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MULTI WALLED CARBON NANOTUBES FOR DESALINATION: PERFORMANCE EVALUATION AND COMPARATIVE STUDIES

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ABSTRACT: With increasing requirement worldwide, the advent of desalination technology using carbon nanotubes to address energy issues seems a practical option. This project intends to provide an in-depth insight on the application of MWCNTs to heighten the performance of seawater desalination in a universal manner. The mechanical and chemical properties of this material to facilitate excellent flux of water transport and salt rejection are outlined. The raw MWCNTs are modified accordingly and subsequent tests are then carried out to study the characteristic changes of MWCNTs. With use of FTC apparatus, desalination trials are then carried out for various samples and concentrations that help in optimization of desalination technique using MWCNTs. Cost effective measures are then analyzed and are modified accordingly. By measuring the TDS before and after we show the efficiency of the desalination process with each sample and concentration. The current hurdles and future challenges related to this technology are also addressed.

KEYWORDS: MWCNT (Multi-Walled Carbon Nanotubes), Desalination, FTC (Flow Through Capacitor), TDS (Total Dissolved Solids)

INTRODUCTION

Nanomaterials are one field of study that has fascinated scientists and engineers over the better part of the last few decades. The broad spectrum of potential applications makes this field all the more significant to present demand. Nanomaterials have a wide range of potential applications including: Construction of harder cutting tools, High density batteries, Improving automobile efficiency, etc. The rapid growth in nanotechnology research has triggered the interest in its biological and environmental applications. Some of the major environmental and biological applications of nanomaterials are: elimination of pollutants, brackish/salt water desalination, longer lasting medical implants, etc.

Water is a basic necessity for life on planet Earth. Unfortunately 98% of the water present on our planet is saline. And of the 2% water available, 90% is frozen in glaciers. There is little doubt that the world needs more drinking water. To meet the rising water demands, desalination of sea water seems to be the most practical solution and it must be given paramount importance[10].

RO technology has become a critical technology to assure the supply of freshwater due to its inherently simple design and operation and to enable it to serve as one of the most energy efficient techniques for seawater desalination purposes[1][3]. In fact, it has been reported that membrane-based desalination accounts for about 44% of the installed capacity of water desalination in the world[2]. Very recently, forward osmosis (FO) and membrane distillation (MD) as well as non-membrane electrochemical technologies such as capacitive deionization (CDI) have been explored for the potentials as alternative desalination technologies to offer low energy consumption while achieving high water recovery. These technologies are emerging to provide wider options, but have yet to find practical and commercialized applications[11]. Research efforts are underway to seek for breakthrough of these technologies to compete with and surpass the performance of conventional RO and thermal desalination[16][17].

CNTs have particularly attracted significant growing attention due to their capability to display superior durability and separation characteristics. The introduction of CNTs constitutes a significant potential break through for the desalination technology[8]. Previous research studies on the transport properties of CNTs have commonly found that the extremely smooth hollowed structure of the nanotubes could facilitate rapid transport of liquid and gas molecules in the channels, hence can favorably offer high flux membrane separation performance[9]. Diameter of the CNTs is the critical dimension to implement physical size exclusion and capillary behavior relevant to the environment systems. Extraordinarily, the small and precise diameter size of CNTs is also proved to reject most ions due to the energy barrier existing at the channel entries hence only water molecules are allowed to permit through the nanotube hollows. The findings from some of the simulation studies have interestingly showed that water can enter narrow hydrophobic interior channels of CNTs, which have been confirmed experimentally and have opened the door to the incorporation of CNTs into membrane to form smooth pores for the desalination applications.

Despite the current modern desalination technology that is using the advantages of CNTs, several challenges and hurdles encountered in the development of this newly emerging technology are still remaining as the major concerns of the worldwide desalination industries. Substantial uncertainty also remains about the technology's environment impact. Therefore, efforts to expand and fully harvest the advantages of CNTs may face great challenge in the near term. With the major focus placed on the utilization of CNTs, this paper aims to apply Multi walled CNTs for desalination of seawater and also incorporating it as a standard desalination technology.

With the constant improvement achieved in all aspects, it is anticipated that it is just the matter of time for this novel material to likely play an essential role in shaping the future trends in water purification research.

