# Rehabilitation of Contaminated Surface and Groundwater for Selected Sites in the Illawarra and Sydney Regions Utilising Nanotechnology

Hamad N. Altalyan, Brian G. Jones, John Bradd

Abstract-A comprehensive study was conducted to examine the removal of inorganic contaminants that exist in surface and groundwater in the Illawarra and Sydney regions. The ability of multiwalled carbon nanotubes (MWCNT), as a generation of membrane technology, was examined using a dead-end filtration cell setup. A set of ten compounds were examined in this study that represent the significant inorganic cations and anions commonly found in contaminated surface and groundwater. The performance of MWCNT buckypaper membranes in excluding anions was found to be better than that of its cation exclusion. This phenomenon can be attributed to the Donnan exclusion mechanism (charge repulsion mechanism). Furthermore, the results revealed that phosphate recorded the highest exclusion value reaching 69.2%, whereas the lowest rejection value was for potassium where no removal occurred (0%). The reason for this is that the molecular weight of phosphate (95.0 g/mol) is greater than the molecular weight of potassium (39.10 g/mol).

*Keywords*—Nanotechnology, buckypaper, carbon nanotube, CNT, multi-walled carbon nanotube, MWCNT, Botany Bay, Russell Vale.

# I. INTRODUCTION

NANOTECHNOLOGY is a promising technology for use in the 21st century that can be applied in various environmental applications. Chemical and physical properties of nanomaterials assist in making this technology one of the leading technologies for water treatment [1], [2] and [3]. Particularly, carbon nanotubes (CNTs) have attracted significant growing attention because of their ability to exhibit superior durability and separation characteristics [4]. Their remarkable mechanical stability, exceptional electrical conductivity and thermal properties allow fluid flow through their interior [5], [6]. In particular, CNT buckypapers have exceptional properties such as natural hydrophobicity, high porosity and very high specific surface area, making them promising candidates for separation applications [7].

The separation of contaminants can be occurred by three mechanisms: adsorption, size exclusion and the electrostatic repulsion. According to [8], more than 95% of the emerging contaminants can be removed by adsorption. Typically, the separation of inorganic contaminants is attributed to size exclusion in addition to Donnan exclusion (a charge repulsion mechanism [9]-[12]). The size exclusion mechanism occurs when the solute size is greater than the pore size of the

membrane. Accordingly, contaminants are removed effectively by a sieving mechanism [11], [13]. The electrostatic repulsion mechanism is another key factor affecting the ability of a CNT membrane to separate charged solutes present in a mixture. According to this mechanism, the ion separation results from the electrostatic interactions between ions and the negatively charged MWCNT membrane [1]. On the other hand, adsorption is considered a dominant mechanism to retain some inorganic contaminants and it is a simple and efficient method for the removal of such contaminants from contaminated water [14]. 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 [14], [15].

The objective of this study was to examine the ability of MWCNT membranes (buckypapers) to remove inorganic contaminants from contaminated surface and groundwater. Experiments were conducted using laboratory-scale and synthesized MWCNT buckypapers. Ten inorganic compounds with molecular weights of less than 100 g/mol and a wide range of ionic and hydrated radii were selected as model inorganic contaminants due to their widespread occurrence in surface and groundwater. Removal efficiency for MWCNT buckypapers was associated with the physicochemical characteristics of inorganic contaminants that concentrate on the capability and effectiveness of this kind of treatment. Significant characterization work has been conducted in this paper to investigate MWCNT buckypaper membranes.

#### A. Study Area

In this study, samples were collected from a leachate pond at Russell Vale and the WGB32 borehole at Botany Bay in the Illawarra and Sydney regions, respectively (Fig. 1).

#### II. MATERIALS AND METHODS

### A. 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 cm<sup>2</sup> (1.8 cm x 2.6 cm). Each experiment used 2 L of sample as the feed solution. Before use, contaminated surface and groundwater samples were collected from a leachate pond at Russell Vale and the WGB32 at Botany Bay. They were

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filtered using a Stericup DuraporeTM 0.45  $\mu$ m (Millipore) filter for separation of colloidal and suspended materials. Following that, 2 L of each filtered sample was used as feed solution for each experiment. In the next step, the dead-end filtration system was operated for at least 24 hours in each experiment to collect an adequate amount of permeate (40 mL - two duplicates), which was then 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).

## B. CNT Membrane

The CNTs used in this investigation were mainly multiwalled thin nanotubes, with 95% C purity, supplied by Nanocyl (Nanocyl-3100). Triton X-100 (T9284, [16]) was supplied by Sigma Aldrich. Dispersion was prepared using milli-Q water (18 M $\Omega$  cm). A hydrophilic 0.22 µm cellulose nitrate [17] 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 I.

## C. MWCNT Membrane Characterization

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.



Fig. 1 Sample sites in the Illawarra (Russell Vale) and Sydney (Botany Bay) regions



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

TABLE I Physical Properties of Buckypapers

PHYSICAL PROPERTIES OF BUCKYPAPERS							
Membrane	Tensile strength (MPa)	Young's modulus (GPa)	Ductility (%)	Thickness (µm)	Electrical conductivity (S/cm)	Resistant ( $\Omega$ )	Contact angle (°)
MWCNT/Triton X-100	$3.4\pm 0.8$	$0.4\pm0.2$	$2.4\pm0.2$	$48\pm2$	$56\pm3$	$5.4\pm0.3$	$50.7\pm4$

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

The surface morphology and cross-section of the buckypaper were examined using a JEOL JSM-7500FA field-emission scanning electron microscope (SEM). Moreover, energy dispersive spectrometer (EDS) analysis was used to examine the distribution of organic compounds deposited on the membrane surface.

The contact angles of MWCNT 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  $\mu$ L milli-Q water droplets on the surfaces of each buckypaper 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 the 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 the buckypapers. The distance between the top and bottom of the 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 until failure. The electrical properties of the buckypaper samples were examined according to a standard two-point probe technique [18].

