

Removal of volatile organic compounds (VOCs) from groundwater by using MWCNT buckypaper membrane

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ABSTRACT

A comprehensive study was conducted to examine the removal of volatile organic compounds (VOCs) which exist in groundwater at Southlands-Botany Bay (Sydney, Australia). The ability of multi-walled carbon nanotubes (MWCNT), as a new generation of membrane technology, was examined using a dead-end filtration cell setup. Experiments were conducted using a buckypaper (BP) created using MWCNT-Trix 1% (w/v) dispersion. Twenty one VOCs with molecular weights between 78.11 g/mol (benzene) and 260.76 g/mol (hexachlorobutadiene) were designated as model organic contaminants because of their widespread occurrence in groundwater.

The results from this study revealed that the highest value of rejection was for tetrachloroethylene reached 88.5 %, while the lowest rejection achieved by the MWCNT buckypaper membrane was for 1,1,2-trichloroethane that amounted to 27.6 %. These values depended on the hydrophobicity and hydrophilicity of the compounds. It was noteworthy that the performance of MWCNT buckypaper membranes in rejecting hydrophilic compounds (carbon tetrachloride, trichloroethylene and tetrachloroethylene) was higher than for hydrophobic compounds (other VOCs which are examined in this study). This is because hydrophobic compounds can be adsorbed onto MWCNT membranes and then diffuse through the bundles, causing significant transport of these compounds across the bundles and the space between the bundles which can be considered as pores.

Keywords: Volatile organic compounds (VOCs), Buckypaper (BP), Carbon nanotube (CNT), Multi-walled carbon nanotube (MWCNT), Nanotechnology

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I. INTRODUCTION

Membrane-based water purifications are well known as a useful technology for a wide range of water and wastewater treatment processes. This is due to their low cost and environmentally acceptable process compared to conventional technologies such as distillation and evaporation which usually suffer from disadvantages such as high cost and their requirement for the use of chemicals that need special handling [1]. Even though these are remarkable features, there is still a need to test a new generation of membranes that may offer more effective solutions to the problems associated with fouling, short service lifetimes and low chemical selectivity [2]. One such material is carbon nanotubes (CNTs), which have exhibited a combination of exceptional mechanical, thermal and electrical properties [3]. Carbon nanotube buckypapers have unique properties such as natural hydrophobicity, high porosity and very high specific surface area, making them promising candidates for separation applications [4].

The separation process of components through a membrane is governed by one or more

mechanisms, including adsorption and size exclusion [5-7]. Adsorption is a dominant mechanism to retain organic contaminants utilizing CNTs. This mechanism is often governed by the relative hydrophilicity or hydrophobicity of the membrane surface, and hydrogen bonding as well as other interactions between solutes and the membrane [8]. It has been found that CNTs are superior adsorbents for removing many kinds of organic contaminants, for instance volatile organic compounds [6, 7], trihalomethanes [9, 10], organic dyes [11], xylene [12], natural organic matter [13], phenols [11], trace polycyclic aromatic hydrocarbons [14] and pesticides [15]. On the other hand, electrostatic repulsion and size exclusion mechanisms govern the rejection of positively charged organic contaminants. The size exclusion mechanism occurs when the solutes size is larger than the pore size of the membrane; as a result contaminants are removed effectively by a sieving mechanism [16, 17]. In the electrostatic repulsion mechanism, the separation results from the electrostatic interactions between ions and the negatively charged MWCNT membrane [18].

The aim of this study was to investigate the removal of VOCs by using a dead-end filtration cell setup. Experiments were conducted using a buckypaper (BP) created using MWCNT-Trix 1% (w/v) dispersion. Twenty one VOCs with molecular weights between 78.11 g/mol (benzene) and 260.76 g/mol (hexachlorobutadiene) were designated as model organic contaminants because of their widespread occurrence in surface and groundwater. Removal efficiency by the dead-end filtration cell setup was linked to the

physicochemical properties of these compounds and focused on the ability and effectiveness of this kind of treatment.

1.1 Study area

In this study contaminated groundwater samples were collected from Botany Bay (Sydney, Australia). In the Botany area samples have been collected from two contaminated sites, namely EWB10D and EWB13D (Fig. 1).

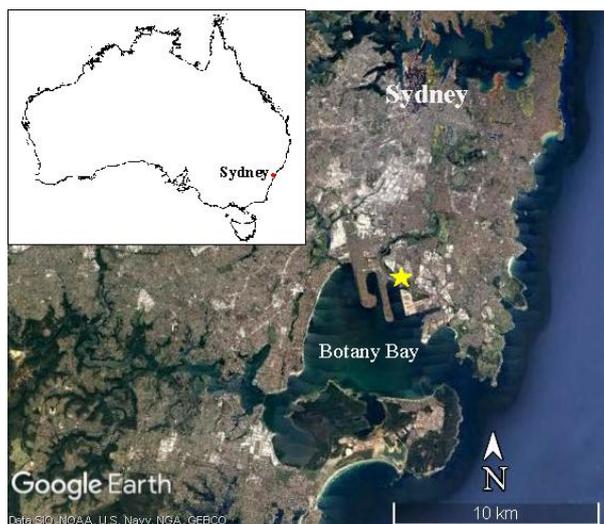


Fig. 1: Image illustrates sample sites (yellow star) in the Sydney (Botany Bay), Australia.

II. MATERIALS AND METHODS

2.1. Dead-end filtration cell setup

A laboratory-scale, dead-end filtration cell was constructed for this study (Fig. 2). The cell had an effective membrane area of 4.68 cm² (1.8 cm x 2.6 cm). The dead end filtration cell setup was completely sealed throughout the experiment to avoid evaporation compounds. Each experiment used 2 L of sample as the feed solution. Following setup, the dead-end filtration system operated for 8 hours in each experiment to collect an adequate amount of permeate (40 mL - two duplicates)

which was analysed to determine the removal efficiency of this system. Compressed air, controlled via an air pressure gauge, was used to force water from the steel reservoir through the cross-flow cell and over the surface of the buckypaper. The flux across the buckypaper was measured by recording the mass of water that passed through the membrane as a function of time using a computer-controlled balance (Mettler-Toledo AB2 with Balancelink software).

