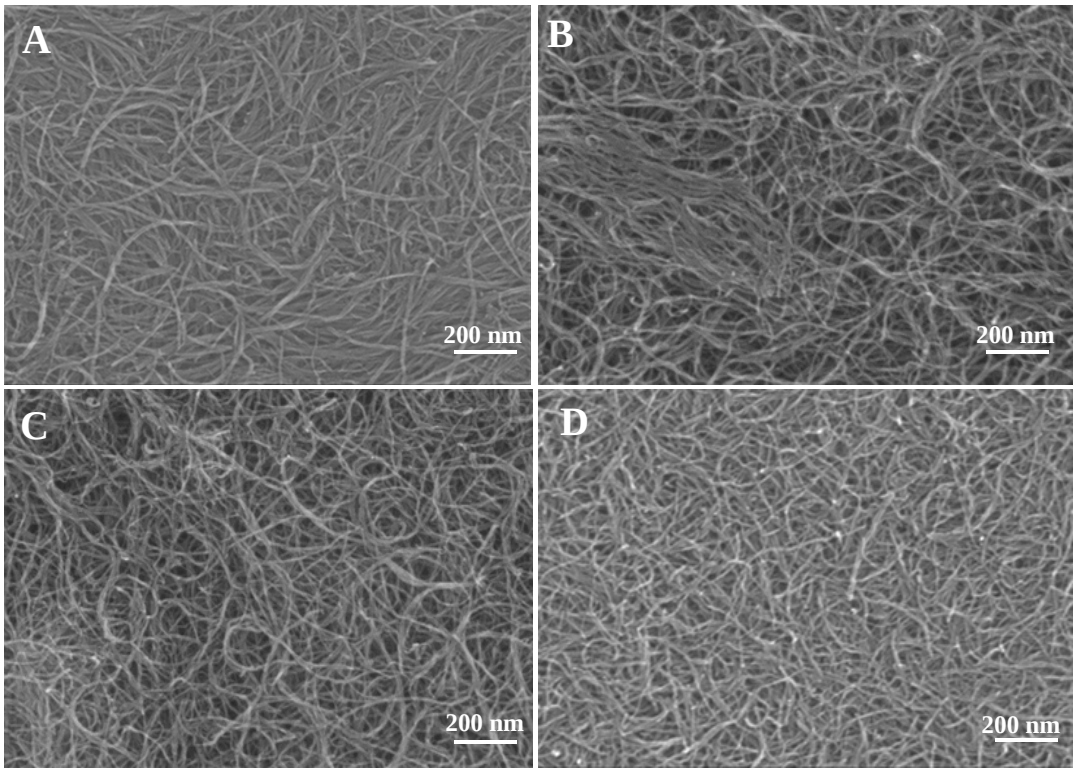

Fig. 1. Scanning electron microscope images of different buckypapers imaged at 70,000 X magnification: (a) MWNT/PTS, (b) MWNT/TSP, (c) MWNT/C6S and (d) MWNT-COOH/Trix.

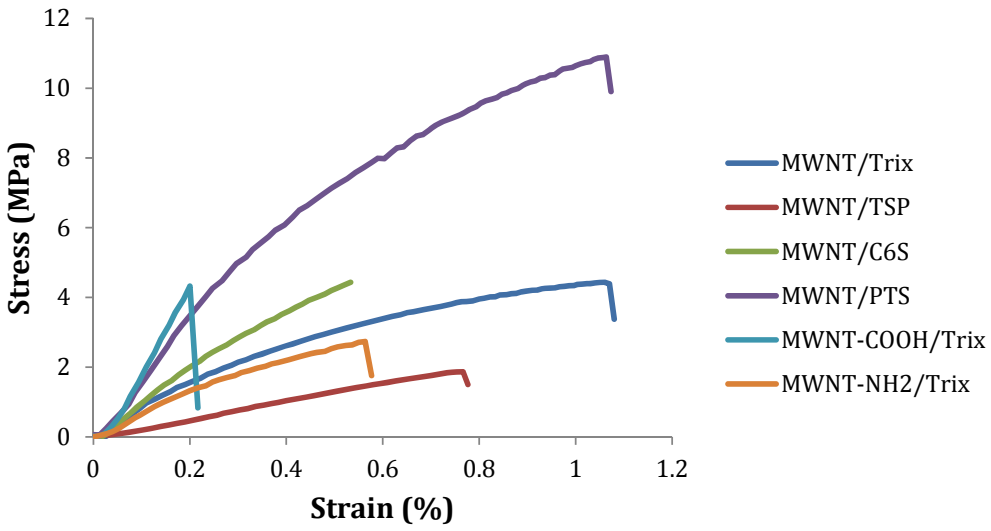

Fig. 2. Representative stress-strain curves for MWNT buckypapers.