To investigate the pore structure and surface morphology of MWCNT buckypapers, Brunnauer, Emmett and Teller (BET) analysed the results of nitrogen adsorption/desorption measurements [19]. This allowed determination of the specific surface area of the buckypapers and the average pore diameter as well which exists throughout the samples. Table II shows surface pore diameter, buckypaper surface area, average internal pore diameter and average nanotube bundle of MWCNT buckypapers. If it is assumed that the surface area is related to the outer surface of large CNT bundles, then the bundle diameter (Dbun) can be calculated using (1):

$$A_s = \frac{4}{\rho N T^{D_{bun}}} \tag{1}$$

where As, Dbun and  $\rho$ CNT are the BET surface area, CNT bundle diameter, and nanotube bundle density (estimated as 1500 kg/m<sup>3</sup>), respectively [20].

	I ABLE II							
	D <sub>SEM</sub> S	D <sub>SEM</sub> Surface Pore Diameter Derived by Image Analysis of SEM Micrographs						
	Buckypaper	$D_{\text{SEM}}(\text{nm})$	ABET (m <sup>2</sup> /g)	DBET (nm)	Dbun (nm)	Interbundle pore volume (%)		
	MWCNT/Trix-100	$65.6\pm80$	$141\pm2$	$27.7\pm2$	$19\pm2$	$86.4\pm2$		
All other parameters are determined through analysis of results obtained from nitrogen adsorption/desorption isotherms.								

# D.Model Inorganic Contaminants

Ten compounds were chosen for this study to represent two major inorganic groups of concern in surface and groundwater samples - namely cations (e.g., mercury, sodium and calcium) and anions (e.g., chloride, nitrate and sulphate). The selection of these model inorganic compounds was also based on their widespread occurrence in aquatic resources and their diverse physicochemical properties (e.g., molecular weight, ionic hydrated radii and hydrophobicity). The main physicochemical properties of these inorganic constituents are shown in Table III. The selected inorganic contaminants include compounds with molecular weights in the range between 22.99 g/mol (paracetamol) and 96.06 g/mol. The retention of these compounds correlated with both charge and hydrated size. Therefore, multivalent ions with large hydrated radii (i.e., Ca2+ and SO42-) were retained more than monovalent ions with smaller hydrated radii (i.e., Cl<sup>-</sup>, K<sup>+</sup> and Na<sup>+</sup> [21], [22]). Additionally, the quantity of charge on the surface of the membrane impacts the degree of electrostatic repulsion and removal of negatively charged solutes [22].

TABLE III MOLECULAR WEIGHT, IONIC AND HYDRATED RADII FOR RELEVANT CATIONS

	A	ND ANIONS		
Ion	Molecular weight (g/mol)	Ionic radius (nm)	Hydrated radius (nm)	Ref.
$Na^+$	22.99	0.095	0.358	[23]
$Ca^{2+}$	40.08	0.100	0.412	[24]
$\mathbf{K}^+$	39.10	0.133	0.331	[23]
$Mg^{2+}$	24.31	0.065	0.428	[23]
$\mathrm{Hg}^+$	200.59	0.119	NA <sup>a</sup>	[25]
$SO_4^{2-}$	96.06	0.215	0.300	[26]
PO43-	95.0	0.223	0.339	[26]
NO <sup>3-</sup>	62.00	0.264	0.335	[23]
Cl	35.45	0.181	0.332	[23]
Br-	79.90	0.195	0.330	[23]

a NA: Not available.

All samples collected before and after filtration using the dead-end filtration system were analysed at Orica Australia Botany Environmental Laboratories. Cations, anions and mercury were analysed by using Inductively Coupled Plasma Optical Emission Spectrometry, Ion Chromatography, Flow Injection Mercury System, Gas Chromatography/Mass Spectrometer and Inductively Coupled Plasma (ICP-OES, IC, FIMS and GC-MS, ICP), respectively. Cations were digested with aqua regia at 95 °C for 2 hours and then analysed with a Perkin Elmer Optima 7000DV ICP-OES (inductively coupled plasma optical emission spectrometry) based on the US EPA Method 200.7. According to this technique, samples are nebulised and the consequent aerosol is transferred to the plasma torch. Production of specific emission spectra for any element is obtained by radio-frequency inductively coupled plasma. The spectra are distributed by a grating spectrometer, and the intensities of the line spectra are checked at definite wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and managed by a computer system. A background correction technique is essential to compensate for mutable background participation on the determination of the analysis. Background has to be measured adjacent to the analysed wavelength during analysis and several interferences must be taken into consideration (USEPA Method.200.7 [27]).

Anions were analysed using Metrohm 881 Compact IC Pro Suppression Ion Chromatography based on "Standard methods for the examination of water and wastewater" [28]. This method is appropriate, after a filtration process to eliminate solid particles using a 0.2 µm pore diameter membrane filter. By this method the common anions such as bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate can be determined. Basically, this method uses a prewashed syringe of 1 to 10 mL capacity equipped with a male luer suitable injecting sample or standard. To flash the loop, we inject sufficient sample many times; for a 0.1 mL sample loop inject at least 1 mL. Following step, we shift ion chromatograph (IC) from load to inject mode. Then, we record peak heights and retention times on a strip chart recorder. After the last peak (SO42-) is performed and the conductivity signal has returned to the base line, another sample can be injected. We compute the concentration of each anion, in milligrams per litre, by referring to the appropriate calibration curve. Otherwise, when the response is shown to be linear, we use (2):

$$C = H \times F \times D \tag{2}$$

where C = mg anion/L, H = peak height or area, F = response factor = concentration of standard/height (or area) of standard, and D = dilution factor for those samples requiring dilution [28].