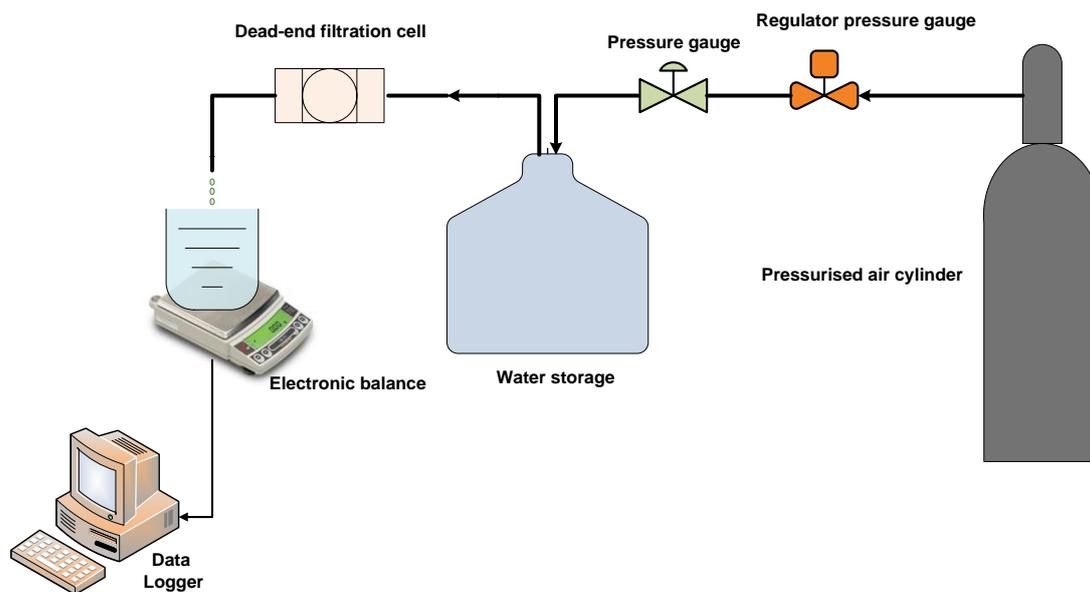


Fig. 2: Schematic diagram of the laboratory-scale dead end filtration cell setup.

2.2. Carbon nanotube (CNT) membrane

The CNTs used in this investigation were mainly multi-walled thin nanotubes, with 95% C purity, supplied by Nanocyl (Nanocyl-3100). Triton X-100 (T9284; [19]) was supplied by Sigma Aldrich. Dispersion was prepared using Milli-Q water (18 MΩ cm). A hydrophilic 0.22 μm cellulose nitrate [20] membrane filter

was provided by Millipore. Only one type of membrane was used as the support material for the preparation of the buckypapers in this project. Small, circular buckypapers were made using polytetrafluoroethylene (PTFE) membranes of ~4.5 cm diameter (with 0.22 μm pores). Physical properties of the buckypapers are illustrated in Table 1.

Table 1: 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.

Membrane	Tensile strength (MPa)	Young's modulus (GPa)	Ductility (%)	Thickness (μm)	Electrical conductivity (S/cm)	Resistant (Ω)	Contact angle (°)
MWNT/Triton X-100	3.4 ± 0.8	0.4 ± 0.2	2.4 ± 0.2	48 ± 2	56 ± 3	5.4 ± 0.3	50.7 ± 4

2.3. MWNT membrane characterisation

An important step that should be considered before the preparation of a buckypaper is to optimise the sonication time used for preparing the CNT dispersion from which the buckypaper will be made. The reason is that the energy input during the sonication process could lead to shorter CNTs and subsequently will unfavourably impact the mechanical and electrical properties of the resulting buckypaper. Therefore, UV-vis-NIR spectra of the dispersion (Triton-X) was acquired between 1000 and 300 nm using a Cary 500 UV-vis-NIR spectrophotometer.

The surface morphology and cross-section of buckypapers was examined using a JEOL JSM-7500FA field-emission scanning electron microscope (SEM). The surface morphology and

distribution of organic compounds deposited on the membrane surface were examined using field-emission SEM on a JEOL JSM-7500FA - (BRUKER-QUANTAX 400), with additional semi-quantitative energy dispersive spectrometer (EDS) analysis.

The contact angles of MWNT buckypapers were measured using the sessile drop technique on a custom device developed by R. Taylor utilising a Dinolite am-211 digital microscope. The contact angles of 2 μL Milli-Q water droplets on the surfaces of the buckypapers were computed utilizing the accompanying Data Physics software (SCA20.1). The mean contact angle was computed using measurements performed on at least five water droplets.

The mechanical properties of buckypapers were measured by using a Shimadzu EZ-S universal testing device with the buckypaper samples cut into small rectangular strips measuring 15 mm by 3 mm and attached into a small paper frame. Five different strips were used to determine the tensile strength of buckypapers. The distance between the top and bottom of buckypaper strips was kept constant at 10 mm. The paper frame was cut between the clamps prior to testing, and the attached samples were then stretched by means of a 10 N load cell, at a strain rate of 1 mm min⁻¹ until failure. The electrical properties of buckypaper samples were examined according to a standard two-point probe technique [21].

Triton-X-100 buckypapers were subjected to BET (Brunauer, Emmett, Teller) analysis to evaluate the surface area of the buckypapers. The samples were annealed underneath argon to burn off the surfactant and cut into small pieces, before being tested using a Micrometric ASAP2010 and a Micrometric ASAP2400.

2.4 Model organic contaminants

Sixteen compounds were used in this study to represent the major organic groups

considered contaminants in groundwater samples – namely volatile organic compounds (e.g. dichloromethane, trichloroethylene, tetrachloroethylene, toluene and benzene). The analysis of these compounds was also based on their widespread occurrence in groundwater and their diverse physicochemical properties (e.g. hydrophobicity and molecular size). Key physicochemical properties of these organic contaminants are shown in (Table 2). The volatile organic compounds had molecular weights between ranging 78.11 g/mol (benzene) and 167.85 g/mol (1,1,2,2-tetrachloroethane). The intrinsic hydrophobicity of these compounds varied significantly, as was reflected by the values of their octanol-water partitioning coefficient (Log K_{ow}) or Log K_{ow} at specific pH (Log D). As can be seen in Table 2, the properties of the selected volatile organic compounds demonstrated that some compounds are hydrophilic (Log D > 2.5) while others are hydrophobic (Log D < 2.5) and ranged between 1.40 and 3.07 (log D at pH 7 and 8). However, most volatile organic compounds which were examined in this study are hydrophobic (Log D < 2.5).

