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Multi-Walled Carbon Nanotubes/Polyacrylonitrile Composite as Novel Semi-Permeable Mixed Matrix Membrane in Reverse Osmosis Water Treatment Process

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***Abstract*—**A novel and simple method is introduced for rapid and highly efficient water treatment by reverse osmosis (RO) method using multi-walled carbon nanotubes (MWCNTs) / polyacrylonitrile (PAN) polymer as a flexible, highly efficient, reusable and semi-permeable mixed matrix membrane (MMM). For this purpose, MWCNTs were directly synthesized and on-line purified by chemical vapor deposition (CVD) process, followed by directing the MWCNT bundles towards an ultrasonic bath, in which PAN polymer was simultaneously suspended inside a solid porous silica support in water at temperature to ~70 ºC. Fabrication process of MMM was finally completed by hot isostatic pressing (HIP) process. In accordance with the analytical figures of merit, the efficiency of fabricated MMM was ~97%. The rate of water reatment process was also evaluated to 6.35 L min^{-1}. The results reveal hat, the CNT-based MMM is suitable for rapid treatment of different forms of industrial, sea, drinking and well water samples.

***Keywords*—**Mixed Matrix Membrane, Carbon Nanostructures, Chemical Vapour Deposition, Hot Isostatic Pressing

I. INTRODUCTION

THE importance of water in life and significant applications of water have caused water treatment to be considered as one of the most important fields [1]-[2]. Physical methods such as coagulation/filtration, forward osmosis, reverse osmosis (RO) and electrodialysis. Progress of these techniques has provided enormous developments in water treatment technology [3]. Among these techniques, microporous and mesoporous membranes, not only purify water from bacteria and viruses, but can simply separate small units of proteins from industrial or agricultural wastewater [6]. Generally, membranes have permeable structure that facilities the separation of impurities based on size and/or physical and chemical properties. Usually, processes with high selectivity have low permeability and vice versa [7]-[8]. Therefore, assessment of permeability and selectivity of membrane has shown asymptotic limitations in separation process using polymeric membrane [9]- [10].Consequently, the development of novel membrane systems is of great importance.

Recent researches reveal that, mixed matrix membranes (MMMs) are considered as suitable membrane for gas separation processes [9]-[10]. When these membrane are fabricated using nanostructured materials such as metal nanoparticles and carbon nanomaterials. Therefore, magic properties of MMM seems to be applicable in water treatment, purification and recycling process. Despite the unique advantageous of MMMs such as high permeability, great selectivity and high practical capabilities as molecular sieving support [11]. In this work, a novel, flexible, low cost and highly efficient semi-permeable MMM is fabricated using multi-walled carbon nanotubes (MWCNTs), mixed with polyacrylonitrile (PAN) polymer for highly efficient water treatment technology.The efficiency of the RO technique is strongly dependent to the property of the semi-permeable membrane according to the following equation [14]:

$$\%E = \left(\frac{C_{\mathrm{ib}}}{C_{if}}\right) * \left\{\frac{Q-Q_p}{Q}\right\} * 100 \tag{1}$$

where E is the efficiency in water treatment process, C_{ib} and C_{if} are the concentrations of impurities in saltwater and untreated water, respectively. Also, Q and Q_p are defined as the flux of inlet and outlet water [14].

Another important factor affecting the velocity of water treatment is the debi of water, passed through the semi-permeably membrane (Q_w). This parameter is strongly affected by the pressure gradient (ΔP) and osmotic pressure (Δπ), at two sides of the semi-permeable membrane, the thickness (L) as well as the active surface area (A) of membrane and finally the technology by which the semi-membrane was fabricated as described by [14]:

$$Q_w = K_w * \frac{A}{L} * \{\Delta P - \Delta\pi\} \tag{2}$$

where K_w is the MMM permeability coefficient for solvent molecule. In this study, for dilute solution, the osmotic pressure was evaluated using the rule of ideal gas ("Morse" equation), i.e. ($\pi V = nRT$) [14].