Mercury was digested with aqua regia at 95 °C for 2 hours, and then analysed using a Perkin Elmer FIMS 400 (Flow injection mercury system) according to Method 7470. Method 7470 is a cold-vapor atomic absorption process accepted for determining the concentration of mercury in mobilityprocedure extracts, aqueous wastes and groundwaters. This vapor atomic absorption technique is based mainly on the absorption of radiation at 253.7 nm by mercury vapour. The mercury is reduced to the elemental status and ventilated from solution in a sealed system. After that, the mercury vapor moves through a cell placed in the light path of an atomic absorption spectrophotometer. Absorbance is calculated as a function of mercury concentration [29].

#### E. Analysis of Basic Water Parameters

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Water parameters were measured using Water Quality Analyser-MODEL 516 and Orion 4-Star Plus pH/conductivity meter in all experiments and during sampling (see Tables IV and V). The measurements were applied at 0-time, one hour and at 8 hours for each experiment.

0.87

1.000 + 387

				TABLETV						
WATER QUALITY PARAMETERS FOR SAMPLES COLLECTED FROM THE LEACHATE IN THE POND AT RUSSELL VALE GOLF COURSE A										
Season	Depth	Turbidity	Dissolved Oxygen	Electrical conductivity	TDS	pН	Temperature	Salinity	SG	Redox
	(m)	(ntu)	(mg/l)	(µS/cm)	(g/l)		(°C)	(ppt)	$(t/m^3)$	(mV)
Spring	0.33	99	3.43	3442	2.129	8.55	15.01	1.72	1.000	+389
Summer	0.42	66.5	10.8	2761	1.66	8.23	21.76	1.45	0.999	+51
Autumn	0.49	178	7.40	2475	1.67	8.27	20.90	1.46	0.999	+500
	TER QUA Season Spring Summer Autumn	TER QUALITY PA   Season Depth   (m) (m)   Spring 0.33   Summer 0.42   Autumn 0.49	TER QUALITY PARAMETERS     Season   Depth   Turbidity     (m)   (ntu)     Spring   0.33   99     Summer   0.42   66.5     Autumn   0.49   178	TER QUALITY PARAMETERS FOR SAMPLES COLI     Season   Depth   Turbidity   Dissolved Oxygen     (m)   (ntu)   (mg/l)     Spring   0.33   99   3.43     Summer   0.42   66.5   10.8     Autumn   0.49   178   7.40	TABLE IV     TABLE IV     TABLE IV     TER QUALITY PARAMETERS FOR SAMPLES COLLECTED FROM THE LEACT     Season   Depth   Turbidity   Dissolved Oxygen   Electrical conductivity     (m)   (ntu)   (mg/l)   (µS/cm)     Spring   0.33   99   3.43   3442     Summer   0.42   66.5   10.8   2761     Autumn   0.49   178   7.40   2475	TABLE IV       TER QUALITY PARAMETERS FOR SAMPLES COLLECTED FROM THE LEACHATE IN       Season     Depth     Turbidity     Dissolved Oxygen     Electrical conductivity     TDS       (m)     (ntu)     (mg/l)     (µS/cm)     (g/l)       Spring     0.33     99     3.43     3442     2.129       Summer     0.42     66.5     10.8     2761     1.66       Autumn     0.49     178     7.40     2475     1.67	TABLE IV       TER QUALITY PARAMETERS FOR SAMPLES COLLECTED FROM THE LEACHATE IN THE       Season     Depth     Turbidity     Dissolved Oxygen     Electrical conductivity     TDS     pH       (m)     (ntu)     (mg/l)     (µS/cm)     (g/l)        Spring     0.33     99     3.43     3442     2.129     8.55       Summer     0.42     66.5     10.8     2761     1.66     8.23       Autumn     0.49     178     7.40     2475     1.67     8.27	TABLE IV     TER QUALITY PARAMETERS FOR SAMPLES COLLECTED FROM THE LEACHATE IN THE POND AT RUSS     Season   Depth   Turbidity   Dissolved Oxygen   Electrical conductivity   TDS   pH   Temperature     (m)   (ntu)   (mg/l)   (µS/cm)   (g/l)   (°C)     Spring   0.33   99   3.43   3442   2.129   8.55   15.01     Summer   0.42   66.5   10.8   2761   1.66   8.23   21.76     Autumn   0.49   178   7.40   2475   1.67   8.27   20.90	TABLE IV     TER QUALITY PARAMETERS FOR SAMPLES COLLECTED FROM THE LEACHATE IN THE POND AT RUSSELL VAL     Season   Depth   Turbidity   Dissolved Oxygen   Electrical conductivity   TDS   pH   Temperature   Salinity     (m)   (ntu)   (mg/l)   (µS/cm)   (g/l)   (°C)   (ppt)     Spring   0.33   99   3.43   3442   2.129   8.55   15.01   1.72     Summer   0.42   66.5   10.8   2761   1.66   8.23   21.76   1.45     Autumn   0.49   178   7.40   2475   1.67   8.27   20.90   1.46	TABLE IV       TER QUALITY PARAMETERS FOR SAMPLES COLLECTED FROM THE LEACHATE IN THE POND AT RUSSELL VALE GOLF       Season     Depth     Turbidity     Dissolved Oxygen     Electrical conductivity     TDS     pH     Temperature     Salinity     SG       (m)     (ntu)     (mg/l)     (μS/cm)     (g/l)     (°C)     (ppt)     (t/m <sup>3</sup> )       Spring     0.33     99     3.43     3442     2.129     8.55     15.01     1.72     1.000       Summer     0.42     66.5     10.8     2761     1.66     8.23     21.76     1.45     0.999       Autumn     0.49     178     7.40     2475     1.67     8.27     20.90     1.46     0.999

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a All data were obtained using Water Quality Analyser (MODEL 516).