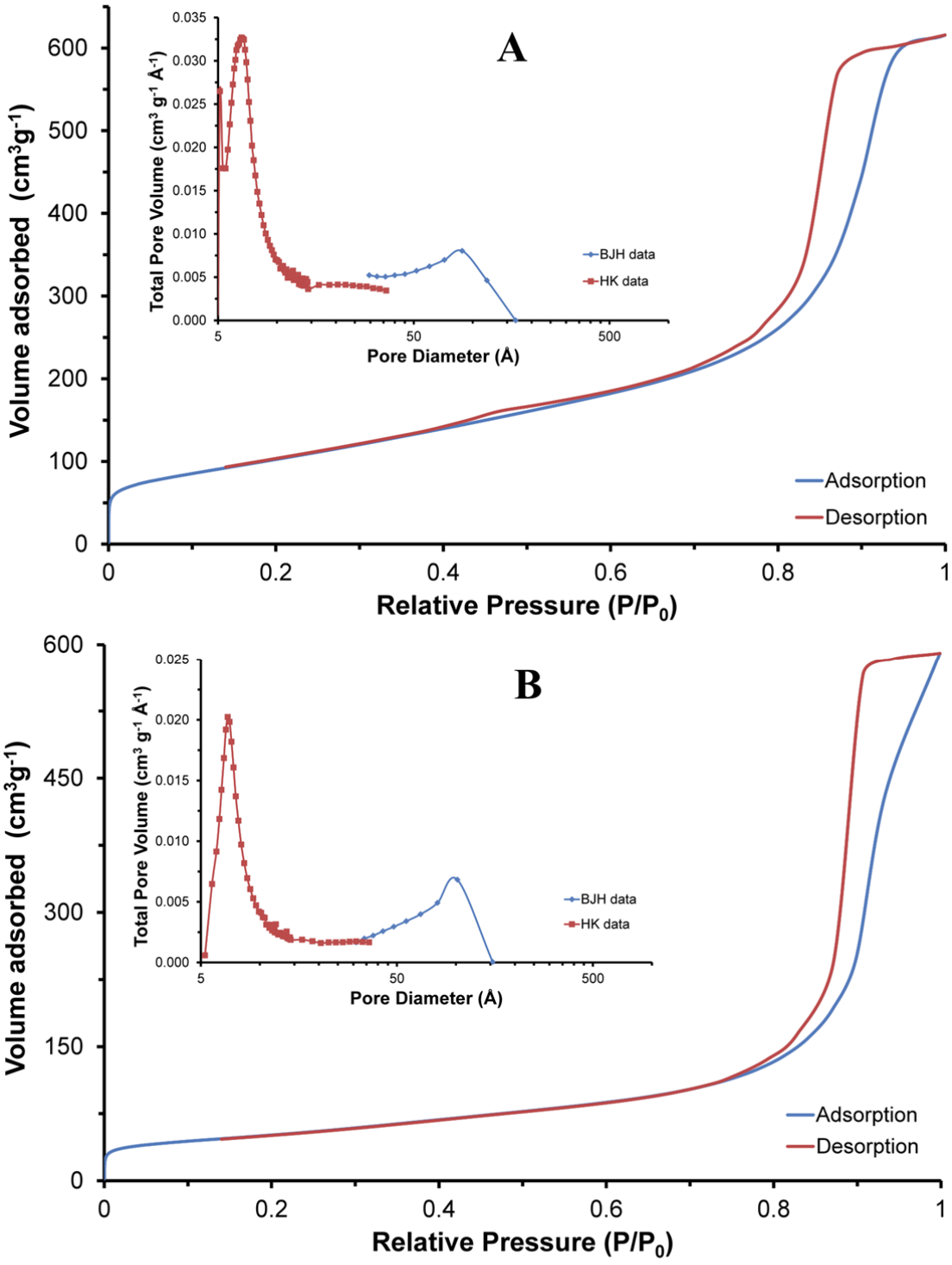

Fig. 3. Nitrogen adsorption (blue) and desorption (red) isotherms for: (a) MWNT-COOH/Trix and (b) MWNT/PTS buckypapers. The insets show the pore size distributions for the buckypapers derived from BJH and HK analysis of the isotherms.