Experimental Procedure

Materials And Reagents

Reagent grade nitric acid and sulphuric acid were obtained from SRL They were used as received without further purification. Multi-walled carbon nanotubes obtained from SRL. All chemicals were of reagent grade and double-distilled water was used throughout the experiments.

Instrumentation

SEM analysis was carried out using FEI Quanta FEG-200 microscope was used. FT-IR results were obtained using Bruker spectrometer. Total dissolved solids was measured using TDS meter of Elico make.

Modification Of Mwcnts

Raw MWCNTs were marked as sample A. 0.35 grams of Sample A was immersed in 20% HNO_3 solution and refluxed for 30 minutes; then was washed several times with distilled water until the washings showed no acidity; and finally was dried at 100 ◦C for 2 hours. The product was marked as sample C. Now, 0.35 grams of sample A was refluxed in concentrated HNO_3 (10 ml) and H_2SO_4 solution (5 ml) for 45 minutes. It was then washed several times with distilled water until the washings show no acidity; and finally it was dried at 100 ◦C for 3 hours, this was marked as sample B. 0.35 grams of sample A was then heated with concentrated H_2SO_4 solution for 30 minutes to obtain sample D. The modifications are tabulated in Table 1

Table 1. Modifications in different samples

Sample	Modification Employed
A	Raw MWCNT
B	10 ml HNO_3& 5ml H_2SO_4- Refluxed for 45 minutes
C	20% HNO_3- refluxed for 30 minutes
D	Sample B – heated with 5ml H_2SO_4

Preparation Of Mwcnt Electrodes

For construction of Electrodes, graphite rods were used as the base. A binding mixture made up of Phenolic resin (90%) and Urotropine (10%) in ratio of 80:20 is used to coat the graphite rods with the MWCNTs. The binding mixture is prepared separately before adding 0.175 grams of each sample of surface modified MWCNT and is consequently coated on the exterior of the graphite rods. The graphite rods were then dried for a considerable amount of time and were tested for their physical properties. The rods are selected in such a way they don't interact with the solution contained in the FTC apparatus. The rods were then used and fabricated according to scaling needs.

FTC APPARATUS

The flow through capacitor (FTC) is an efficient means of chemical-free Total Dissolved Solids (TDS) reduction using electrically charged plates to remove ions. Its primary application thus far has been household water purification. The FTC delivers high purification, high recovery and long life. It resists scaling, and requires no routine maintenance or chemicals. It also is capable of removing "problem" ions such as arsenic, perchlorate, metals, nitrate, and sulfate, which have been proven to be harmful. It purifies up to 98% of hardness and salt from tap and brackish feed waters.

The FTC consists mainly of two carbon electrodes and a DC power source. Water flows through the narrow gap of the FTC, and anions as well as cations are removed via adsorption on the electrodes under the influence of an applied electric field. By simply controlling the applied voltage, the ions can be released thereby regenerating the cell. Chemical-free operation, low operating and maintenance costs, long lifetime, high recovery, low pressure-drop and the ability to remove harmful impurities distinguish the FTC.

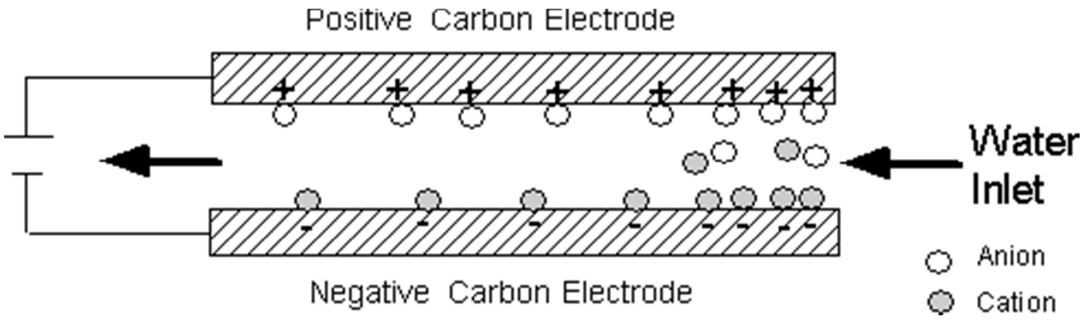

Fig 1 . FTC electrode mechanism

CONSTRUCTION OF FTC APPARATUS

The FTC apparatus is shown in the Fig 4. Graphite foil was used as an inert current collector on the backside of MWCNT electrode, and the electrodes were separated by the separator into anode/cathode pairs. Saltwater solution was passed through the capacitor at a flow rate of 10 ml min^{-1}.