105.1

7.75

Winter 0.50

TABLE V WATER QUALITY PARAMETERS FOR SAMPLES COLLECTED FROM THE WGB32 BOREHOLE LOCATED NEAR THE TENNIS COURTS OUTSIDE THE FENCELINE AT ORICA AUSTRALIA IN BOTANY BAY

			ORI	CA AUSTRALIA IN BOTA	NYDA	Y				
Season	Depth	Turbidity	Dissolved Oxygen	Electrical conductivity	TDS	pН	Temperature	Salinity	SG	Redox
	(m)	(ntu)	(mg/l)	(µS/cm)	(g/l)		(°C)	(ppt)	$(t/m^3)$	(mV)
Spring	5.75	2.1	2.41	8000	5.84	10.5	19.35	4.97	1.002	+540
Summer	5.80	2.6	1.47	7250	5.79	10.55	21.4	4.91	1.001	- 44
Autumn	5.75	2.5	1.42	7667	5.34	11	21.86	4.89	1.002	- 43
Winter	5.38	1.8	0.80	8000	5.58	10.57	19.45	4.77	1.002	+533
14.1.1.1		I	A	1.51()						

a All data were obtained using Water Quality Analyser (MODEL 516).

### F. The Dead-End Filtration Experimental Protocol

Typically, the dead end filtration system does not need the high pressure used in pressure driven membrane filtration system (such as reverse osmosis/nanofiltration) 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 cm<sup>2</sup> (2 cm  $\times$  3 cm) with a channel height of 2 mm and the membrane s supported by a layer made from stainless. Only 2 L of a solution containing contaminated groundwater was used as feed solution after filtration using a Stericup DuraporeTM 0.45 µm Millipore filtration to remove colloidal and suspended materials. Two duplicates (40 mL) from permeate and feed samples were collected after 1 hour and at 8 hours of filtration in order to examine inorganic contaminants that exist in surface and groundwater. All samples collected from both feed and permeate were sent directly [1] to Orica Australia Botany Environmental Laboratories for analysis. The removal rate is defined by (3):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{3}$$

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

#### III. RESULTS AND DISCUSSION

#### A. SEM-END Analysis

1.104 7.99

The surface morphology of MWCNT buckypapers was examined using field-emission SEM on a JEOL JSM-7500FA -BRUKER-QUANTAX 400, and cross-sections were viewed as well. Fig. 3 shows SEM images of MWNT buckypapers prepared using Triton X-100 before (virgin) and after use (fouled) as a membrane. The surface morphology of the MWCNT buckypaper appears to consist of small bundles of tubes and an abundance of small pores (Fig. 3A) which agrees well with the results of a study conducted by [30]. In contrast, it was observed that some flattening of the MWCNT bundles in Fig. 3B occurred due to adsorption of contaminants. Also, the cross-sectional images of MWCNT buckypapers display clearly what has been seen in Fig. 4, where Figs. 4A and 4B show the structure and size of the tubes and pores in the MWCNT membrane. As seen in Fig. 4A, the MWCNT buckypaper seems to contain small bundles of tubes and an abundance of small pores. On the other hand, the MWCNT buckypaper bundles were flattened after use as a membrane because of adsorption of contaminants (Fig. 4B). Moreover, it is clear from Fig. 4A that the MWCNT buckypaper membrane possesses a large number of regularly sized pores, with software image analysis revealing an average surface pore diameter of  $65.6 \pm 8$  nm (Table II) which is similar to that obtained

previously for comparable buckypapers produced using MWCNTs [5], [19].



Fig. 3 SEM images of the (A) virgin MWCNT buckypaper and (B) MWCNT buckypaper fouled by leachate from the Russel Vale Pond in winter



Fig. 4 SEM images of the (A) virgin MWCNT buckypaper and (B) MWCNT buckypaper fouled by leachate from the Russel Vale pond in winter



Fig. 5 EDS data for the virgin MWNT-Triton X-100 membrane (A and B).

To investigate the distribution of elements deposited on the membrane surface, MWCNT buckypapers were also analysed using SEM with an additional semi-quantitative EDS. An example of SEM-EDS images obtained for virgin and fouled MWCNT buckypaper membranes is shown in Figs. 5 and 6. The EDS spectrum of MWCNT buckypapers (Fig. 5B) shows peaks corresponding to titanium and aluminium in addition to a large amount of carbon and a reasonable amount of oxygen as part of the membrane composition and, therefore, these elements were detected in all samples (virgin and fouled). The presence of aluminium and titanium is not surprising as they are used during fouling of MWCNTs via the Nanocyl process. On the other hand, as observed in the corresponding Figs. 5B and 6B, the oxygen content is enhanced significantly. These results suggest that a considerable number of carboxyl groups have been introduced onto the surface of the buckypaper during synthesis of the MWCNTs. A high level of calcium was found in the fouled membrane (Fig. 6B) due to the ability of calcium to complex with carboxyl groups which are very common at the surface of CNTs. Also, a low level of magnesium was found in the fouled membrane (Fig. 6B) and this can be attributed to the exclusion process for this cation via the size exclusion mechanism and consequent diffusion into the membrane surface [31].



Fig. 6 EDS data for the MWNT-Triton X-100 membrane fouled by leachate from the pond at Russell Vale in spring (A and B)

B. Removal of Inorganic Contaminants by MWCNT Buckypaper Membrane

To investigate the potential of these MWCNT materials for filtration applications, it is essential to determine whether they exhibit any selectivity in their permeability towards dissolved solutes. It is noteworthy that only a few studies have been performed previously using buckypapers prepared from MWNTs [6], [32], [33]. Thus, as a first step towards remedying this situation, many experiments were conducted on samples collected in different seasons from the leachate pond at Russell Vale and the WGB32 borehole at Botany Bay to evaluate the ability of MWCNT-Triton-X-100 buckypapers to remove inorganic contaminants from contaminated surface and groundwater. Permeate and feed samples of 250 mL and 100 mL were collected before and after 24 hours of filtration to analyse for cations and anions, respectively.

