Fabrication and Characterization Membrane Prepared from Oxidized Multiwall Carbon Nanotube/Nylon 6 Composite

تصنيع وتوصيف غشاء محضر من متراكب انابيب الكاربون متعددة الجدران النانويه المؤكسده/نايلون

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Abstract:

Mixed matrix nanofibres membranes were prepared, characterized, studied and evaluated for performance and properties in this research. Acid oxidized Multiwall carbon nanotubes MWCNTs embedded in Nylon 6 as matrix polymer were the materials used to create the prepared membranes. Through; the electrospinning process, the hydrophilicity of the membrane was enhanced by blending (MWCNTs) due to migration of functionalized MWCNTs into the membrane surface. Scanning electron microscopy SEM and morphology studies showed that average fiber diameters produced were about 72-193 nm and average pore size 183 - 226 nm . It was found that as fiber diameter decreases high porosity and small pore size will be created and increasing the amount of functionalized MWCNTs leads to increase of pure water flux. The MWCNT blended with Nylon 6 membranes showed better antibactericidal ability as compared to the neat Nylon 6 membranes. Water filter media with a high rejection ratio against heavy metal ions reached (80%) at (0.8 wt. % MWCNT) membrane. Addition of MWCNTs forms a membrane with high mechanical strength (4.158MPa) of Nylon/ 0.8 wt. % MWCNT.

Key Words: Nanofibrous, Electrospinning, Lead Nitrate, Sodium Chloride, Adsorption, carbon nanotube, Antibacterial Activity, Escherichia Coli.

الخلاصه

في هذا البحث حضرت أغشية مخلوطه من البوليمر والياف نانويه وتم توصيفها ودراسة وتقييم أدائها وخصائصها،انابيب الكاربونيه النانويه المتعددة الجدران المؤكسده حمضيا" MWCNTs غمرت في بوليمرالنايلون 6 كمادة اساس حيث استخدمت هذه الانابيب لتحضير الغشاء. عززت خاصية ألفة الماء (تبللية) للاغشيه بخلط أنابيب الكاربون MWCNTs حيث يعزى لتكون رابط من انابيب االكاربون مفعل MWCNTs الى سطح الغشاء خلال عملية البرم الكهربائي. دراسة المورفولوجيه بالمجهر الالكتروني الماسح أظهرت أن معدل قطر الالياف المنتجه كان بحدود 139-72 نانومتر ومعدل حجم المسامات 183-226 نانومتر، وجدأن قطر الالياف ينقص بزيادة المساميه تكون مسامات بحجم صغير. زيادة اضافة انابيب الكانون النانوية المفعلة MWCNTs تؤدي الى زيادة كمية تدفق الماء النقي. أن أضافةMWCNT المخلوطة لأغشية النايلون6 أظهرت قدرة المضاده للبكتريا أفضل بالمقارنة مع الأغشية نايلون 6النقيه. أوساط تصفية المياه بارتفاع نسبة الرفض ضد ايونات المعادن الثقيلة وصلت (80٪) في غشاء (0.8 نسبه وزنيه٪ أنابيب الكاربون النانويه. أضافة الانابيب الكاربونيه الناونيه متعددة الطدران تمنح الاغشيه المحضره متانه ميكانيكه عاليةوصلت (4.158ميكاباسكال) لغشاءمن النايلون / بأضافة وزنيهبالوزن0.8 ٪ من الانابيب النانويه.

Introduction

Several scientific researchers investigate and studied the properties and the application of carbon nanotube (CNTs). This nanomaterial attracts researchers for exploration to their properties [1- 6]. The physical, mechanical, electrical and thermal properties of carbon nanomaterials had extreme range and that gives these materials the power of usage in different applications [1, 2]. These materials had been used as advanced reinforcing fillers for high-strength, light-weight and functional polymer nanocomposites because of their extraordinary properties [7, 8]. Enhancement