NaCl was removed by applying a direct voltage of 3V between the collectors. The main advantage of this method of desalination over Reverse Osmosis (RO) is that constant pressure need not be applied to the membrane surface. A constant potential difference across the two electrodes is sufficient . Various trials were carried out with varying concentrations. Desalination process was also carried out for raw MWCNT for optimization purpose. The output voltage was measured with a scaled version of voltmeter. Various trials were carried out with varying concentrations. Desalination process was also carried out for raw MWCNT for optimization purpose. The output voltage was measured with a scaled version of voltmeter. The flow through capacitor (FTC) is an efficient means of chemical-free Total Dissolved Solids (TDS) reduction using electrically charged plates to remove ions. It resists scaling, and requires no routine maintenance or chemicals. It also is capable of removing ions such as arsenic, perchlorate, metals, nitrate, and sulfate, which have been proven to be harmful. It purifies up to 98% of hardness and salt from tap and brackish feed waters.

TEST AND MEASUREMENT

Before conducting the desalination process, initial TDS was measured for the contaminated water sample. The electrodes of the FTC apparatus is then immersed in this water sample and potential difference of 3 Volts is maintained. This procedure lasts for 20 minutes with continuous inspection at intervals of 5 minutes each. The water sample is then retrieved and the final TDS is measured.

RESULTS AND DISCUSSIONS

EFFECT OF MODIFICATION ON MWCNTS

The Figures 2 and 3 show the Fourier Transform Infrared Analysis of the raw MWCNTs(sample A) as well as the modified MWCNT(Sample B). FTIR is commonly used to investigate functional groups. The extent of functionalization will alter the wettability of MWCNTs in various surfactants and may thus alter its toxicity.

