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Development of New Filter with Surface Modified MWCNTs

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Abstract: In the development of membrane technologies, it needs a better understanding of the material characteristics and its mechanism for the improved membrane systems. This study focuses on the low energy consumption and time-saving system in which several membrane filters are coated by ultrasonic using Multi-Walled Carbon Nano Tube (MWCNT) solutions. The MWCNTs were modified by chemical oxidation and mechanical treatment to improve membrane performance. The morphological and structural analysis was carried out by using the transmission electron microscope (TEM) and raman spectroscopy. Dispersion characteristics of the prepared fluids were examined by UV/Vis/NIR spectrophotometer at operating wavelengths range from 250 to 900 nm. The particle size of the filtrate was investigated by particle size analyzer using incoming samples with a consistent size. In these results, it was confirmed that the mechanically treated filter was more effective than other filters by chemical methods. It is expected that any other membrane filter system can be applied.

Key Words : Filter, MWCNT, Pore Size, Particle Size, Coating

1. Introduction

Lack of freshwater has been issued as a big challenge in this industry. Desalination of the polluted water has been utilized to produce fresh water for the human. The principal desalination method is based on membrane separation through reverse osmosis (RO).[1] However, there are many desalination technologies such as membrane, geothermal, solar desalination.[2-4] Many of nano-structured RO membranes were reported because of its unique permeability characteristics. In particular, the carbon nanotube (CNT) based membranes have been investigated over the decade.[5-7] Many kinds of research have been conducted to benefit from the various CNT properties and fabricate membranes.[8-10] These kinds of nanoporous materials have a huge potential in water desalination because it has a high water permeability and salt rejection characteristic. CNT which is well-aligned can make as robust pores in membranes for water desalination and decontamination applications.[11~14] Its structure makes frictionless transport of water molecules, and this makes them suitable for the high fluxing separation techniques. CNT functionalized to a higher degree form more homogeneous polymer solutions, which can make

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greater improvements of membrane characteristics.[15)] Moreover, proper pore size can make energy barriers at the entries of channel, rejecting salt ions and permitting water via nanotube hollows.[5)] The purpose of this study is to investigate the effective coating method. Particle size of filtrate was investigated by particle size analyzer using incoming samples that have a certain size. Furthermore, the effect of chemical modification method and mechanical method for MWCNTs are studied to determine a more acceptable way to improve desalination. In this work, it shows the best-modified MWCNTs as a membrane source.

2. Experimental details materials

2.1 Material

The MWCNT which is about 20 nm diameter, ~5 μm lengths, with greater than 95% purity, less than 3% impurities were used in this experimental study (Carbon Nanomaterial Technology Co., Ltd, South Korea). The chemicals, the concentrations (63%) of Nitric acid (HNO_3), the concentrations (98%) of the Sulfuric acid (H_2SO_4), were used for treatment processes. A base fluid for preparing nanofluids are used by Distilled water (DW). The Membrane filter with 2.5 ㎛ was used for coating.

2.2 Preparation of MWCNTs

The treated MWCNTs were prepared by using chemical and mechanical treatment methods in this study. For the chemical treatment, surface modification of MWCNTs was performed with 1:3 volume ratio of the mixture of concentrated nitric acid (HNO_3) and sulfuric acid (H_2SO_4). Pristine MWCNTs were suspended in mixture of acids with an ultrasonication (1510E-DTH, Branson Ultrasonic Corporation 41, Danbury, CT 06813, USA) at room temperature. Next oxidation reaction at 100°C for 100 minutes on a magnetic stirrer (Hot plate stirrer, SMSH-20A, Scilab Korea., Ltd.). The sample was filtered and rinsed with distilled water until the pH value reached to 7.0 and then dried in a furnace. The acid treated sample with H_2SO_4/HNO_3 was designed as C-CNT. For the mechanical treatment, grounding MWCNTs were made by using planetary ball mill (A planetary ball mill, HPM-700, provided by Haji Engineering, Gimhae, Korea) which grind to MWCNTs. Mono-sized (3.0 mm) spherical zirconia (ZrO_2) balls were used as the collision medium. The agitator-applied rotation speed is 500 RPM for 1h under wet condition.[16)] It is denoted as M-CNT for mechanically treated MWCNTs.