Table 2: Summary of relevant physiochemical properties of selected volatile organic compounds

Compound	CAS no.	Formula	MW (g/mol)	Log K _{ow} ^a	Log D ^a at pH 7	Log D ^a at pH 8
Vinyl chloride (Chloroethene)	75-01-4	C ₂ H ₃ Cl	62.50	1.69	1.69	1.69
1,1-Dichloroethene	57-53-4	C ₂ H ₂ Cl ₂	96.94	2.05	2.05	2.05
DCM: Dichloromethane	75-09-2	CH ₂ Cl ₂	84.93	1.40	1.40	1.40
cis-1,2 Dichloroethene	156-59-2	C ₂ H ₂ Cl ₂	96.94	2.14	2.14	2.14
1,1-Dichloroethane	75-34-3	C ₂ H ₄ Cl ₂	98.96	1.76	1.76	1.76
Chloroform	67-66-3	CHCl ₃	119.38	1.94	1.94	1.94
1,1,1-Trichloroethane	71-55-6	C ₂ H ₃ Cl ₃	133.40	2.35	2.35	2.35
CTC: Tetrachloromethane (Carbon Tetrachloride).	56-23-5	CCl ₄	153.82	2.92	2.92	2.92
1,2-Dichloroethane	107-06-2	C ₂ H ₄ Cl ₂	98.96	1.65	1.65	1.65
Benzene	71-43-2	C ₆ H ₆	78.11	2.18	2.18	2.18
TCE: Trichloroethylene (Trichloroethene)	79-01-6	C ₂ HCl ₃	131.39	2.57	2.57	2.57
Toluene	108-88-3	C ₇ H ₈	92.14	2.72	2.72	2.72
1,1,2-Trichloroethane	79-00-5	C ₂ H ₃ Cl ₃	133.40	1.92	1.92	1.92
PCE: Tetrachloroethylene (Tetrachloroethene or Perchloroethene)	127-18-4	C ₂ Cl ₄	165.83	3.07	3.07	3.07
1,1,2,2-Tetrachloroethane	79-34-5	C ₂ H ₂ Cl ₄	167.85	2.33	2.33	2.33

^a Reference source: SciFinder Scholar, data calculated using Advanced Chemistry Development (ACD/Labs) Software V8.14 for Solaris (1994–2007 ACD/Labs).

2.5. Volatile organic compounds analysis

All samples collected before and after using the NF/RO filtration system were analysed at ORICA Botany Environmental Laboratories. VOCs were analysed using a Shimadzu purge and trap/gas chromatography/mass spectrometer detector based

on USEPA methods 5030 and 8260. Method 5030 can be utilised for most volatile organic compounds that have boiling points below 200°C and are insoluble or somewhat soluble in water. This method can include volatile water-soluble compounds; nevertheless, quantification limits (by

GC or GC/MS) are roughly ten times higher due to poor purging efficiency [22]. On the other hand, method 8260 is utilised to determine volatile organic compounds in a range of solid waste matrices. This method is appropriate for nearly all types of samples, irrespective of water content, containing numerous air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils and sediments [23]. This method has an inert gas bubbled through a portion of the aqueous sample at room temperature, and the volatile components are efficiently conveyed from the aqueous phase to the vapor phase. In the subsequent step, the vapor is swept through a sorbent column where the volatile

components are adsorbed. After purging is finished, the sorbent column is heated and back flushed with inert gas to desorb the components onto a gas chromatographic column [22].

2.6. Analysis of basic water parameters

The temperature, turbidity, dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS), salinity, density, (SG) and redox (water quality parameters) were measured using Water Quality Analyser-MODEL 516 during sampling (see Table 3 and Table 4). On the other hand, the temperature, conductivity and pH were measured using an Orion 4-Star Plus pH/conductivity meter in all experiments. The measurements were applied at 0 time, one hour and at 8 hours for each experiment.

Table 3: Water quality parameters for samples which were collected from EWB10D at Southlands-Botany Bay

Depth (m)	Turbidity (ntu)	Dissolved Oxygen (mg/l)	Electrical conductivity (µS/cm)	Total Dissolved Solids (g/l)	PH	Temperature (°C)	Senility (ppt)	Density (g/cm ³)	SG (t/m ³)	Redox (mV)
6.7	19.5	3.78	4270	3.73	4.6	22.03	2.28	999	1.000	- 107

^aAll data were obtained using Water Quality Analyser (MODEL 516).

Table 4: Water quality parameters for samples which were collected from EWB13Dat Southlands-Botany Bay

Depth (m)	Turbidity (ntu)	Dissolved Oxygen (mg/l)	Electrical conductivity (µS/cm)	Total Dissolved Solids (g/l)	PH	Temperature (°C)	Senility (ppt)	Density (g/cm ³)	SG (t/m ³)	Redox (mV)
4.49	19.5	3.78	1553	1.37	4.4	22	0.60	997	0.998	- 193

^aAll data were obtained using Water Quality Analyser (MODEL 516).

2.7. The dead-end filtration experimental protocol

Typically, the dead end filtration system does not need the high pressure as used in pressure driven membrane (such as RO/NF filtration system) and the appropriate pressure for this type of membrane is often less than 1 kPa. The cross-flow cell used in this study has an effective membrane area of 6 cm² (2 cm × 3 cm) with a channel height of 2 mm supported by a layer made from stainless to support this membrane. The system was completely sealed to avoid evaporation of compounds. Only 2 L of a solution containing contaminated

groundwater was used as feed solution after filtration using a StericupDuraporeTM 0.45 µm Millipore filtration to investigate the removal volatile organic compounds. Permeate and feed samples of 40 mL (two duplicates) were collected after 1 hour and at 8 hours of filtration to analyse volatile organic compounds. All samples collected from both feed and permeate were sent immediately to ORICA Botany Environmental Laboratories for analysis. The rejection rate is defined by the equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\%$$

where C_p and C_f are the permeate and the feed concentrations, respectively.

III. RESULTS AND DISCUSSION

3.1. SEM-EDS and AFM analysis

Average roughness was studied by 3D topographic analysis (see Figs 3 and 4). The AFM image (Fig.3) of the carbon nanofibrous films shows that the vertically aligned CNTs have an average diameter of ~294 nm and length of 10 μm . In this image, the brightest area presents the highest point of the membrane surface and the dark regions indicate valleys and this can be seen clearly in Fig. 5[24]. The amount of MWCNTs in the composite membrane is an important factor

affecting the morphology, so the image in Fig.3 indicates that the roughness of the membrane was somewhat smoothed by adding 0.1 wt % MWCNT to the composite membrane. This result supports the conclusion reached in a previous study [18]. In this later study the roughness of the MWCNT membrane was reduced by adding 0.04 wt % MWCNT to the polymer matrix. Following that, the roughness increased significantly after adding 0.2 wt % and once again reduced by adding 0.04 wt %.

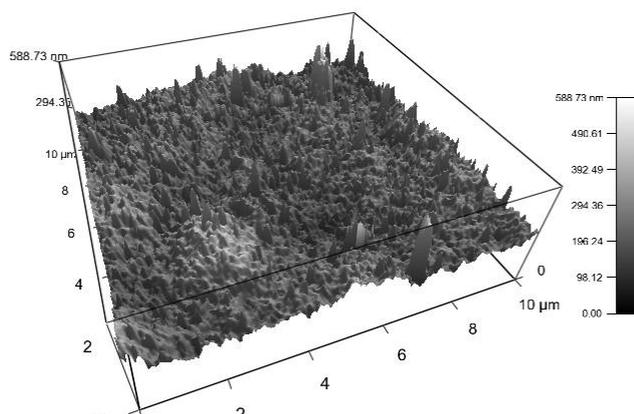


Fig. 3: Surface topography image of MWCNT/Triton X-100 buckypaper.