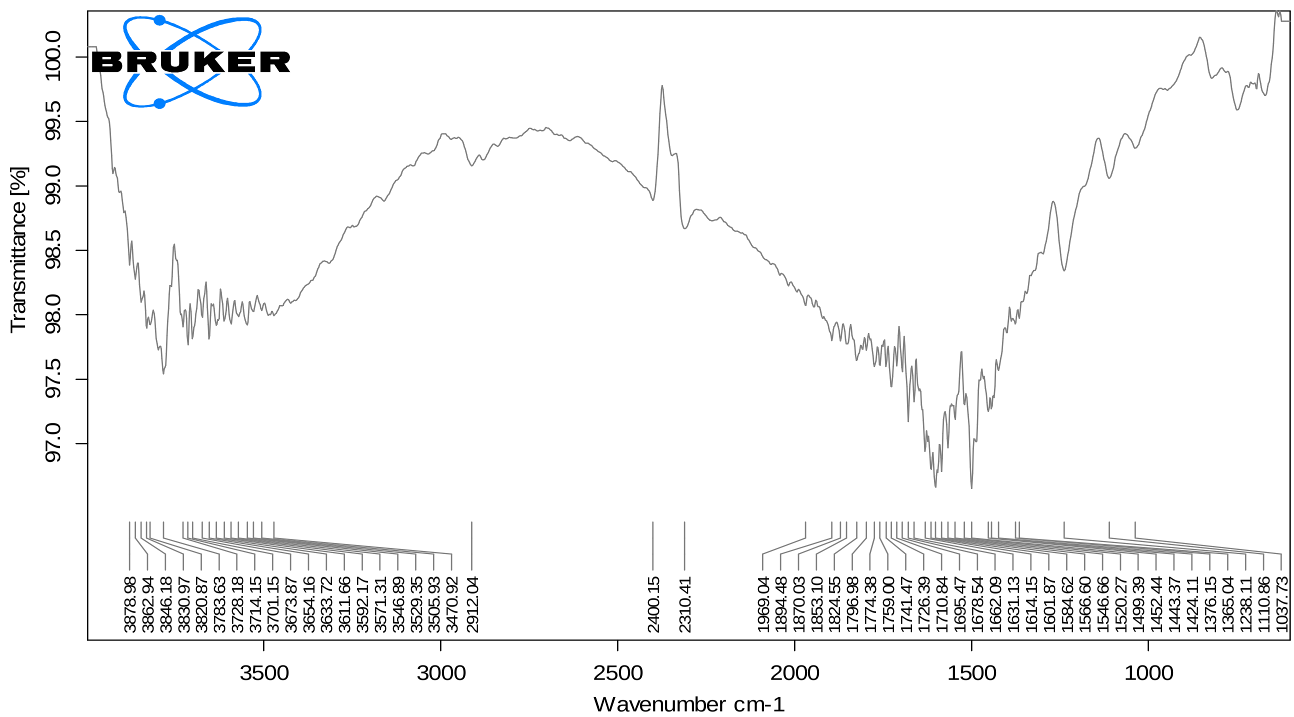

Fig 2 FTIR Analysis of raw MWCNT sample (Sample A)

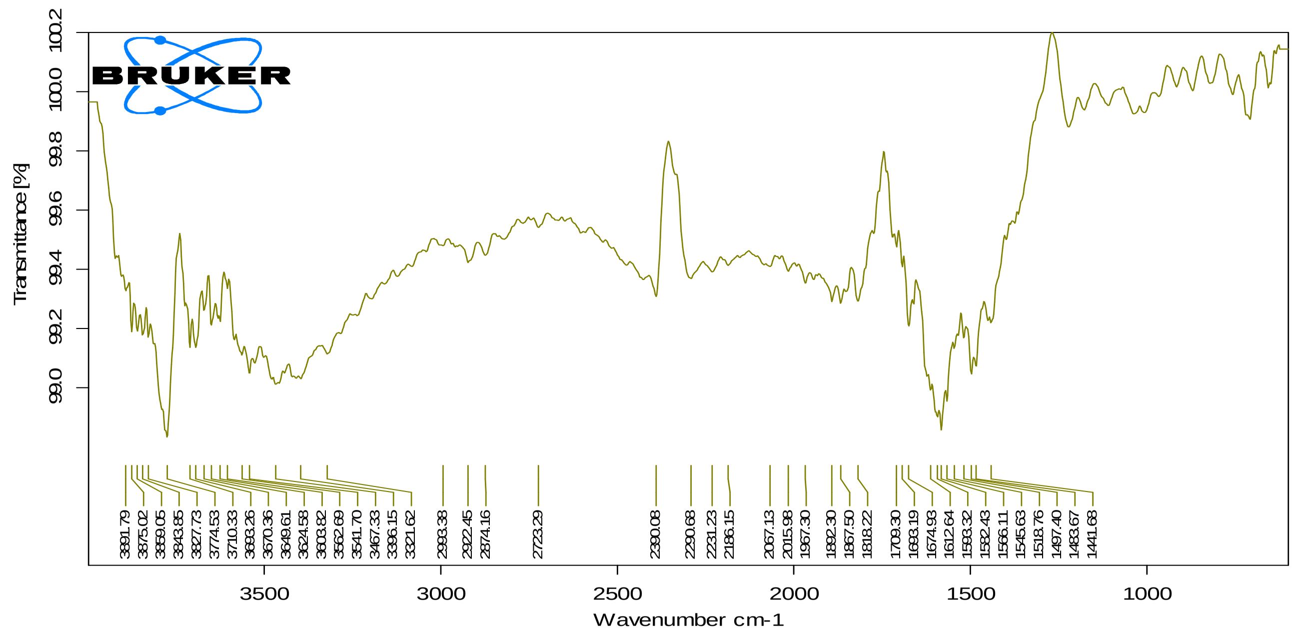

Fig 3. FTIR Analysis of Modified MWCNT sample (Sample B)

The modification take into consideration here is that of Sample B, which was refluxed in 10 ml HNO_3& 5ml H_2SO_4 for 45 minutes It is observed that there is only one additional peak formation in the modified sample when compared to the FTIR of raw MWCNT. This peak forms at approximately 1750. cm^{-1} wave number. This shows that there is no functional group attached to the modified sample other than anhydrides. Hence this shows that there is no detrimental effect of any functional group which can be observed during the desalination process.