2.3 Preparation coating of membrane filter

Nanomaterials are not dispersed well in aqueous solution as they are subjected to a very large surface area, forcing strong Van der Walls.[17-18)] Carbon nanotubes are naturally hydrophobic and aggregate, therefore non-homogeneous and unstable in the aqueous solution with steady conditions. Chemical functionalization typically involves treating chemicals at high temperatures on top or sidewall areas of carbon nanotubes. As a result of the above, functional groups are added to the defected areas on the nanotube surface, which makes carbon nanotubes more hydrophilic.[19-20)] Mechanical treating can reduce particle agglomeration by using the grinding method. It is known that the decreased agglomeration of carbon nanotubes would disperse better in the base fluid[21~22)]. Through the above processes, it was prepared the nanofluid to coat the membrane filter, and the incoming nanofluid sample for filtration was made by using stainless steel nanoparticles. The 0.1 wt% of the nanofluids were treated for 1h by ultrasonic (Branson Ultrasonic Corporation 41, Danbury, CT 06813, USA). The membrane filters were soaked into the nanofluids. Then, the samples in the nanofluid were treated by

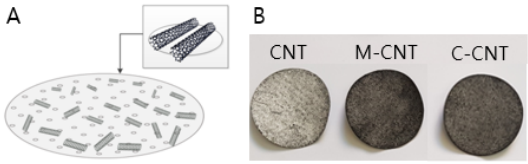

Fig. 1 (A) Schematic (B) Each sample picture

ultrasonic to make a better coating. As a result, it was investigated for three filters: pristine CNT coated filter, M-CNT coated filter and C-CNT coated filter. Fig. 1(A) shows the schematic design with CNT coated on a membrane filter, and 1(B) shows completed each filter.

3. Experimental results and discussion

3.1 Morphological Surface Analysis of MWCNTs

The morphological characteristics of MWCNTs were observed by TEM (JEM-2100 F, JEOL; Tokyo, Japan) in this study. The light source in a TEM is an electron beam that accelerates at high speeds in a high vacuum state (1×10-4 or higher). The electron beam penetrates the sample and goes through a series of electromagnetic or electrostatic fields, and finally is projected with a focus on the fluorescent plate or photographic film. TEM interacts with the incident light and composes an electron sample. TEM is a device obtaining a light field image, dark field image, diffraction pattern, etc. by using certain parts of beam when the electron enters the sample after interaction. As mentioned above, structure information in the sample can be obtained mostly through the diffraction pattern, dark field image, and bright field image. With high-scaling images of approximately 1.5 million magnifications, the microstructure of the sample can be directly observed. It is also useful for observing common crystal fault structures.

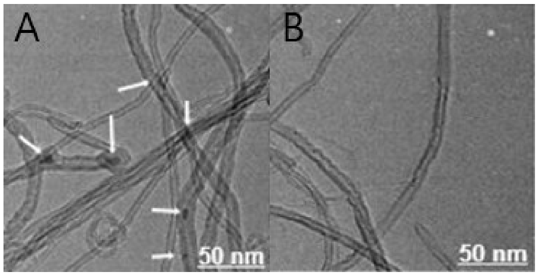

Fig. 2 TEM images of the pristine and chemical treated MWCNTs.
(A) Pristine CNT, (B) C-CNT