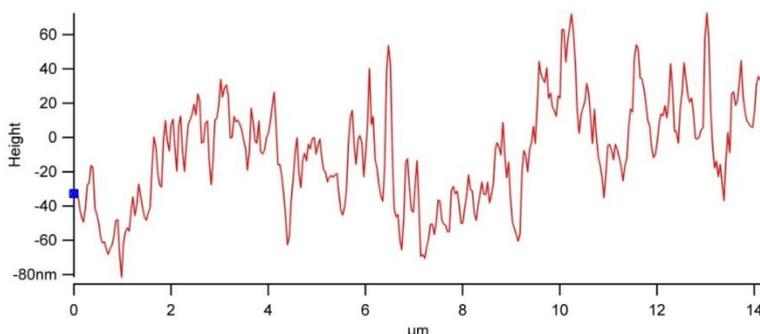


Fig.4: Section graph of MWCNT/Triton X-100 buckypaper.

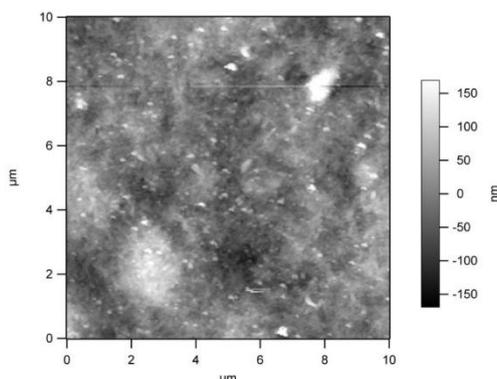


Fig. Error! No text of specified style in document.: Plan view image of SIM membrane surfaces reconstructed from AFM roughness statistics for MWCNT/Triton X-100 buckypaper.

The surface morphology and cross-section of MWCNT buckypapers was studied using a JEOL JSM-7500FA field-emission scanning electron microscope (SEM). Fig. 6 shows SEM images of MWCNT buckypapers prepared using Triton X-100 before (virgin) and after use (fouled) membrane. The surface morphology of the MWCNT buckypaper seems to show small bundles of tubes and an abundance of small pores (Fig. 6A)

and this agrees well with the results of a study conducted by Cottinet et al. [25]. Also from Fig. 6A, it can be seen that the buckypapers are composed of randomly dispersed MWCNTs, which tangle through the van der Waals force and form a uniform porous structure. On the other hand, it was observed that some flattening of the MWCNT bundles occurred in Fig. 6B and 6C due to adsorption of contaminants.

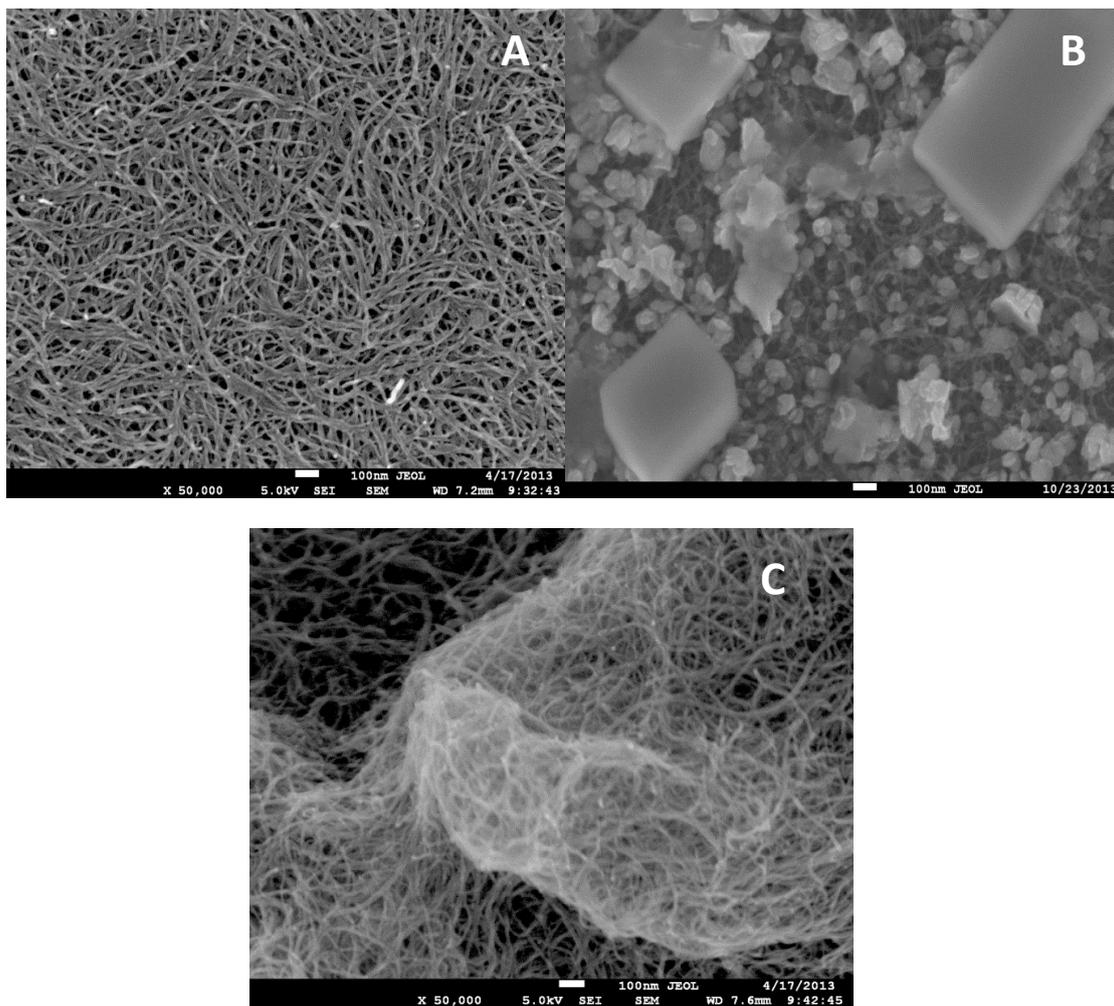


Fig.6: SEM images of the (A) virgin MWCNT buckypaper; (B) MWCNT buckypaper membrane fouled by EWB10D and (C) MWCNT buckypaper membrane fouled by EWB13D at Sutherland Botany Bay.

Furthermore, the cross-sectional images of MWCNT buckypapers show clearly what has been seen above, where Fig. 7A, 7B and 7C show the structure and size of the tubes and pores in the MWCNT membrane as well. As seen Fig. 7A, MWCNT buckypapers appear to consist of small bundles of tubes and an abundance of small pores. In contrast, the MWCNT bundles were flattened after the MWCNT buckypaper membranes were used due to adsorption of

pollutants (Fig. 7B and 7C). Moreover, from Fig. 6A it is clear that the MWCNT buckypaper membrane possesses a large number of regularly sized pores, with software image analysis [using a JEOL JSM-7500FA field-emission SEM] revealing an average surface pore diameter of 65.6 ± 2 nm which is similar to that obtained previously for comparable buckypapers produced using MWCNTs [26, 27].