SEM ANALYSIS

Scanning Electron Microscope with high resolution is powerful instrument for imaging of fine structures of materials and nanoparticles fabricated by the nanotechnology. For MWCNTs observation and their morphological analysis the F E I Quanta FEG 200 – High Resolution Scanning Electron Microscope was used Fig 4 and 5 shows the SEM images of Sample A and Sample B containing Raw and Acid refluxed MWCNTs. The resolution of secondary electron image (SEI) of the microscope is 2.0 and 5.0 µm at accelerating voltage 20 kV. Magnification is in the range of 15000x to 40000x. The MWCNTs in Figure 5 were found to be more randomly dispersed with MWCNT bundle formation at few regions. It therefore means that MWCNT dispersion in the refluxed sample is finer than that in raw MWCNTs. The results obtained from SEM and EDX shows the surface characterization, determination of the chemical composition and degree of purity of multi walled carbon nanotubes. Also these results showed that the

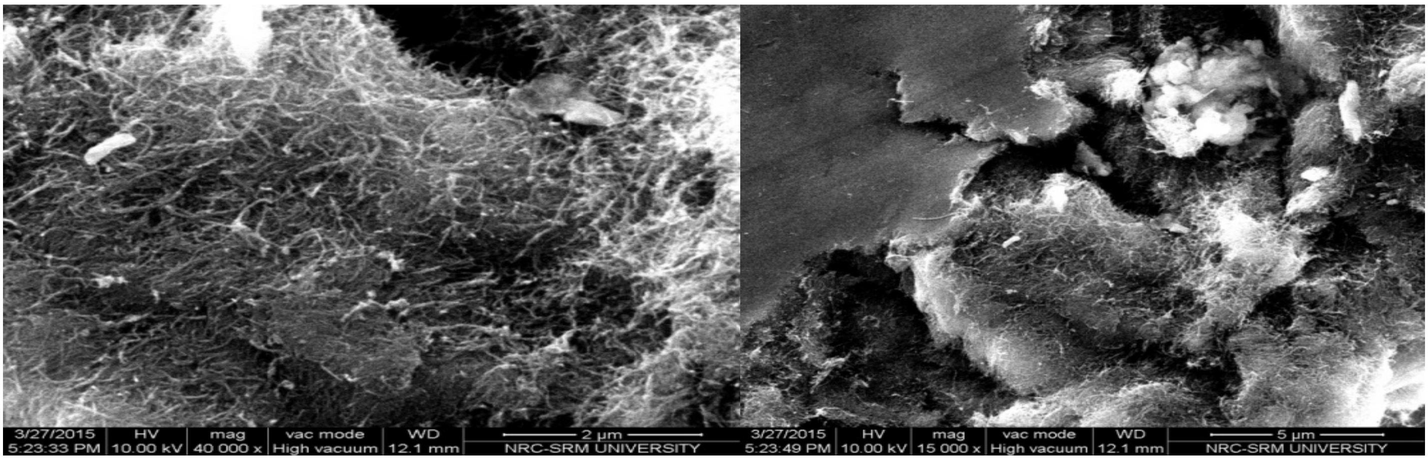

Fig.4 SEM Images of Sample A/Raw MWCNTs

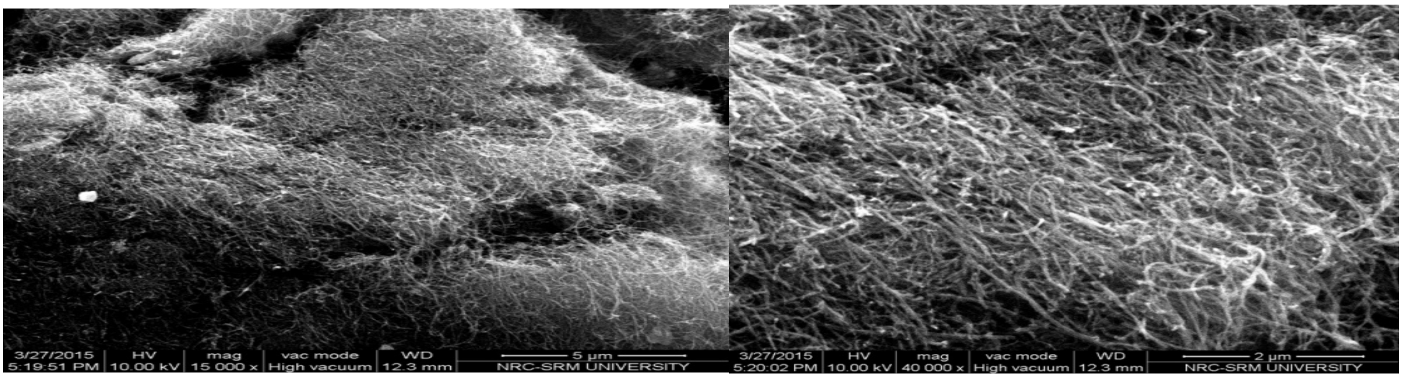

Fig.5 SEM Images of Sample B/Modified MWCNTs