#### 1) Leachate Pond at Russell Vale Golf Course

Contaminated surface water is represented by samples collected from the leachate pond at Russell Vale Golf Course in the Illawarra area. The removal efficiency for MWCNT buckypapers are reported in Table VI and Fig. 7. The results from Fig. 7 showed that the performance of the MWCNT buckypaper membranes in exclusion anions was higher than that of its exclusion of cations. This phenomenon can be explained by the Donnan exclusion mechanism (charge repulsion mechanism); the anion separation resulting from the electrostatic interactions between the negative charge of the anions and the negative charge on the MWCNT membrane [1]. The molecular weight of the anions is greater than the cations (except for mercury, which was not detected in contaminated surface water samples at Russell Vale) and ranged between 35.45 g/mol (Cl<sup>-</sup>) and 96.06 g/mol (SO4<sup>2-</sup>), whereas the molecular weight of the cations ranged between 22.99 g/mol (Na<sup>+</sup>) and 40.08 g/mol (Ca<sup>2+</sup>; see Table II). This may give an added reason for the higher exclusion of anions than cations. Also as seen in Fig. 7, it was notable that the rejection of calcium was high compared to other cations and this is attributed to the fact that it has a large molecular weight (40.08 g/mol), while other cations for example sodium and magnesium have smaller molecular weights (22.99 g/mol and 24.31 g/mol respectively). Consequently, calcium was rejected by the size exclusion mechanism and according this mechanism size variation can determine which ions are able to pass through the membrane pores by diffusion [31]. Furthermore, the results in Fig. 7 revealed that calcium recorded the highest value of exclusion reaching 51%, followed by phosphate 47.8%, then magnesium 19.4%, while the lowest value of rejection was for potassium where no removal occurred (0%). This can be explained by divalent and multivalent ions with their large hydrated radii (i.e., Mg<sup>2+</sup>, Ca<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup>) were excluded more than monovalent ions with smaller hydrated radii (i.e., K<sup>+</sup> [21]). Lastly, it is observed that the exclusion rate of the model foulants was similar in all seasons.

TABLE VI OVERALL REMOVAL EFFICIENCY OF THE SELECTED INORGANIC COMPOUNDS DETECTED IN CONTAMINATED SURFACE WATER FROM THE LEACHATE POND

	IN RUSSE	LL VALE					
Common 1	Removal (%)						
Compound	Summer	Autumn	Winter	Spring			
Chloride	8.7	4.8	7.7	20.7			
Bromide	3.8	4.8	7.1	5.7			
Nitrate	16.7	11	5.3	4.7			
Phosphate	47.8	50	45	30			
Sulphate	5.7	1.6	4.6	8.3			
Sodium	6	5.1	3.7	3.2			
Potassium	0	0	0	0			
Magnesium	16.1	19.4	14.3	11.8			
Calcium	14.3	35.9	22.4	51			
Total Mercury a	ND	ND	ND	ND			

a ND: Not detected.



Fig. 7 Overall removal efficiency of the selected inorganic compounds detected in contaminated surface water at Russell Vale: The MWCNT-Triton-X-100 buckypaper membrane filtration

experiment was conducted at 140 kPa and a temperature of 20 °C. Samples were collected after 24 hours of filtration

#### 2) WGB32 Borehole at Botany Bay

The performance of MWCNT membranes in excluding the model foulants in samples from the WGB32 borehole are reported in Table VII and Fig. 8. The situation here, when investigating the efficiency of MWCNT buckypaper membranes to remove inorganic contaminants, is not much different when contaminated groundwater samples collected from this site are compared to contaminated surface water samples collected from the leachate pond at Russell Vale. The findings from Fig. 8 display that the performance of MWCNT buckypaper membranes in excluding anions were better than that of its cation exclusion. This phenomenon can be attributed to the Donnan exclusion mechanism (charge repulsion mechanism); the anions separation resulting from the electrostatic interactions between negative charges on the anions and the MWCNT membrane [1]. Furthermore, the results in Fig. 7 revealed that phosphate recorded the highest exclusion value reaching 69.2%, whereas the lowest exclusion value was for potassium where no removal occurred (0%). The reason for this is that the molecular weight of phosphate (95.0 g/mol) is greater than the molecular weight of potassium (39.10 g/mol). Also, as shown in Fig. 8, it was noteworthy that the removal of phosphate was high compared to other anions followed by sulphate, nitrate then chloride. This can be explained by multivalent ions with large hydrated radii (i.e., PO<sub>4</sub><sup>3-</sup>) were excluded more than monovalent ions with smaller hydrated radii (i.e., Cl<sup>-</sup>; [21]). In case of cations, the highest value of exclusion was for magnesium that reached 15%, followed by mercury 13.7% then calcium 7.4% and after that sodium 4.3%, while the lowest value of exclusion was for potassium where no removal occurred (0%). This can be explained since ions with large hydrated radii (i.e., Mg<sup>2+,</sup> Hg<sup>+</sup> and Ca<sup>2+</sup>) were retained more than ions with smaller hydrated radii (i.e., Na<sup>+</sup>; [21]). Finally, it is observed that there is no relationship between seasonal effects using MWCNT buckypaper. This is quite clear from Fig. 7, where the removal of the model foulants was similar in all seasons.

#### C. Performance of the MWCNT Buckypaper Membrane

To investigate the performance of MWCNT buckypaper membranes, it is important to study the membrane permeate flux as a function of filtration time for samples collected in different seasons and from different sites (i.e., leachate pond at Russell Vale Golf Course and the WGB32 borehole at Botany Bay).