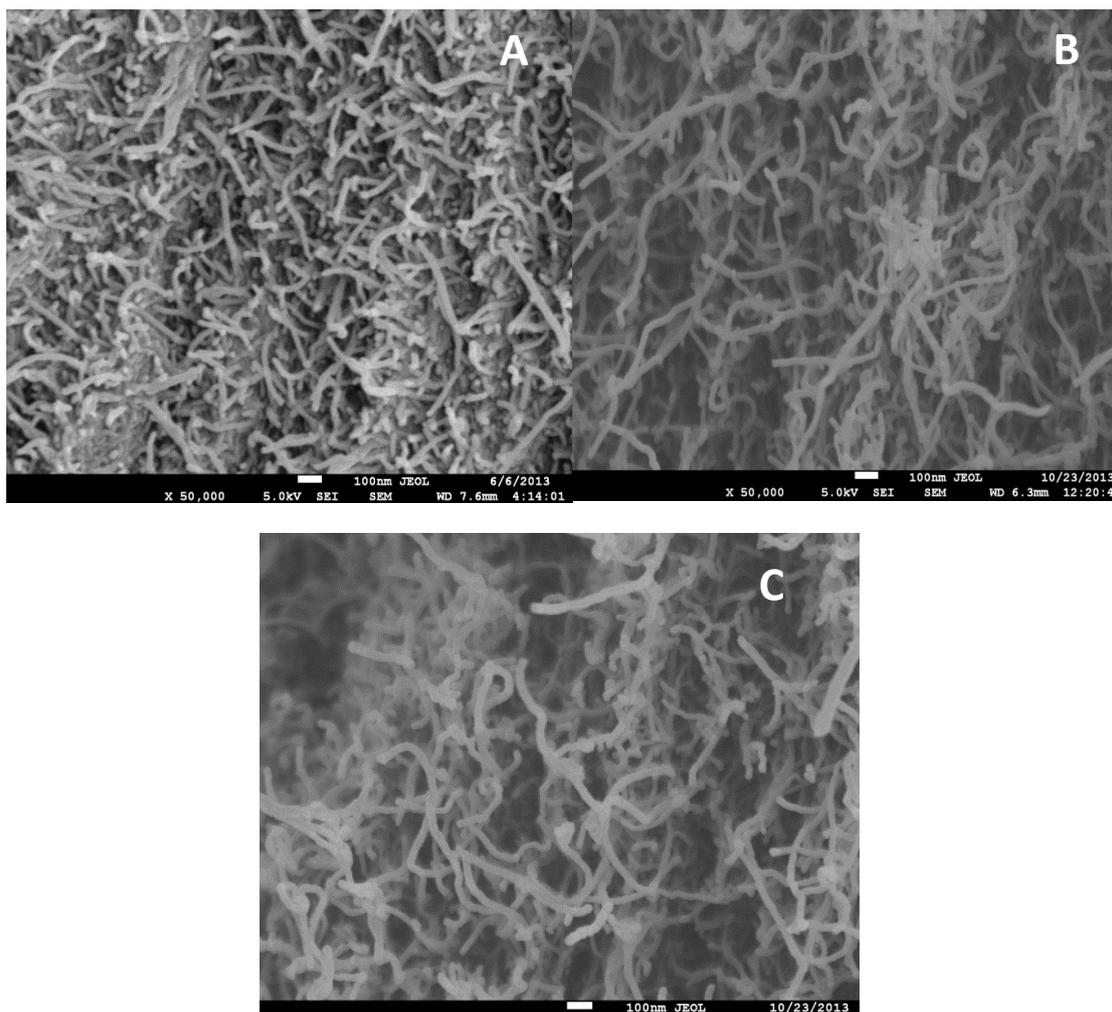


Fig.7: SEM images cross-section (A) virgin MWCNT buckypaper; (B) MWCNT buckypaper membrane fouled by EWB10D and (C) MWCNT buckypaper membrane fouled by EWB13D at Sutherland Botany Bay.

To investigate the distribution of elements deposited on the membrane surface, MWCNT buckypapers were also analysed using SEM with additional semi-quantitative energy dispersive spectrometer (EDS). SEM-EDS images obtained for MWCNT buckypaper virgin and fouled membranes are shown in Figs 8, 9 and 10. The EDS spectrum of MWCNT buckypapers (Fig. 8) shows peaks corresponding to titanium and aluminum in addition to the high amount of carbon and a reasonable amount of oxygen as parts of the membrane composition which therefore were detected in all samples (virgin and fouled). The presence of aluminum and titanium is not surprising as these elements are used during the synthesis of MWCNTs via the Nanocyl process. Also the presence of iron (Fig. 10)

is not surprising as iron catalysts are used during synthesis of MWCNTs via the Nanocyl process. The amount of chlorine found was high in MWCNT membrane fouled by EWB10D and somewhat higher in MWCNT membrane fouled by EWB13D and this can be attributed to the rejection process for this compound by the size exclusion mechanism (see Fig. 9 and 10). A small level of calcium was found in the fouled membrane (Fig. 9) due to the ability of calcium to complex with carboxyl groups which are very common at the surface of MWCNTs. A considerable amount of sodium and sulphate was found in the fouled membranes (Figs 9 and 10) and this can be attributed to the rejection process for these cations via the size exclusion mechanism and consequent diffusion in the membrane surface [28].

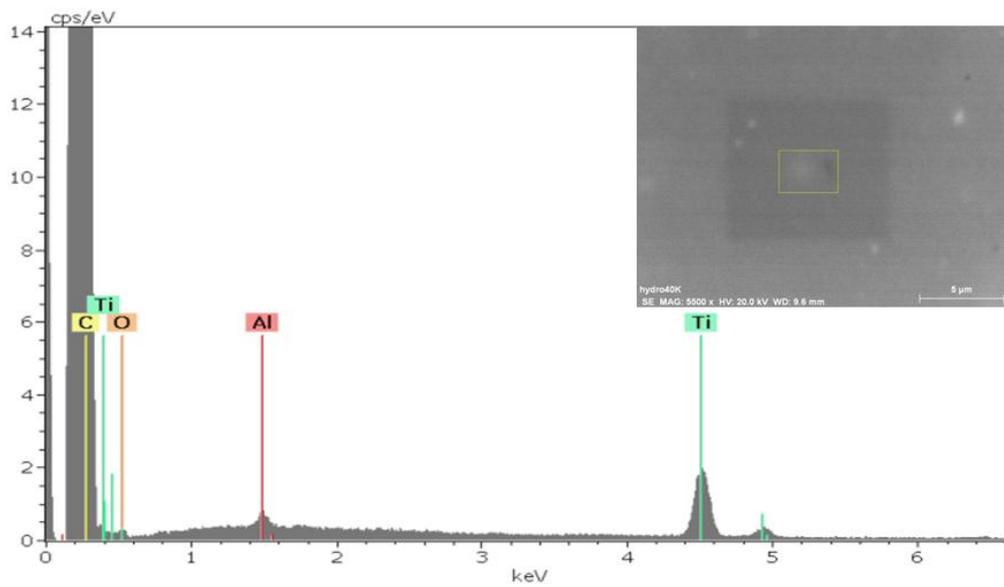


Fig.8:EDS data of the virgin MWCNT/Triton X-100 buckypaper membrane.