MWCNTs when treated with 10 ml HNO_3& 5ml H_2SO_4 .Refluxed for 45 minutes is best suited for obtaining high purity MWCNTs and without any defects in its structure. These results prove to be important in the scalability of the process. These results are also important in analyzing the efficiency range of the process for different modified samples

Effect Of Modification On Desalination

Desalination studies were conducted for Sample A and Sample B on contaminated water sample of known initial TDS (886.2ppm). Characteristic studies over time were conducted for the water sample with the MWCNT electrodes placed inside the apparatus under 3 volts potential difference. The results are tabulated in Table 2

Table 2: Effect of MWCNT modification on desalination

Time (minutes)	Concentration of Sample A(ppm)	Concentration of Sample B(ppm)
5	886.6	886.6
10	863.4	760.5
15	839.2	678.5
20	825.7	659.2

Plotting of concentration of sample A and sample B against time gives the desalination curve as shown in Fig 6

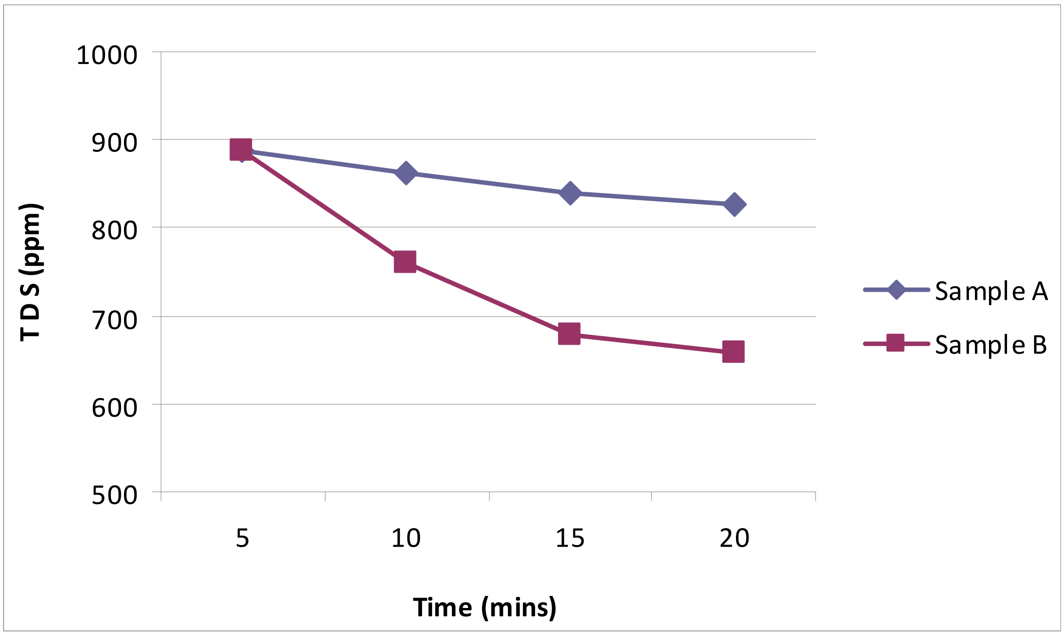

Fig 6 TDS curves of Sample A (Raw MWCNT) and Sample B (Modified MWCNT)