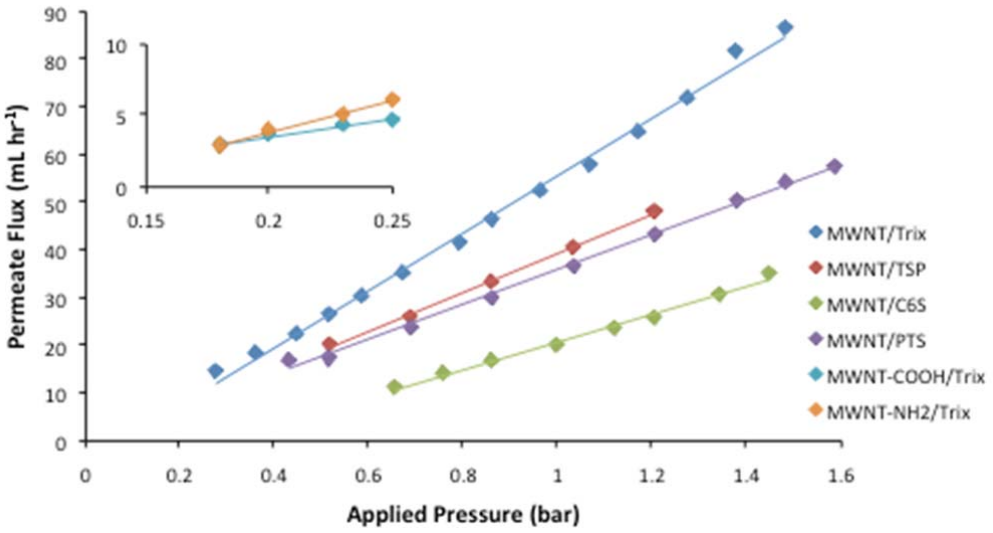

Fig. 4. Effect of applied pressure on the permeate flux (*J*) of different buckypapers.

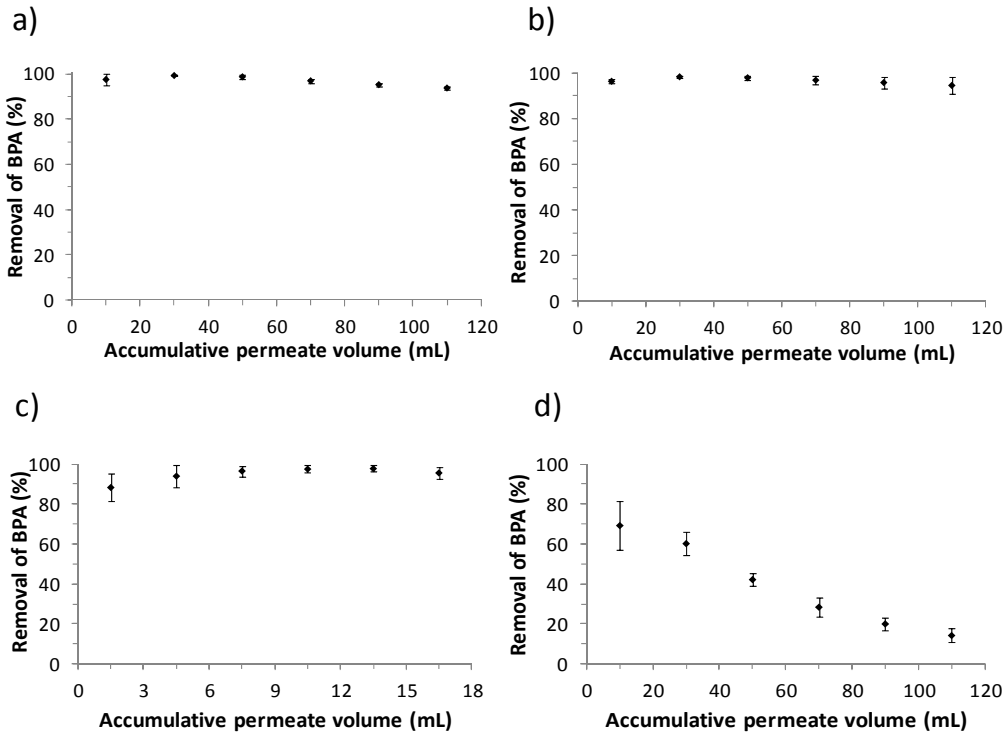

Fig. 5. Average bisphenol A removal obtained using different buckypaper membranes: (a) MWNT/Trix, (b) MWNT-NH_2/Trix, MWNT-COOH/Trix and (d) MWNT/PTS. In each case the feed solution contained 180 mL of 685 μg/L bisphenol A. The error bars represent the standard deviations obtained from experiments performed in triplicate for all buckypapers except MWNT-NH_2/Trix, for which duplicate experiments were performed. The total numbers of bed volumes of permeate that passed through each buckypaper were: 1430 (MWNT/Trix); 1080 (MWNT-NH_2/Trix); 210 (MWNT-COOH/Trix) and 1110 (MWNT/PTS).