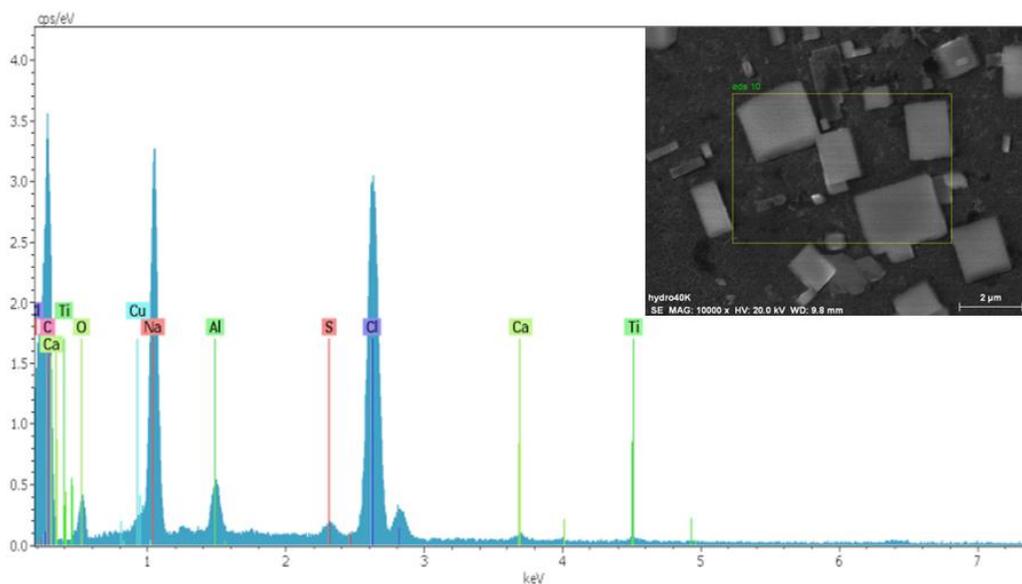


Fig.9:EDS data of the MWCNT/Triton X-100 buckypaper membrane fouled by EWB10D.

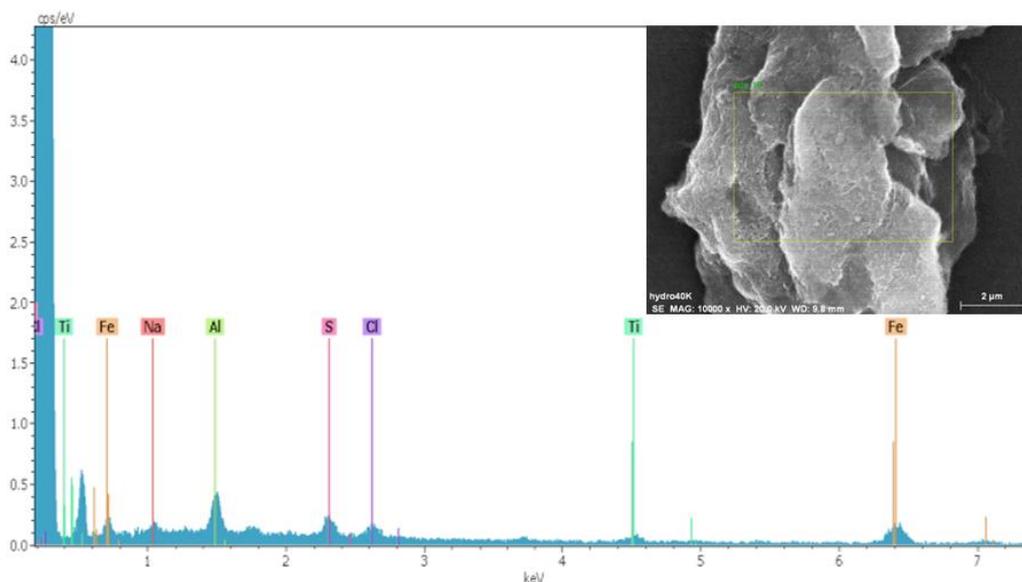


Fig.10:EDS data of the MWCNT/Triton X-100 buckypaper membrane fouled by EWB13D.

3.2. Removal of volatile organic compounds by MWCNT buckypaper membrane

To examine the ability of MWCNT buckypaper membranes to remove volatile organic compounds from contaminated groundwater, several experiments were conducted for samples collected from EWB10D and EWB13D at Southlands-Botany Bay.

3. 2. 1. EWB10D at Southlands Botany Bay

The removal efficiency of MWCNT buckypaper membrane for EWB10D is reported in Table 5 and Fig. 11. Because of strong van der Waals interactions, MWCNT adhere to each other and form bundles, and the space between the bundles can be considered as pores, which provided more adsorption sites. Consequently, MWCNT exhibited higher adsorption efficiency for VOCs to some extent, however it still less than the efficiency of pressure driven membranes (RO/NF) in rejecting VOCs. It was remarkable that the performance of MWCNT buckypaper membranes in rejecting hydrophilic compounds [(Log D > 2.5), carbon tetrachloride, trichloroethylene and tetrachloroethylene] was higher than hydrophobic compounds [(Log D < 2.5), for other VOCs which are demonstrated in Table 5]. According to Nghiem et al. [29] the removal of some hydrophobic compounds can be much lower than that predicted based only on a steric hindrance transport model. It can be explained that hydrophobic compounds can adsorb on a MWCNT membrane and then diffuse

through the bundles, resulting in significant transport of these compounds across the bundles and the space between the bundles which can be considered as pores. On the other hand, because hydrophilic compounds do not adsorb to the MWCNT membrane, hydrophilic VOCs can be effectively rejected by MWCNT membranes using size exclusion mechanism or through the non-electrostatic interactions which include hydrophobic interactions and hydrogen bonding. These results also support the findings from other previous studies [30, 31].

It is notable that the highest rejection achieved by a MWCNT buckypaper membrane was for tetrachloroethylene when it reached 88.5 % whereas the lowest rejection achieved by MWCNT buckypaper membrane was for 1,1,2-trichloroethane that amounted to 27.6 %. According to [32] tetrachloroethylene has the highest Log D of the model foulants (3.07) and consequently it is considered to be a hydrophilic compound and it can be effectively rejected by a MWCNT buckypaper membrane using steric hindrance or size exclusion mechanisms, while the Log D of 1,1,2-trichloroethane was (1.92) and it is classified as a hydrophobic compound and it can adsorb onto a MWCNT buckypaper membrane and then diffuse through the bundles, resulting in the lower removal for this compound compared to tetrachloroethylene.