II. EXPERIMENTAL

MWCNTs (40-60 nm) and carbon nanofibers (CNFs) with 250-300 nm internal diameter, were synthesized by chemical vapour deposition (CVD) method at temperatures to ~1300 ºC in argon atmosphere using hydrocarbon such as acetylene gas as the source of carbon and ferrocene (Merck, Darmstadt,

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Germany) as the source of iron nanoparticles. The schematic representing the design of water treatment instrument by RO method is shown in Fig. 1. This system consists of two identical, 80-liter containers; distinctly half filled with untreated and treated water.

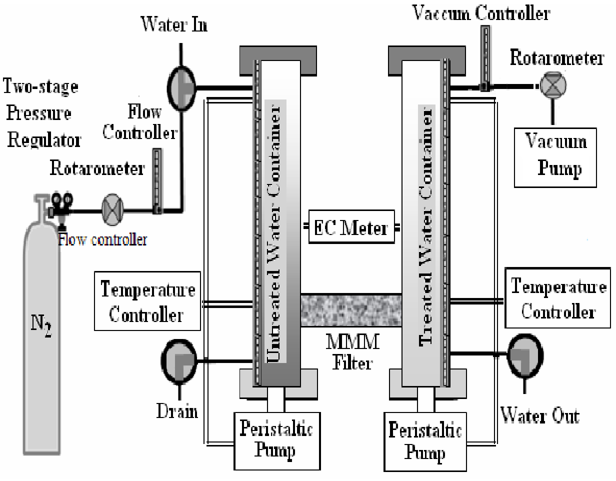


Fig. 1 Schematic representing the water treatment process

These two containers were connected with each other through horizontal glass tubing, packed with semi-permeable MMM. The temperature of water inside each container was controlled using cooling and heating systems by Ni-Cr thermocouples as thermal detector. To have homogeneous water solution as well as to prevent from any temperature gradient, water inside each container was independently stirred via circulation of water using two peristaltic pumps. To control the pressure of water through RO process, the pressure of untreated water was controlled via purging nitrogen gas through a rotarometer. Also, the pressure of treated water was controlled using a vacuum pump (2-stage Edwards E2M2 Company, Crawley Sussex, England) through a vacuum controller. In this system, the rate (flux) of treated water was evaluated via ranging the volume of each container. Also, the rate of water treatment process was measured using two lab-made EC meters.

A. Procedure

Prior starting water treatment process, each container was at most half filled with both untreated and treated water, individually. Then, the temperature of each untreated and treated water sample was set to ~25°C and ~8 °C, respectively, followed by circulation of water using peristaltic pump. After controlling the temperature, the pressure inside each untreated and treated water container was set to ~3.5 and ~0.05 bar, respectively. Finally, the flux of water, passed through the semi-permeable MMM, was evaluated via measuring the volume of water increased during water treatment, followed by evaluation of the rate of water treatment process using EC meters. The efficiency of the fabricated MMM for water treatment was evaluated by COD test

III. RESULTS AND DISCUSSION

In this work, RO method was selected as the method of choice for water treatment and purification. Briefly, RO process is a physical technique, in which partially pure solvent is produced from an impure solution using a semi-permeable membrane [11].This is because of significant advantageous of RO process such as simplicity, high efficiency and capability to industrialize this method, compared to other treatment methods such as forward osmosis [4]- [5], electrodialysis. As clearly observed according to the Table I, more efficient and also longer lifetime are evaluated forMWCNT-based MMM, compared to that fabricated using SWCNTs, CNFs, or fullerene. Selection of MWCNTs in the construction of MMM is related to high defect, edge planes and presence of large amounts functional groups such as -OH and -COOH in the CVD-synthesized MWCNT matrix [12]. critical conditions such as HIP process are needed to control the mechanical stability of the MMM [13]. These parameters depend on the temperature, pressure, number of cycle, and time duration of HIP process.As reported (Table I), the average lifetime of each CNT-based MMM is almost ~1 year without decrease in the efficiency, permeability and also without need any pretreatment.