TABLE VII
OVERALL REMOVAL EFFICIENCY OF THE SELECTED INORGANIC COMPOUNDS
DETECTED IN CONTAMINATED GROUNDWATER WATER FROM THE WGB32
BOREHOLE IN BOTANY BAY

Boitanole ne Boinni Bill							
Compound	Removal (%)						
Compound	Summer	Autumn	Winter	Spring			
Chloride	15	12.5	13.6	16.4			
Bromide <sup>a</sup>	ND	ND	ND	ND			
Nitrate	17.5	13.3	16.7	12.7			
Phosphate	69.2	48.5	20	32			
Sulphate	22.5	5	6.5	7.2			
Sodium	4.2	2.8	4.3	1.3			
Potassium	0	0	0	0			
Magnesium	15	12.5	15	12.5			
Calcium	2.9	3.6	7.4	3.8			
Total Mercury	13.7	17.1	6.9	13.6			

a ND: Not detected.



Fig. 8 Overall removal efficiency of the selected inorganic compounds detected in contaminated groundwater water in the WGB32 borehole at Botany Bay: Experiments were conducted at 140 kPa and temperature of 20 °C. Samples were collected after 24 hours of filtration

## 1) Leachate Pond at Russell Vale Golf Course

Fig. 9 shows the evolution of the membrane permeate flux as a function of filtration time. As shown in Fig. 9, it is observed that the flux was better for samples that were collected in winter and spring seasons compared to samples collected in summer and autumn seasons. In particular, the flux was the lowest for samples that were collected in the summer season and this can be attributed to existing living cells such as extracellular organic matter (EOM) that is released from algae. In the summer season, higher temperatures participate significantly in the growth of algal blooms and the chance to release EOM becomes more probable. This extracellular, mucilaginous slime material can elevate resistance to filtration [34]. It has been found that characteristics of EOM can impact the specific resistance developed in membrane filtration in particular when it is present in the feed reservoir [35].

The results in Fig. 9 revealed that the highest flux was during the winter and ranged between~ 48-50 L.m<sup>2</sup>.h, followed by spring ( $\cdot$  46-48 L.m<sup>2</sup>.h) and autumn ( $\cdot$  38-40 L.m<sup>2</sup>.h) and with lowest flux found in summer season and ranged between ( $\cdot$  20-25 L.m<sup>2</sup>.h). Also, it is remarkable that after using MWCNT

buckypaper as a membrane in this study the flux was linear and stable in all studied seasons. This can be explained by the porosity of MWCNT the membrane (~65.6 nm) being higher than the porosity of other membranes such as (nanofiltration and reverse osmosis membranes).



Fig. 9 Permeate flux of the MWCNT buckypaper membrane as a function of filtration time for samples collected from the leachate pond at Russell Vale: Experiment was conducted at 140 kPa and temperature of 20 °C

### 2) WGB32 Borhole at Botany Bay

Samples collected from the WGB32 borehole represent contaminated groundwater. Fig. 10 displays the progress of the membrane permeate flux as a function of filtration time. The situation here is not much different when contaminated groundwater samples collected from this site are compared to contaminated surface water samples collected from the leachate pond at Russell Vale. Results in Fig. 10 indicate that the flux was good for samples collected in all seasons, even those collected during the summer season. Because these samples were collected from a well and therefore there was no favourable opportunity for the algal growth and photosynthesis, and the subsequent high release of EOM [35]. If EOM is available, mucilaginous slime material can increase resistance to filtration [34]. It has been found that the characteristics of EOM can influence the specific resistance developed in membrane filtration, in particular when it is present in the feed reservoir [35].

The results in Fig. 10 show that the highest value of flux was in the winter and ranged between~ $53-56 \text{ L.m}^2$ .h, followed by spring (~49-51 L.m<sup>2</sup>.h) and autumn (~41-47 L.m<sup>2</sup>.h) with the lowest value found in summer (~29-37 L.m<sup>2</sup>.h). Furthermore, it is noteworthy that the flux through the MWCNT buckypaper

membrane in this study was linear and stable in all seasons. It can be concluded that, since samples from this site were collected from a well, the colloidal and suspended substances in these waters were slightly less compared to the contaminated surface water samples collected from the leachate pond at Russell Vale. Consequently, the flux while using the MWCNT membrane here was much better than the flux for samples collected from the leachate pond at Russell Vale due to lack of fouling effects.



Fig. 10 Permeate flux of the MWCNT buckypaper membrane as a function of filtration time for samples collected from the WGB32 borehole at Botany Bay: Experiment was conducted at 140 kPa and temperature of 20  $^{\circ}$ C

## D.Flux Decline

Comparison between permeate flux decline through MWCNT membranes for samples collected from the leachate pond at Russell Vale and the WGB32 borehole at Botany Bay is shown in Table VIII. Considerable permeate flux decline was observed with the MWCNT membranes for samples which were collected in summer season from both the leachate pond and WGB32 due to fouling of the membranes. This can be explained since the porosity of the MWCNT membrane (65.6 nm) is higher than the porosity of other membranes nanofiltration and reverse osmosis membranes and thus the possibility of fouling due to retention of contaminants is much less for the MWCNT membrane. Moreover, the CNT membrane has antifouling, self-cleaning and reusable functions [36] and this means a lack of likelihood of fouling for the MWCNT membranes.

TABLE VIII
COMPARISON BETWEEN PERMEATE FLUX DECLINE OF MWNT MEMBRANES
FOR SAMPLES COLLECTED FROM THE LEACHATE POND AT RUSSELL VALE
AND THE WGB32 BOREHOLE AT BOTANY BAY

AND THE WGB32 BOREHOLE AT BOTANY BAY							
Season	Permeate Flux Decline for	Permeate Flux Decline for					
	MWNT-Leachate pond (%) <sup>a</sup>	MWNT-WGB32 (%) <sup>b</sup>					
Autumn	5	4.7					
Winter	4	5.3					
Spring	4.2	3.9					
Summer	20 °	21.6 <sup>d</sup>					

a / b Data calculated using: Flux Decline (%) =  $\left(1 - \frac{J}{I_0}\right) \times 100$ .

c Caused by EOM.

d It could be attributed to the changes in the effluent organic matter seasonally produced during the biological stage.