of polymer nanocomposites in mechanical and thermal properties had been always an aim and that can be done by homogeneous dispersion and strong interfacial interaction between the filler and the polymer matrix [7]. These materials can be functionalized and that will provides efficient stress transfer between the nanometric carbon and the polymer matrix and this can be done by preventing aggregation in the polymer matrix and providing a better dispersion of the nanomaterials [3, 5]. Also, at the surface of nanometric carbon, very strong type of interfacial bonding with the polymer matrix at the surface of nanometric carbon will be created by the functional groups [4, 7].
Nylon 6 can be considered as an important engineering thermoplastic because of its good thermal stability, good mechanical strength and its semi crystalline form [9-12]. This polymer type, which behave as poly-electrolytic in acid solution is very suitable for electrospinning processing [13]. The nanofibers obtained from the electrospinning process with such polymer offers the possibility to collect particles actively on nanoscale [8].

Experimental

1. Materials and Methodes

Materials used in this research were: Nylon 6 (molecular weight for repeat unit 113.16 (g/mol), formic acid (Sigma-Aldrich Co. (USA)), Multi walled Carbon nanotubes MWCNT (Cheap Tubes Co., Canada, with outer diameter 10-30 nm, 5-10 nm inner diameter and length 10-3 µm) . Lead nitrate $Pb(NO_3)_2$ (fluka chemika Germenay), Sodium chloride (NaCl) (Edutek Chemicals, India). All agents were used without further purification.

2. Preparation of Nylon 6 / MWCNTs Solutions
The preparation of WMCNT/Nylon 6 was consisted of two stages: Modification of Carbon nanotube by acidic treatment and blended with Nylon 6.

I. Carbon Nanotube Modification: The first step to produce the MWCNTs/Nylon 6 blend membranes is to create a homogeneous MWCNTs solution in solvent before adding Nylon 6 polymer. In spite of the strongly hydrophobic and very low solubility of MWCNTs in all solvents, MWCNTs surface was treated with strong acid to get over such problems, i.e. concentrated (H_2SO_4) and (HNO_3) to create hydrophilic functional groups. The surfaces of MWCNTs usually have carboxyl groups which show good dispersion in polar organic solvents, so two method were used for such case. Prepare 3 gm of modified MWCNTs was done by using a (500 ml) of ((3M) HNO_3/H_2SO_4 (1/3, v/v)) were mixed with 3 gm of raw MWCNTs and sonicate for 1 hr. The mixtures then were reflex in an oven for 12 hr. at a temperature 100 ^oC . 10 liters of deionized water were used then to dilute the solution and filtration for it was also done. Reaching the neutral pH was done by using rinsed with deionized water [14]. Then the modified MWCNTs dried for 12 hr. at 50 ^oC [15]. The modified MWCNT have been tested by X-ray to explain the effects of acidic treatment on prepared MWCNTs .

2.Solution preparation; The Nylon6 solutions containing multi walled carbon nanotube were prepared initially by adding the MWCNTs with the percentages (0.2, 0.4, 0.6, and 0.8 wt.%) which were dispersed in formic acid by magnetic stirring at room temperature for 3hr. to disrupt possible agglomerates.

3. Electrospinning; Stainless steel needle tip with (22 gauge) which equipped with 10 ml syringe was used to store the prepared electrospun solution. The operating parameters while the electrospinning were: 25 kV voltage, 0.5 ml/ hr flow rate, 0.7 mm needle tip diameter and 15 cm distance between electrodes. The electrospinning process took 4 hr. time and these parameters

will be fixed for all following solutions. The electrospinning operations were done at room temperature (30 °C) and humidity (25-30 %). The diameter of the prepared electrospun nanofiber was 12.4 cm . The electrospinning process was carried out by (Bio-electrospinning/ Electrospray system ESB-200), (Nano NC, South Korea).

4**.** Characterization: Studying the morphology of the produced nanofibers was done by scanning electron microscopy (Model: VEGA3 LM –TESCAN). All specimens of produced nanofibers were tested under low pressure in all (SEM) tests; the pressure was enough, so there was no need for any more of sample gold ion sputtering coating to chive conductivity in the surface of the specimens in SEM tests. Specimen conductivity was measured by (model (C and 7110 inolab)). A Viscometer of type (DV-II- pro) was used to measure solution viscosity at room temperature. Surface tensiometer with the model (JYW-200A- laryee technology. Co) and a ring of platinum were used to measure solution surface tension. Electrical conductivity device of model (C and 7110 inolab) was also used to measure solution electrical conductivity.