Table Error! No text of specified style in document.: Overall removal efficiency of the selected volatile organic compounds (VOCs) which were detected in EWB10D at Sutherland-Botany Bay.

Compound Name	Rejection @ 8hr-MWCNT (%)
Vinyl Chloride	69.2
1,1-Dichloroethene	75.0
Dichloromethane	62.5
trans-1,2-Dichloroethene	82.4
1,1-Dichloroethane	66.0
cis-1,2-Dichloroethene	67.4
Chloroform	61.1
1,1,1-Trichloroethane	40.0
Carbon tetrachloride	87.8
1,2-Dichloroethane	45.5
Benzene	70.0
Trichloroethylene	82.6
1,1,2-Trichloroethane	39.1
Tetrachloroethylene	88.5
Chlorobenzene	60.0
1,1,2,2-Tetrachloroethane	45.0
Hexachlorobutadiene	50.0

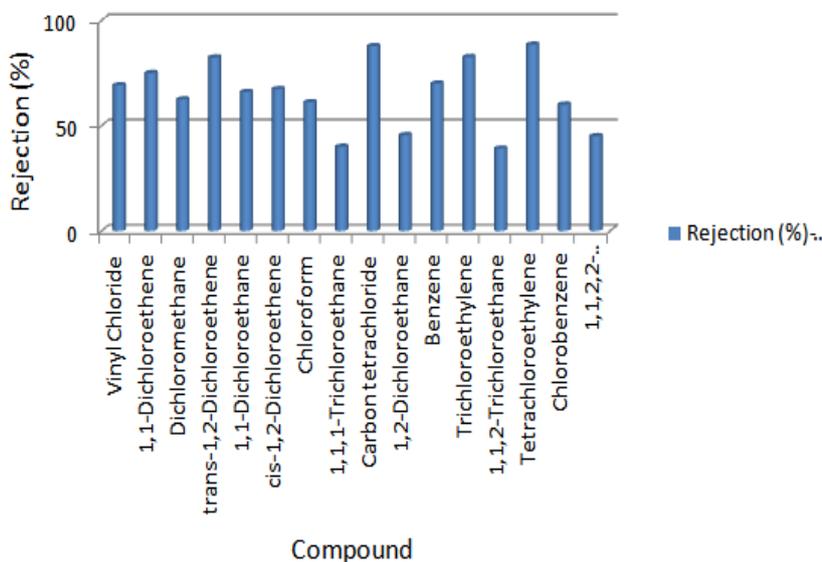


Fig. 11: Overall removal efficiency of the selected VOCs which were detected in contaminated groundwater at EWB10D. MWCNT/Triton X-100 buckypaper membrane filtration experiment was conducted at 140 kPa. Samples were collected after 8 hours of filtration.

3. 2. 2. EWB13D at Southlands Botany Bay

The removal efficiency of the MWCNT buckypaper membrane for EWB13D is reported in Table 6 and Fig. 12. It is clear that the removal efficiency of MWCNT here is less than its

efficiency when used to retain the VOCs detected in the EWB10D site. The results presented in Table 6 and Fig. 12 confirm the results given in 3.2.1; nevertheless there are some differences between them based on the difference in concentrations of model foulants at this site compared with the

previous site (EWB10D). It was noteworthy that the performance of the MWCNT buckypaper membrane in rejecting hydrophilic compounds (tetrachloroethylene, carbon tetrachloride, trichloroethylene and trichloroethylene) was higher than for hydrophobic compounds (the other VOCs which are shown in Table 6). The reason for this phenomenon has been explained above in part 3.2.1 [29].

The highest rejection achieved by a MWCNT buckypaper membrane was for tetrachloroethylene that reached 77.3 % whereas the lowest rejection achieved by MWCNT buckypaper membrane was for 1,2-dichloroethane that reached 33.1 %. It can be elucidated that tetrachloroethylene has the highest Log D of the model foulants (3.07) and thus it is classified as a hydrophilic compound and it can be effectively rejected by a MWCNT buckypaper membrane using size exclusion mechanisms or through the non-electrostatic interactions which include

hydrophobic interactions and hydrogen bonding, while the Log D of 1,2-Dichloroethane was only 1.65 and it is considered to be a hydrophobic compound and it can adsorb onto the MWCNT buckypaper membrane and then diffuse through the bundles, resulting in the lower removal for this compound compared to tetrachloroethylene [32].

Lastly, it is observed that the rejection rates for VOCs at both sites EWB10D and EWB13D do not reach as high a value after using a MWCNT membrane compared to a pressure driven membrane (RO/NF). This can be attributed to the pore diameter of MWCNT (24 ± 1) which is large and consequently allows some contaminants to pass through the MWCNT membrane. Remarkably, the small and precise diameter size of CNTs is demonstrated to reject most ions because of the energy barrier present at the channel entries and therefore only water molecules are allowed to pass through the nanotube hollows [33, 34].

Table 6: Overall removal efficiency of the selected organic compounds (VOCs) which were detected in EWB13D at Sutherland Botany Bay.

Compound Name	Rejection @ 8hr-MWCNT (%)
Vinyl Chloride	66.7
1,1-Dichloroethane	50.0
cis-1,2-Dichloroethene	57.1
Chloroform	45.8
Carbon tetrachloride	75.0
1,2-Dichloroethane	33.1
Benzene	50.0
Trichloroethylene	74.2
1,1,2-Trichloroethane	40.0
Tetrachloroethylene	77.3
1,1,2,2-Tetrachloroethane	33.3

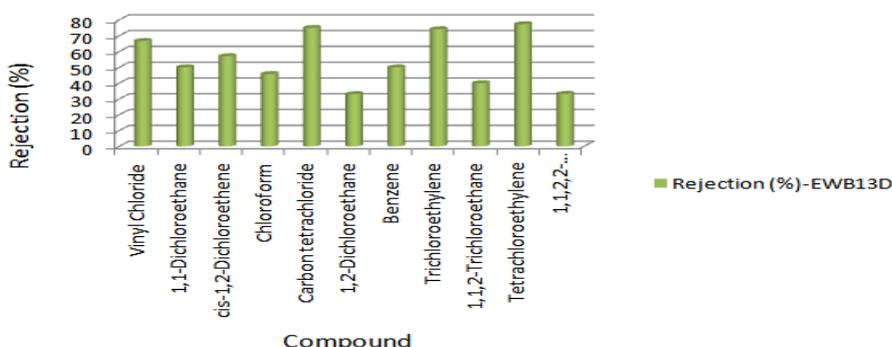


Fig.12: Overall removal efficiency of the selected VOCs which were detected in contaminated groundwater at EWB13D. MWCNT-Triton-X-100 buckypaper membrane filtration experiment was conducted at 140 kPa. Samples were collected after 8 hours of filtration.