#### IV. CONCLUSIONS

Results reported in this study indicate that the performance of the MWCNT membrane in removing inorganic contaminants detected in samples collected from the leachate pond and the WGB32 borehole was low in all seasons. This was due to the high porosity of the MWCNT buckypaper membrane. It is observed that the performance of MWCNT buckypaper membranes in excluding anions was greater than that for its cation exclusion. This can be explained by the Donnan exclusion mechanism; the anion exclusion resulted from the electrostatic interactions between the negative charge of anions and the negative charge of the MWCNT membrane. The results in this study revealed that the highest value of rejection was for multivalent and divalent ions (PO4<sup>3-</sup>, Ca<sup>2+</sup>) while the lowest value of rejection was for monovalent (K<sup>+</sup>). This can be elucidated since multivalent and divalent ions with large hydrated radii (i.e., PO43-, Ca2+) were excluded more than monovalent ions with smaller hydrated radii (i.e., K<sup>+</sup>). Furthermore, it is remarkable that the MWCNT buckypaper membrane gave a linear and stable flux in all studied seasons. It can be deduced that this phenomenon is related to the higher porosity of the MWCNT membrane (~65.6 nm).

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#### References

- Vatanpour, V., Madaeni, S.S., Moradian, R., Zinadini, S., Astinchap, B., Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite. Journal of Membrane Science, 2011. 375(1–2), 284-294, doi:10.1016/j.memsci.2011.03.055.
- [2] Asha, P.T., Nanotechnology for sustainable water treatment a review.

Materials Today: Proceedings, 2021, 1-6, doi:10.1016/j.matpr.2021.05.629.

- [3] Ojemaye, M.O., Adefisoye, M.A., Okoh, A.I., Nanotechnology as a viable alternative for the removal of antimicrobial resistance determinants from discharged municipal effluents and associated watersheds: a review. Journal of Environmental Management, 2020, 275, 111234, 1-17, doi:10.1016/j.jenvman.2020.111234.
- [4] Goh, P.S., Ismail, A.F., Ng, B.C., Carbon nanotubes for desalination: Performance evaluation and current hurdles. Desalination, 2013, 308, 2-14, doi:10.1016/j.desal.2012.07.040.
- [5] Dumée, L.F., Sears, K., Schutz, J., Finn, N., Huynh, C., Hawkins, S., Duke, M., Gray, S., Characterization and evaluation of carbon nanotube Bucky-Paper membranes for direct contact membrane distillation. Journal of Membrane Science, 2010. 351, (1–2), 36-43, doi:10.1016/j.memsci.2010.01.025.
- [6] Yogita, B., Pandey, G., Bhoj, A., Tharmavaram, M., Rawtani, D., Recent advancements in practices related to desalination by means of nanotechnology. Chemical Physics Impact, 2021, 100025, 1-18, doi:10.1016/j.chphi.2021.100025.
- [7] Dumée, L.,Germain, V., Sears, K., Schutz, J., Finn, N., Duke, M., Cerneaux, S., Cornu, D., Gray, S., Enhanced durability and hydrophobicity of carbon nanotube bucky paper membranes in membrane distillation. Journal of Membrane Science, 2011, 376(1–2), 241-246, doi:10.1016/j.memsci.2011.04.024.
- [8] Rathi, B.S., Kumar, P.S., Application of adsorption process for effective removal of emerging contaminants from water and wastewater. Environmental Pollution, 2021, 280, 116995, doi:10.1016/j.envpol.2021.116995.
- [9] Yaroshchuk, A.E., Non-steric mechanisms of nanofiltration: superposition of Donnan and dielectric exclusion. Separation and Purification Technology, 2001, 22–23, 143–158. doi:10.1016/S1383-5866(00)001593.
- [10] Teixeira, M.R., Rosa, M.J., Nyström, M., The role of membrane charge on nanofiltration performance. Journal of Membrane Science, 2005, 265(1–2), 160-166, doi:10.1016/j.memsci.2005.04.046.
- [11] Verliefde, A.R.D., Cornelissen, E.R., Heijman, S.G.J., Verberk, J.Q.J.C., Amy, G.L., Van der Bruggen, B., Van Dijk, J.C., The role of electrostatic interactions on the rejection of organic solutes in aqueous solutions with nanofiltration. Journal of Membrane Science, 2008, 322(1), 52-66. doi:10.1016/j.memsci.2008.05.022.
- [12] Bolong, N., Ismail, A.F., Salim, M.R, Matsuura, T., A review of the effects of emerging contaminants in wastewater and options for their removal. Desalination, 2009, 239(1–3), 229-246. doi:10.1016/j.desal.2008.03.020.
- [13] Chen, S.-S., Taylor, J.S., Mulford, L.A., Norris, C.D., Influences of molecular weight, molecular size, flux, and recovery for aromatic pesticide removal by nanofiltration membranes. Desalination, 2004, 160(2), 103-111, doi:10.1016/S0011-9164(04)90000-8.
- [14] Liu, X., Wang, M., Zhang, S, Pan, B., Application potential of carbon nanotubes in water treatment: a review. Journal of Environmental Sciences, 2013, 25(7), 1263-1280. doi:10.1016/S1001-0742(12)60161-2.
- [15] Li, Y.-H.,Ding, J., Luan, Z, Dia, Z., Zhu, Y., Xu, C., Wu, D., Wei, B., Competitive adsorption of Pb2+, Cu2+ and Cd2+ ions from aqueous solutions by multiwalled carbon nanotubes. Carbon, 2003, 41(14), 2787-2792, doi:10.1016/S0008-6223(03)00392-0.
- [16] Dolar, D., Gros, M., Rodriguez-Mozaz, S., Moreno, J., Comas, J., Rodriguez-Roda, I., Barcelo, D., Removal of emerging contaminants from municipal wastewater with an integrated membrane system, MBR– RO. Journal of Hazardous Materials, 2012, 239–240(0), 64-69, doi:10.1016/j.hazmat.2012.03.029.
- [17] Loncnar, M., Zupancic, M., Bukovec, P., Justin, M.Z., Fate of saline ions in a planted landfill site with leachate recirculation. Waste Management, 2010, 30(1), 110-118, doi:10.1016/j.wasman.2009.09.010.
- [18] Blighe, F.M., Hernandez, Y.R., Blau, W.J., Coleman, J.N., Observation of Percolation-like Scaling-Far from the Percolation Threshold-in High Volume Fraction, High Conductivity Polymer-Nanotube Composite Films. Advanced Materials, 2007, 19, 4443-4447, doi:10.1002/adma.200602912.
- [19] Sweetman, L.J., Synthesis, Characterisation and Applications of Carbon Nantube Membrane Containing Macrocycles and Antibiotics, PhD thesis, 2012, University of Wollongong, Wollongong, Australia, 1-188, https://ro.uow.edu.au/theses/3815/.
- [20] Frizzell, C., In het Panhuis, M., Coutinho, D., Balkus, K., Minett, A., Blau, W., 2005, Reinforcement of macroscopic carbon nanotube structures by polymer intercalation: the role of polymer molecular weight