5. Contact angle measurement**:** The wettability of the electrospun mats was measured with deionized water contact angle measurements. Contact angle meter with the type (CAM 110, Germany) was used. Deionized water was automatically dropped onto the membrane. Measurement was carried out in 3 seconds.

6. Permeability test: Experiments were carried out at a temperature (23-24 °C). Tests were done and conducted by using high pressure cross flow filtration system. Measuring pure water flux and salt rejection were the used method that characterized Nylon 6 with various additives membranes. Membranes were exposed to a pressure to the value of 1 bar for 50 min .. They were placed with a shim and a mesh structured spacer to eliminate pressure polarization. They were pressurized with a mechanical pump controlled by pressure regulators and then the pressure was lowered to the operating pressure 1-6 bars . The permeable flux was calculated by equation (1).

$$J = \frac{V}{A} * T \qquad (1)$$

Where (J) is the permeable flux ($L/m^2 \times h$), (V) is the volume of permeate (liter), (A) is the effective membrane surface area (m^2) and (T) is the time (hr.). The salt rejection was determined using atomic absorption device (-AA-7000 atomic absorption spectrophotometer, Shimadzu). The rejection of salts was obtained by:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad (2)$$

Where (C_p) and (C_f) are ion concentration in permeate and feed, respectively, (R) is rejection as a percentage. Figure (2) shows the system used in this process. During the rejection test three cells was used of membranes (three layers) on one layer of microfiber.

7. Mechanical strength measurement**:** Mechanical properties of the electrospun membrane were measured by a tensile mechanical tester with the type (Tinus Olsen, H50 KT). A 5 N load cell was used in that device. Specimen thicknesses were measured by an optical microscope. Specimens with the dimensions 10 mm width and 100 mm length were tested and the extension rate at the room temperature was (0.5 mm/min). The experiments were carried three times to calculate the average value of the result.

8. Antimicrobial test

A. Antibacterial activity test (Disc diffusion method): Bacteria were grown aerobically in nutrient broth at (37 ºC) for (12 hr.) [16]. Cells were washed and suspended in distilled water until reaching

the final concentration of (10^6 CFU/mL). The antimicrobial susceptibility of MWCNTs / Nylon 6 nanofibers was evaluated using the disc diffusion method. "Muller - Hinton agar" was prepared from a commercially available dehydrated medium according to manufacturer's instructions. The dried surface of "Muller Hinton agar" plate was inoculated with (*E.coli*) by swabbing over entire the sterile agar surface. Two forms of nanofiber sterilized membrane samples were cut into small standard circles (6 mm in diameter) for each circle and placed on the surface of the inoculated media. The first form of nanofiber membrane is contains additive and other one without additive which was used as a control. The plates were incubated at (37 ºC) for (24 hr.). Incubation plates, then were examined in order to identify clear zones on growth characteristic for antibacterial activity (halos around the fragments).

B. Antibacterial activity test (Optical density method): The antibacterial activity of electrospun nanofibers membrane was also tested by immobilizing nanofiber onto filters of a Millipore under vacuum filtration. A test water sample was prepared by inoculating (1×10^8 cells/ml) *E.coli* into (250 ml) of sterile normal saline water sample (0.85% (NaCl) in (100 ml) distilled water). Water samples then were filtered through the membrane. After this step the optical density of the solution was measured by (UV) spectrophotometer (UV-1800 spectrophotometer, shimadzu) at (450 nm) wavelength. The number of bacteria was indirectly measured by optical density in an ultraviolet (UV) – visible spectrometer and the antibacterial activity were evaluated quantitatively with the following equation [17]:

$$Antibacterial\ activity\ (efficiency) = \frac{A-B}{A} \times 100\% \qquad (3)$$

Where A and B are the numbers of surviving cells in the control and test samples, respectively.