TABLE I
EFFECT OF DIFFERENT CARBON NANOSTRUCTURES ON THE PERFORMANCE OF MMM IN WATER TREATMENT PROCESS. (1)

MMMs	SWCNTs	MWCNTs	CNFs	Fullerene
Rate (2)	3.1	3.6	1.7	2.9
Rate (3)	5.84	6.35	3.12	4.09
%E	86.47	96.76	89.88	86.01
Kw×10^{-4} (4)	1.92	4.69	6.26	1.81
COD (5)	7.11	3.16	35.72	28.19
H (6)	1.67	0.32	2.74	1.90
Δπ (7)	1.84	0.35	3.02	2.10
A (8)	832±3	813±2	813±2	795±4
Lifetime (9)	~1.5	>2	~1	~1.5

(1) Results are the average of three independent analyses.
(2) EC gradient versus time for treated water, ΔEC/Δt.
(3) Debi, the volume of water versus time passed through the MMMs, ΔV/Δt.
(4) (Lgm^{-1}Atm^{-1})
(5) Chemical oxygen demand in parts per million (ppm).
(6) Total hardness. (ppm)
(7) Osmotic pressure based on total harness of water using the "Morse" equation ($\pi V=nRT$) (atm) [12]-[13] at 25 °C.
(8) Active surface area, (m^{2}Kg^{-1}).measured by nitrogen adsorption using a thermogravimetric analyzer.
(9) (Year)

The efficiency of various carbon-based MMM is also reported in Table I. As shown, maximum efficiency (~97%) was evaluated for MWCNT-based MMMs, revealing the importance of active surface area, morphology and the edge planes of MWCNTs as active site for treatment process using RO technique. Scanning electron microscopic (SEM, XL-30 FEG, Philips, 20 KV) and atomic force microscopic (AFM, DME-SPM, version 2.0.0.9) images of MWCNT/PAN-based MMM are shown in Fig. 2 and Fig. 3, respectively.

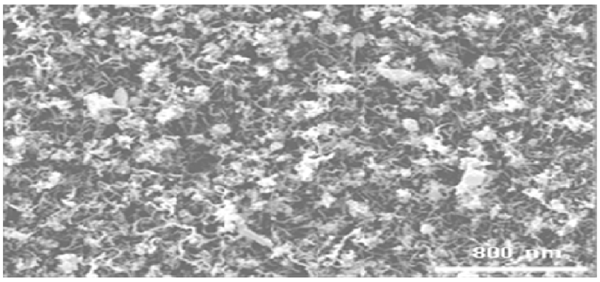


Fig. 2 Characterization of MWCNT-based MMM including SEM image

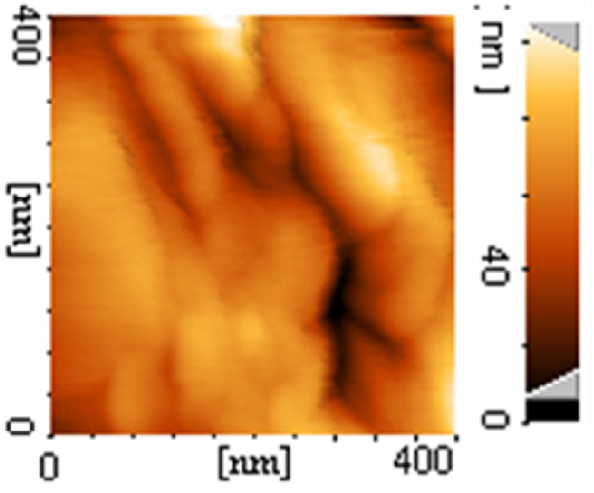


Fig. 3 Characterization of MWCNT-based MMM includingAFM image

Normal distribution of MWCNTs in PAN precursor is clearly evaluated according to the SEM and AFM images.also reveals the capability of the flexible and semi-permeable MMMs for treating different forms of water including industry, sea, river and drinking water as shown in Table II.

TABLE II

REAL SAMPLE ANALYSIS USING MWCNT-BASED MMM

Real sample	Rate(1)×10^{-3}	Rate(2)	Efficiency%
Wastewater	4.2	2.73	95.34
Sea water	4.6	3.19	92.06
Domestic water	3.1	6.35	96.76
River water	3.8	5.62	96.21
Industrial water	5.3	2.11	89.47

(1) EC gradient versus time for treated water, ΔEC/Δt.
(2) Debi, the volume of water versus time, passed through the MMMs, ΔV/Δt.

The potential of fabricated semi-permeable MMMs was also evaluated for quantitative analyses of different ions including K^+, Na^+, M^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, HCO^{3-}, and also parameters such as pH and total dissolved solids (TDS) in different forms of treated water samples as shown in Table III.