and chain conformation. Physical Review B, 72, 245420, 1-8.

- [21] Richards, L.A., Richards, B.S., Schäfer, A.I., Renewable energy powered membrane technology: Salt and inorganic contaminant removal by nanofiltration/reverse osmosis. Journal of Membrane Science, 2011, 369(1-2), 188-195, doi:10.1016/j.memsci.2010.11.069.
- [22] Xu, P., Drewes, J.E., Bellona, C., Amy, G., Kim, T.U., Adam, M., Heberer, T., Rejection of emerging organic micropollutants in nanofiltration-reverse osmosis membrane applications. Water Environment Research, 2005, 77(1), 40-48, doi:10.2175/106143005×41609.
- [23] Nightingale, E.R., Phenomenological theory of ion solvation. Effective radii of hydrated ions, Journal of Physical Chemistry, 1959, 63(9), 1381-1387, doi:10.1021/j150579a011.
- [24] Volkov, A.G., Paula, S., Deamer, D.W., Two mechanisms of permeation of small neutral molecules and hydrated ions across phospholipid bilayers. Bioelectrochemistry and Bioenergetics, 1997, 42(2), 153-160, doi:10.1016/S0302-4598(96)053097-0.
- [25] Haynes, W.M., Bruno, T.J., Lide, D.R., CRC Handbook of Chemistry and Physics, 94th Edition, 2013, CRC Press, Boca Raton, FL, USA.
- [26] Kiriukhin, M.Y., Collins, K.D., Dynamic hydration numbers for biologically important ions. Biophysical Chemistry, 2002, 99(2), 155-168, doi:10.1016/S0301-4622(02)001053-9.
- [27] Martin, T.D., Brockhoff, C.A., Creed, J.T., EMMC Methods Work Group, Method-200.7, Revision 4.4: Determination of metals and trace elements in water and wastes by inductively coupled plasma atomic emission spectrometry., U.S. EPA1994, Cincinnati, Ohio, USA.
- [28] APHA Standard methods for the examination of water and wastewater. 21st Edition ed. 2005, American Public Health Association/American Water Works Association/Water Enveronment Fedration, Washington DC, USA.
- [29] U.S. EPA. Metod.7470A (SW-846): Mercury in liquid waste (manual cold-vapor technique), Revision 1. U.S. EPA 1994, Washington DC, USA.
- [30] Cottinet, P.J., Souders, C., Tsai, S.Y., Liang, R., Wang, B., Zhang, C., Electromechanical actuation of buckypaper actuator: material properties and performance relationships. Physics Letters A, 2012, 376(12–13), 1132-1136, doi:10.1016/j.physleta.2012.02.011.
- [31] Sweetman, L.J., Synthesis, Characterisation and Applications of Carbon Nantube Membrane Containing Macrocycles and Antibiotics, PhD thesis, 2012, University of Wollongong, Wollongong, Australia, 1-188, https://ro.uow.edu.au/theses/3815/.
- [32] Van der Bruggen, B., Koninckx, A., Vandecasteele, C., Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration. Water Research, 2004, 38(5), 1347-1353, doi:10.1016/j.waters.2003.11.008.
- [33] Alshahrania, A.A., Al-Zoubi, H., Neghiem, L.D., in het Panhuis, M., Synthesis and characterisation of MWNT/chitosan and MWNT/chitosancrosslinked buckypaper membranes for desalination. Desalination, 2017, 418, 60-70, doi:10.1016/j.desal.2017.05.031.
- [34] Deshpande, B.D., Agrawal, P.S., Yenkie, M.K.N., Dhoble, S.J., Prospective of nanotechnology in degradation of waste water: a new challenges. Nano-Structures & Nano-Objects, 2020. 22, 1-20, doi:10.1016/j.nanoso.2020.100442.
- [35] Kwon, B., Park, N., Cho, J., Effect of algae on fouling and efficiency of UF membranes. Desalination, 2005, 179, 203–214, doi:10.1016/j.desal.2004.11.068.
- [36] Babel, S., Takizawa, S., Ozaki, H., Factors affecting seasonal variation of membrane filtration resistance caused by Chlorella algae. Water Research, 2002, 36(5), 1193–1202, doi:10.1016/S0043-1354(01)00333-5
- [37] Das, R., Al, M.E., Hamid, S.B.A., Ramakrishna, S., Chowdhury, Z.Z., Carbon nanotube membranes for water purification: a bright future in water desalination. Desalination, 2014, 336, 97-109, doi:10.1016/j.desal.2013.12.026.