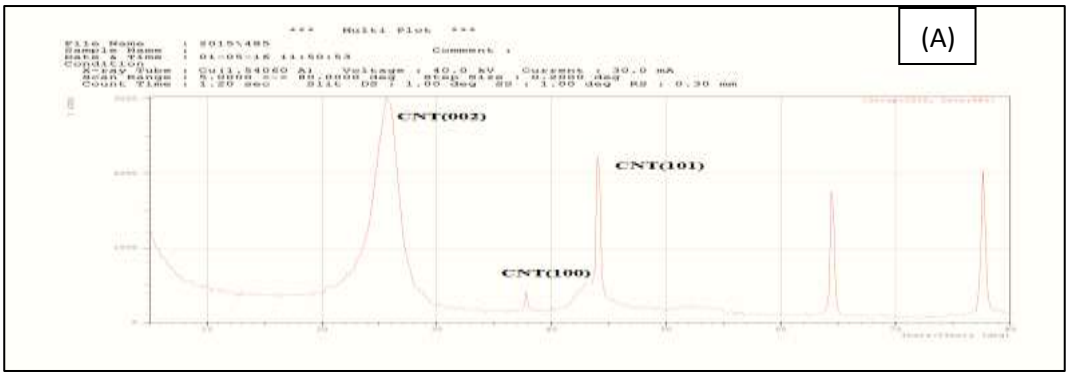
Results and discussion

I. **X-ray Diffraction:**

Figure (3) shows the X-ray diffraction patterns of as-synthesized and functionalized of MWCNTs . As described in the previous works [18], the significant diffraction pattern of MWCNTs is appeared at (2θ) is about (26 °). The (2θ) peaks correspond to (002) reflection planes or also known as interlayered spacing between adjacent graphite layers, respectively. The (002) reflection peaks was observed at the same (2θ) values in both as-synthesized and functionalized MWCNTs diffractions. Interestingly, the intensity of diffraction peak at (002) in acid functionalized MWCNTs was increased as compared to the raw MWCNTs .

Furthermore, from XRD patterns of the functionalized MWCNTs samples, it was observed that the XRD patterns were similar to the as-synthesized MWCNTs . Thus, the structure of MWCNTs is protected even after undergoing the treatment as confirmed from XRD analysis previously [18].

II. Properties of spinning solutions: The effect of Mullitwall carbon nanotube MWCNTs addition on the viscosity of the Nylon 6 / MWCNTs solution is shown in table (1). The least viscosity of the solution and the thinnest fiber diameter will be determined by SEM results. The electrical conductivity increased with increasing the weight percent of additives. In the solution of Multiwall carbon nanotube, increasing the concentration (wt. %) of MWCNTs will lead to create more conductive pathways in nylon.



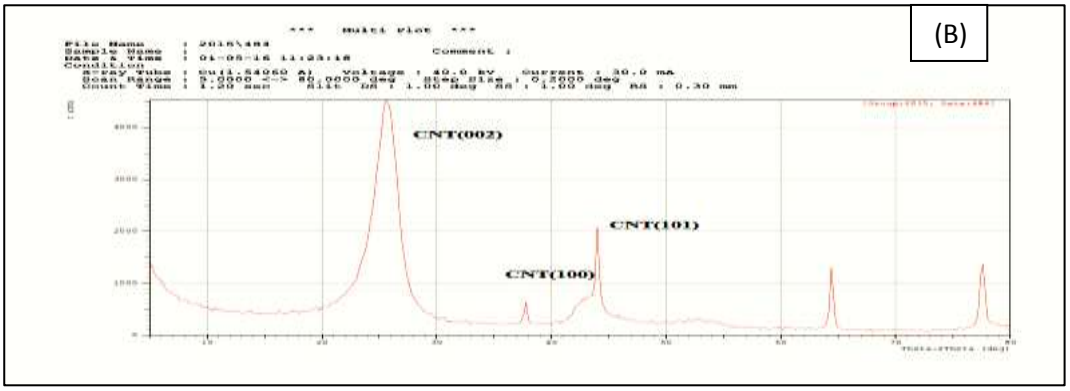


Figure (1): X-ray of (A) raw carbon nanotube, (B) acidic modification carbon nanotube by ((1/3) HNO_3/H_2SO_4).