TABLE III

QUANTITATIVE ANALYSES OF TREATED WATER SAMPLES. (1)

Real sample	*Waste water*	*Sea water*	*Domestic water*	*River water*	*Industrial water*
K^+	0.08	0.06	0.04	0.12	0.18
Na^+	4.8	2.0	0.91	1.12	5.72
Mg^{2+}	5.2	3.0	2.8	3.1	8.0
Ca^{2+}	5.5	4.8	4.1	4.7	9.5
SO_4^{2-}	7.5	5.7	3.6	3.7	10.0
Cl^-	4.2	2.4	1.0	2.1	5.9
HCO_3^-	7.1	4.6	3.8	4.0	8.9
pH	7.22	7.50	7.27	7.21	7.45
TDS (2)	1761	1440	632	652	1856

(1) Unit of each data is in ppm (mg l^{-1}).
(2) Total Dissolved Solids (TDS)

also parameters such as Mg^{2+}, Ca^{2+}, Cl^-, pH and total dissolved solids (TDS) in different forms of feed water(before treated via MMM) and treated water via MMM samples as shown in Table IV.

TABLE IV

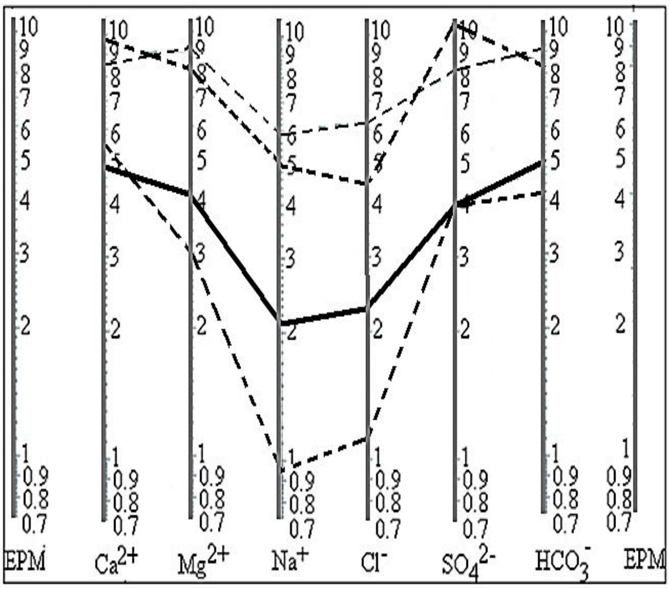
QUANTITATIVE ANALYSES OF TREATED WATER SAMPLES. (1)

Real sample	Wastewater	Domestic water	River water	Industrial water
Mg^{2+}(3)	21.30±0.06	9.12±0.06	18.63±0.08	36.81±0.09
Mg^{2+} (4)	5.22±0.05	2.84±0.06	3.12±0.05	8.02±0.05
Ca^{2+} (3)	36.18±0.10	24.06±0.09	38.43±0.10	71.82±0.11
Ca^{2+} (4)	5.53±0.09	4.11±0.11	4.74±0.13	9.53±0.17
Cl^- (3)	19.06±0.09	24.09±0.15	31.40±0.05	109.72±0.17
Cl^-(4)	4.23±0.09	1.04±0.15	2.14±0.05	5.92±0.17
PH (3)	7.62	7.37	7.35	8.63
PH (4)	7.22	7.27	7.21	7.45
TDS (2,3)	3405	1483	5911	28303
TDS (2,4)	1761	632	652	1856

(1) Unit of each data is in ppm (mg l^{-1}).
(2) Total Dissolved Solids (TDS).
(3)Feed water
(4) Treated water

Also,Fig. 4 shows the "Schoeller" diagrams related to several drinking water samples, treated by PAN/MWCNT-. based MMM

As shown, the fabricated MMM has enough potential for removal of various anions and cations specially Cl^- and Na^+. Therefore, fabricated MMM is considered as high efficient,high flexible and semi-permeable membrane for water treatment process. RO process using CNT-based MMMs has some significant advantageous such as simplicity, high sensitivity and permeability, flexibility and high efficiency.



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