3. 3. Performance of MWCNT buckypaper membrane

To examine the performance of MWCNT buckypaper membranes, it is essential to study the membranes permeate flux as a function of filtration time for samples that were collected from two different sites (EWB10D and EWB13D) from the Southlands Botany Bay contaminated groundwater.

3. 3. 1. EWB10D at Southlands-Botany Bay

Fig. 13 displays the evolution of the membrane permeate flux as a function of filtration time. As seen in this figure, it is observed that flux was excellent during use of a MWCNT buckypaper and this is illustrated clearly by the continued linear and constant flux throughout the duration of the experiment. It can be explained that samples at this site were collected from wells; this means that the colloidal and suspended substances existing in these waters were few and as a result gave a high efficiency for this membrane. Another reason for explaining this phenomenon is the critical pore diameter of CNTs. Many previous studies indicate

that there is a critical pore diameter of $\sim 7 \text{ \AA}$ (0.7 nm), above which ions and water will pass but below which they will not [35-38]. Particularly, the pore diameter of MWCNT in this study was above 7 \AA ($\sim 28 \text{ nm}$) and that means the MWCNT passed water and some contaminants according to this theory. Furthermore, the results in Fig. 13 revealed that the value of flux was high, linear and stable when a MWCNT buckypaper was used as a membrane and ranged between $\sim 115\text{-}118 \text{ L.m}^2\text{.h}$. Compared to NF-90 and ESPA2 membranes, the flux through these membranes was roughly half the flux of the MWCNT membrane and ranged between $\sim 35\text{-}52.6 \text{ L.m}^2\text{.h}$ (in case of NF-90 membrane) and $\sim 51.7\text{-}52.6 \text{ L.m}^2\text{.h}$ (in case of ESPA2 membrane)[40]. This can be explained by the porosity of the MWCNT membrane ($\sim 28 \text{ nm}$) being greater than the porosity of the NF-90 and ESPA2 membranes (0.68 nm and non-porous respectively) and this also confirms what has been inferred above.

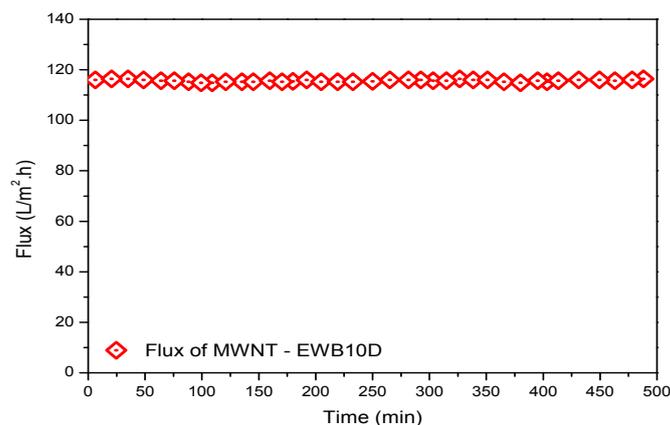


Fig.13: Permeate flux of MWCNT buckypaper membrane as a function of filtration time. Experiment was conducted at 140 kPa. Samples were collected after 8 hours of filtration.

3. 3. 2. EWB13D at Southlands-Botany Bay

Fig. 14 shows the evolution of the membrane permeate flux as a function of filtration time for EWB13D. The findings shown in Fig. 14 confirm the results concluded for EWB10D. Also here it is observed that the flux was exceptional during the use of the MWCNT buckypaper and this is demonstrated clearly by the continued linear and constant flux during filtration time as explained in the previous section. Additionally, the results in Fig. 14 revealed that the flux was high, linear and stable when the MWCNT buckypaper was used as a membrane and ranged between $\sim 116\text{-}119 \text{ L.m}^2\text{.h}$. In contrast, the flux was somewhat lower and not as stable when NF-90 and ESPA2 were used as membranes to separate VOCs from contaminated samples; they ranged between $\sim 27\text{-}52.6 \text{ L.m}^2\text{.h}$ and $\sim 45\text{-}52.6 \text{ L.m}^2\text{.h}$, respectively [40]. This can be attributed to the fact that the porosity of MWCNT membrane was high (28 nm) compared to the low porosities of the NF-90 and ESPA2 membranes (0.68 nm and non-porous respectively). This is fully consistent with many previous studies, which see pore size of the membrane playing a significant role in determining the membrane performance, in particular the flux [1, 33, 39].

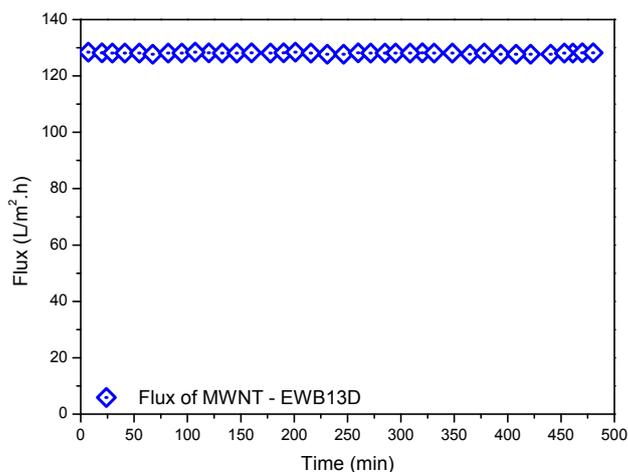


Fig.14: Permeate flux of MWCNT buckypaper membrane as a function of filtration time. Experiment was conducted at 140 kPa. Samples were collected after 8 hours of filtration.

IV. CONCLUSIONS

Results reported in this study indicate that MWCNT exhibited higher adsorption efficiency for VOCs to some extent, nevertheless it still less than the efficiency of NF-90 and ESPA2 membranes in rejecting VOCs [40]. It was noteworthy that the performance of MWCNT buckypaper membranes in rejecting hydrophilic compounds (carbon tetrachloride, trichloroethylene and tetrachloroethylene) was higher than hydrophobic compounds (the other VOCs which are examined in this study). This is because hydrophobic compounds can adsorb onto MWCNT membranes and then diffuse through the bundles, causing significant transport of these compounds across the bundles and the spaces between the bundles which can be considered as pores. Conversely, because hydrophilic compounds do not adsorb onto the MWCNT membrane, hydrophilic VOCs can be effectively rejected by a MWCNT membrane using size exclusion mechanisms or through the non-electrostatic interactions which include hydrophobic interactions and hydrogen bonding. The results in this study revealed that the highest value of rejection was for tetrachloroethylene that reached 88.5 % while the lowest rejection achieved by MWCNT buckypaper membrane was for 1,1,2-trichloroethane that amounted to 27.6 % and these values depend on the hydrophobicity and hydrophilicity of the compounds.

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