This leads to increase the mobility and density of charge carriers and will increase the electrical conductivity.This explanation agrees with (J. Wang et al.) [19], whom explained that MWCNTs addition will form conductive pathways in the polymer and that will improve the electrical conductivity. Table (1) shows the effect of MWCNTs on electrical conductivity of the polymeric solution. The increase in the percentage of additive solution will not lead to an increase in additive ratio only, but also lead to reduce the polymeric content which reduces the surface tension of solutions with increasing the additives.

III. Electrospun Membrane Characterization

Figure (2-a) demonstrates the surface morphology of nanofibers electrospun of (Nylon 6). All nanofibers shows continuous and smooth fibrous structure and homogeneous morphology, with an average diameter 139 nm obtained from the histogram drawn from SEM image analysis and calculated as shown in figure (2-b) for average fibers diameters**.**

Table (1): The electrospinning solution properties (these average values after three time test)

Concentration of (MWCNT wt. %)	Electrical conductivity (mS/cm)	Viscosity (cP)	Surface tension (mN/m)
0	**4.0**	**692**	**34.43**
0.2	**4.3**	**510**	**34.30**
0.4	**4.9**	**420**	**33.90**
0.6	**5.8**	**411**	**33.50**
0.8	**6.7**	**389**	**33.30**

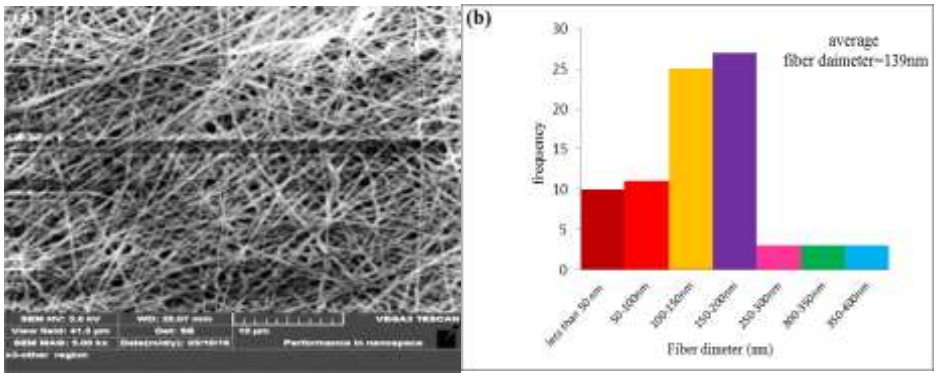


Figure (2): (a) SEM image of pure (Nylon 6) nanofibers membrane, (b) fiber diameter distribution.

Figure (3-a) presents the SEM image for (Nylon / 0.8wt. % MWCNT) membrane and the slight and very small swelling appearing inside the fibers indicates the presence of MWCNTs on or inside the fiber surface where the MWCNTs bonded to the polymer chain by functional group that formed after acid treatment of CNTs). The average fiber diameter of the Nylon / 0.8 wt. % MWCNT membrane was 72 nm , as shown in figure (3-b).

The contact angle of the Nylon 6 membranes decreased with an addition of MWCNTs as illustrated in figure (4), suggesting that the MWCNTs additives gave a hydrophilic property on the Nylon 6 membrane surface. All the functionalized membranes showed increasing in the hydrophilic character with an increase in porosity of the membranes. It reveals that, the membrane interconnectivity between the sub-layers increases with an increased number of surface pores. The above results demonstrated the flux increases due to increased hydrophilicity and pore connectivity.