Fig. 2 shows the TEM image of Pristine MWCNTs and chemical treatment MWCNTs. Particle impurities attached to carbon fiber surface as part of the synthesis process. This shows that pristine MWCNTs contain impurities such as graphitic, metal catalysts and amorphous carbon (white arrows in Fig. 2(A)). Catalyst particles are clearly embedded in the tips or tube cores of pristine CNTs.[17),23)] In this study, a mixture solution of acids and oxidants was used for the treatment process. Thus, the impurities structure was removed from MWCNTs, the tips of the nanotubes were opened after chemical treatment and the morphology of tubular structure could still observe in Fig. 2(B), which suggests that the structure of C-CNT had not deteriorated. This implies that the structure of MWCNTs has not been changed even after the treatment process. The Raman spectrometer (HR Micro Raman spectrometer, LaRAM HR800 UV, HORIBA JOBIN YVON, Kyoto, Japan) can measure the detector of a Czerny-turner type with a focal distance of 800mm and obtains resolving power of $0.3cm^{-1}$. It is a system which can measure from the UV area to the Near IR area and without calibration for optical aberration, using a mirror instead of a Lens. The Raman spectrometer confirms the structural changes of the Chemical treatment CNTs and shows the highest intensity values of the two properties in the Raman analysis D-band $1330cm^{-1}$

and G-band 1585cm^{-1}. The D band indicates the structural defects in graphitic, which is not ill-organized due to the sp^3 hybridization carbon. Also, the G band indicates tangential C=C stretching vibrations due to the integrity of hexagonal sp^2 hybridization carbon.[23-24] Highest intensity values mean that chemical structures such as C=O, O-H and C-O-H are altered or created during the oxidation of the pristine CNT. Due to the functional group's generation on the surface of the pristine CNT, intensity ratio of the D-band and G-band was increased. The value of (I_D/I_G) is a result that the chemical treatment CNT has a larger functional group than the pristine CNT. After chemical treatment process, the intensity of the D-band increased compared to that of the pristine CNT, and this indicates the production of mixed carbon with functional groups attached. In this study, the Raman spectrum could determine that C-CNT was functionalized as seen in the Fig. 3.

3.2 Dispersion of MWCNTs

The UV/Vis spectrum (UV/Vis/NIR Spectrophotometer, U-4100, HITACHI, Tokyo, Japan) shows the absorbance values of solution for the dispersion. Dispersibility means the level of absorbed light. As the number of molecules and the surface area increase, the area that absorbs light increases. This results in the ability to determine dispersion.[18] Dispersion graph shows the reflectivity measurement results in an incident angle of 45° for a YAG laser, showing the reflection properties of S$^-$ and P$^-$ polarized lights from the mirror of a microfabricator. Each reflectance indicates nearly 100% at 1064nm and is measured with precise polarization characteristics. Therefore, the dispersion of MWCNTs is indicated by UV/VIS absorption spectra and can generally be determined that higher absorbance results in better dispersion.[25] Fig. 4 shows the UV-vis spectrum of the pristine CNT, the mechanical treatment CNT, and the chemical

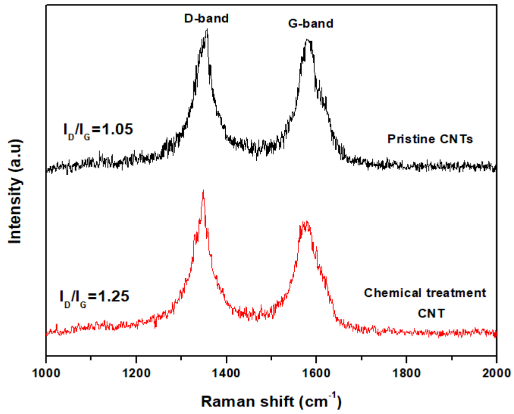

Fig. 3 Raman spectra of pristine and various treated MWCNTs.

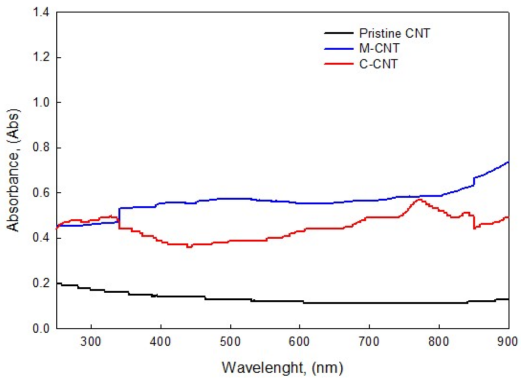

Fig. 4 UV-Vis spectra of pristine and various treated MWCNTs nanofluids.

treatment CNT. C-CNT showed a higher absorption value than the pristine CNT. Chemical treatment allows functional groups to be inserted into the defect sites. Functional groups make to the CNT more hydrophilic and reduce the interactions of Van der Waals forces between the CNT, which facilitates the separation of carbon nanotube bundles into individual nanotubes. A large surface area M-CNT reduced the Van der Waals force interaction which allowed us to conclude M-CNT to be highly decentralized than the hydrophilic properties of C-CNT significantly. Through this experiment, it was concluded that surface treatment is essential for the dispersion of nanofluids. The measured absorption value results showed that C-CNT was the largest, followed by M-CNT and Pristine CNT.