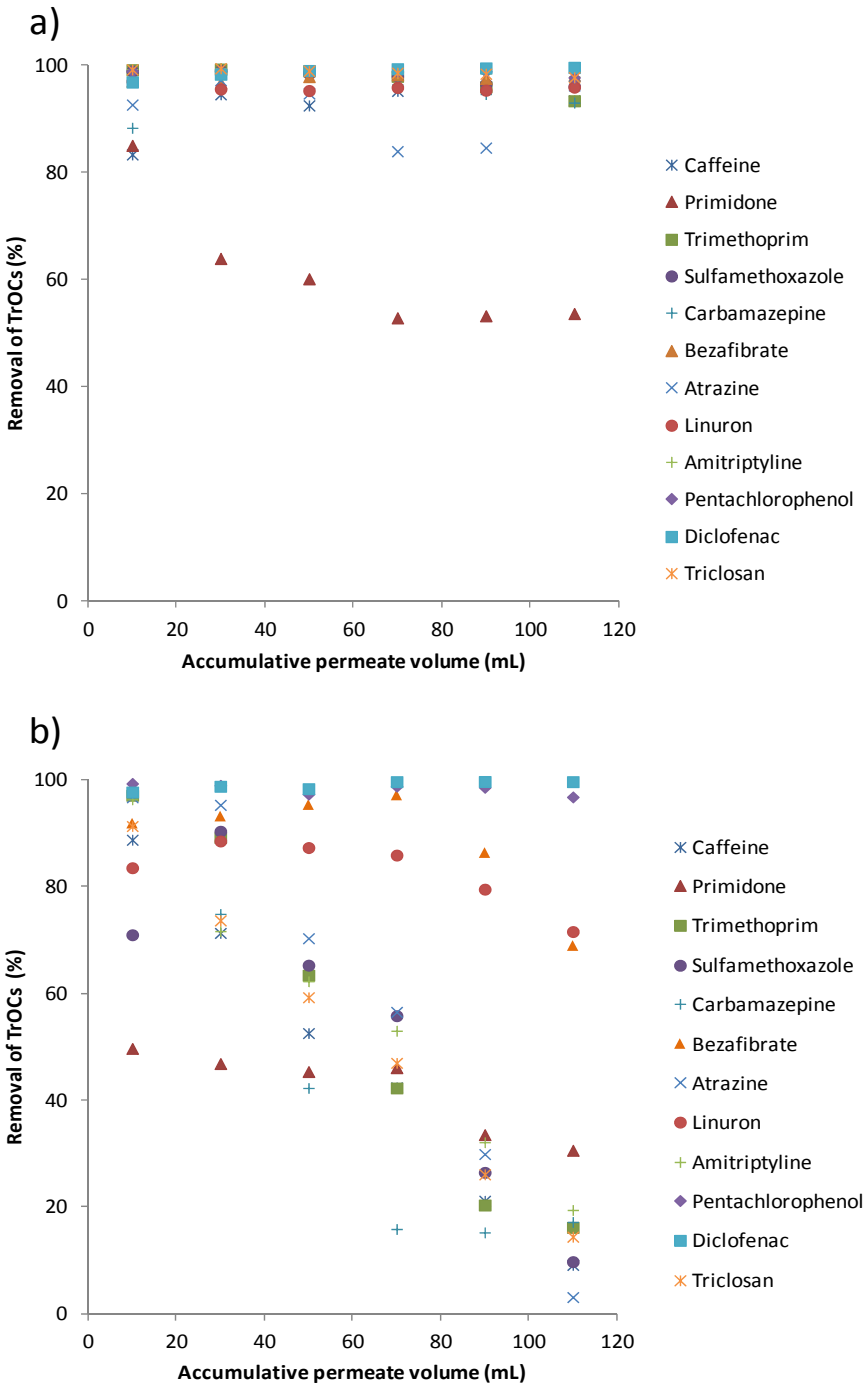

Fig. 6. Efficiency of removal of selected trace organic contaminants (TrOCs) using: (a) MWNT/Trix and (b) MWNT/PTS. For each experiment the feed solution contained twelve different TrOCs each at a concentration of 50 µg/L. The total

numbers of bed volumes of permeate that passed through each buckypaper were: 1430 (MWNT/Trix); and 1110 (MWNT/PTS).