Conclusion

MWCNTs were modified successfully by using acid treatment. The surface morphologies of the modified samples were studied by using FEI Quanta FEG 200 Scanning Electron Microscope and FTIR. It is observed that the modification of MWCNT largely enhances the desalination performance of this novel material. Samples C and D were discarded because the de-acidification process failed to separate the MWCNT from the acid used for reflux. From this project, it has been confirmed that Sample A (Raw MWCNT) can be used as a material for desalination and the Total Dissolved Solid content of the water sample reduced from 886.6 ppm to 825.7 ppm. But, it has been proved that Sample B has a much superior efficiency and performance characteristics as it reduced to 659.2 ppm. Since this method employs a simple potential difference instead of maintaining a high constant pressure in the case of Reverse Osmosis, this understates that the running costs of this technique is very low making this a highly economical and favorable method for desalination of seawater

REFERENCES

[1] A. Matin, Z. Khan, S.M.J. Zaidi, M.C. Boyce, Biofouling in reverse osmosis membranes for seawater desalination: phenomena and prevention, Desalination281 (2011) 1–16.

[2] F. Macedonia, E. Curcio, E. Drioli, Integrated membrane systems for sea water desalination: energetic and exegetic analysis, economic evaluation, experimental study, Desalination 203 (2007) 260–276.

[3] A. Matin, Z. Khan, S.M.J. Zaidi, M.C. Boyce, Biofouling in reverse osmosis membranes for seawater desalination: phenomena and prevention, Desalination281 (2011) 1–16.

[4] A. Matin, Z. Khan, S.M.J. Zaidi, M.C. Boyce, Biofouling in reverse osmosis membranes for seawater desalination: phenomena and prevention, Desalination281 (2011) 1–16.

[5] F. Macedonia, E. Curcio, E. Drioli, Integrated membrane systems for sea water desalination: energetic and exegetic analysis, economic evaluation, experimental study, Desalination 203 (2007) 260–276.

[6] C. Fritzmann, J. Lowenberg, T. Wintgens, T. Melin, State-of-the-art of reverseosmosis desalination, Desalination 219 (2007) 1–76.

[7] P.S. Goh, A.F. Ismail, B.C. Ng - Carbon nanotubes for desalination: Performance evaluation and current hurdles

[8] L. Shi, J. Xie, H. Liu, H. Yang, C. Li, W. Zhu, A method about seawater desalination using flow through capacitor with carbon nanotube electrode, Patent No. CN1463927A, 2003

[9] Dengsong Zhang, Liyi Shi, Jianhui Fang, Kai Dai, Xuanke Li - Preparation and desalination performance of multiwall carbon Nanotubes

[10] Review of Water resources and desalination technologies - James E. Miller

[11] R. Sheikholeslami, Strategies for future research and development in desalination-challenges ahead, Desalination 248 (2009) 218–224.

[12] UN Water, Coping with water scarcity, A Strategic Issue and Priority for System- Wide Action, 2006.

[13] 2030 Water Resources Groups, Charting Our Water Future-Economic Frameworks to Inform Decision-Making, 2009.

[14] UNGA, United Nations Millennium Declaration, United Nations General Assembly, United Nations, A/RES/55/2, 9, 2000.

[15] F. Macedonio, E. Drioli, A.A. Gusev, A. Bardo, R. Semiat, M. Kurihara, Efficient tech- nologies for worldwide clean water supply, Chem. Eng. Process. 51 (2011) 2–17.

[16] M.S. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature 452 (2008) 301–310.

[17] B. Penate, L. Garcia-Rodriguez, Current trends and future prospects in the design of seawater reverse osmosis desalination technology, Desalination 284 (2012) 1–8.

[18] International Desalination Association, Desalination in 2008 global marker snapshot, 21st GWI/International Desalination Association Worldwide Desalting Plant Inventory, 2008.

[19] S.K. Pillai, S.S. Ray, M. Moodley, Purification of multi-walled carbon nanotubes, J. Nanosci. Nanotechnol. 8 (12) (2008) 6187–6207.

[20] A.F. Ismail, P.S. Goh, J.C. Tee, S.M. Sanip, M. Aziz, A review of purification techniques for carbon nanotubes, Nano 3 (2008) 127–143.

[21] M.S. Mauter, M. Elimelech, Environmental applications of carbon-based nanomaterials, Environ. Sci. Technol. 42 (2008) 5843–5859.