3.3 Particle size analysis

Particle size of filtered solution was investigated through dynamic Light Scattering of particle size analysis (Particle Size & Zeta Potential Analyzer, NANO ZS, Malvern analytical Instrument Ltd., Malvern, United Kingdom). Dynamic Light Scattering (DLS) is used to measure particles and molecular size. DLS measures the spread of moving particles in Brownian motion and replaces these measurements with size and distribution size using the Stokes-Einstein relationship. Non-Invasive Back Scatter (NIBS) technology is applied to provide the highest sensitivity, maximum size, and concentration range. The experimental conditions were set to Viscosity (cP): 0.8872, Dispersant RI: 1.330 and Count Rate (kcps) was set to 2.1 at a temperature of 25°C. As seen in the Fig. 5, The X-axis means as follows: Water for distilled water; Membrane for the only membrane filter without CNT coated; CNT for the filter coated with MWCNTs that are not surface treated; and M-CNT and C-CNT for the membrane filter coated with each surface treated CNT. Each filtration experiment result is as below; Membrane 1952 (r.nm), CNT 1317 (r.nm), C-CNT 651.9 (r.nm), and M-CNT 126 (r.nm). The average

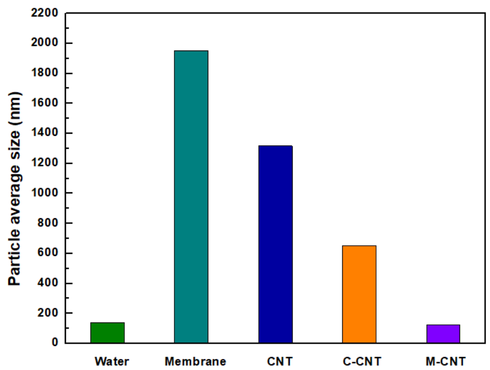

Fig. 5 Particle size of incoming solution

particle size of the standard distilled water is 140.6 Z-Average (r.nm) and the incoming solution is stainless nanofluid. As a result, filtered solution's particle average size of M-CNT is smaller than others.

4. Conclusions

In this study, we researched effective filtration system of Micro-nanomaterials which can affect negative influence on marine environment. A conclusion can be summarized as follows: The surface of the MWCNT has been modified in two different ways (chemical treatment and mechanical treatment) to increase the dispersion and facilitate adsorption of the Membrane filter. The filter that adsorbed mechanically treated CNT with a greater surface area due to grinding had the highest filtration efficiency, however, the dispersion of chemically treated CNT with hydrophilic properties had low filtration efficiency, even though the dispersibility was similar to mechanical CNT. The filtration efficiency of the Pristine CNT filters increased by 32.5% compared to Membrane, while C-CNT and M-CNT increased 50.5% and 90.4% respectively compared to CNT filter. The filtration efficiency of M-CNT shows the best value of 93.5% higher than Membrane filter The performance of the filter that adsorbed the surface modified CNT was better than that of the filter coated the pristine CNT, and this result demonstrated the performance of Membrane filter by coated CNTs which can replace the expensive micro Membrane filter.

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Author contributions

J. Y. Park and H. M Jeong; Conceptualization, J. Y. Park. and Y. H. Park.; Data Curation, J. Y. Park. and H. M Jeong; Formal Analysis, Methodology, J. Y. Park and Y. H. Park.; Investigation, H. M Jeong; Validation, J. Y. Park; Writing – Original Draft Preparation, H. M Jeong; Writing – Review and Editing.

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