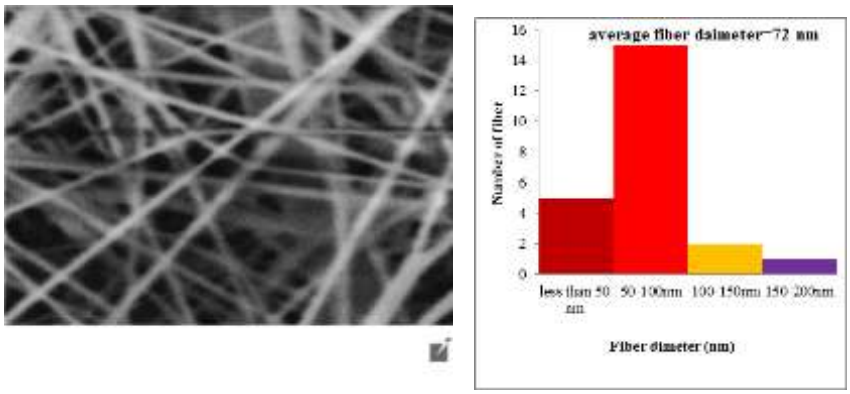


Figure (3): (a) SEM image of 0.8 wt. % MWCNT/ Nylon 6 nanofibers membrane, (b) fiber diameter distribution.

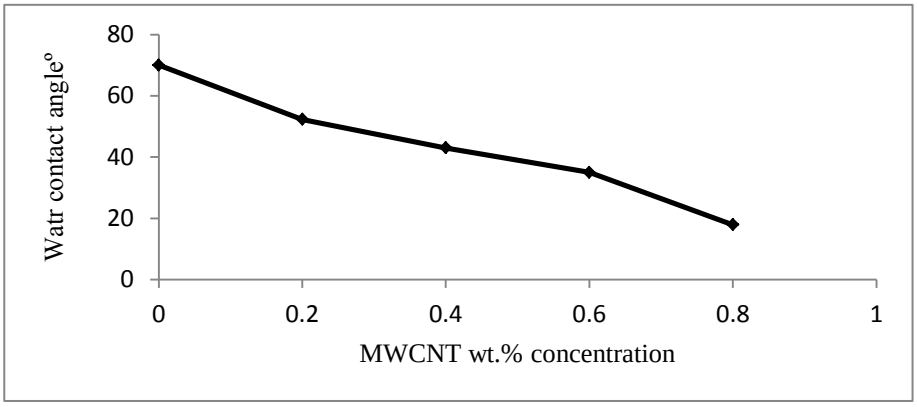


Figure (4): Water contact angle variations of various (Nylon / MWCNT) electrospun nanofibrous membranes.

Figure (5) shows behavior of pure water flux permeation with time at room temperature and 1 bar membrane pressure. It can be seen that the pure water flux permeation of Nylon 6/ MWCNTs nanofiber membrane decreases with time from (2037.063 to 1293.53 L /m^2.hr) for pure Nylon membrane.

Figure (5) shows that flux has been improved as the concentration of MWCNTs increased due to the latter works to increase the hydrophilicity of membrane; whereas the relationship between flux and pressure are explained in figure (6). Figure (6) shows that when an increase in pressure is happening the pure water flux is increased, because of flux directly proportional to the pressure drop across the membrane as shown in figure (6) and the same behavior for all membrane is noticed as the pressure increased.

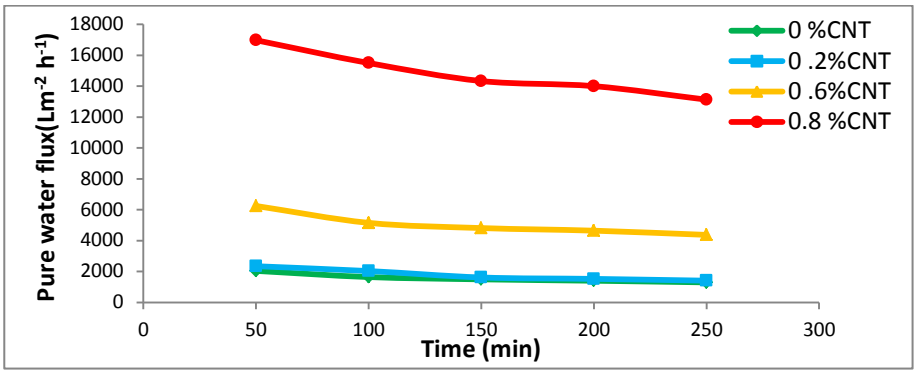


Figure (5): Pure water permeation flux with time of Nylon 6 /MWCNT nanofiber membrane at room temperature and (1 bar) pressure.

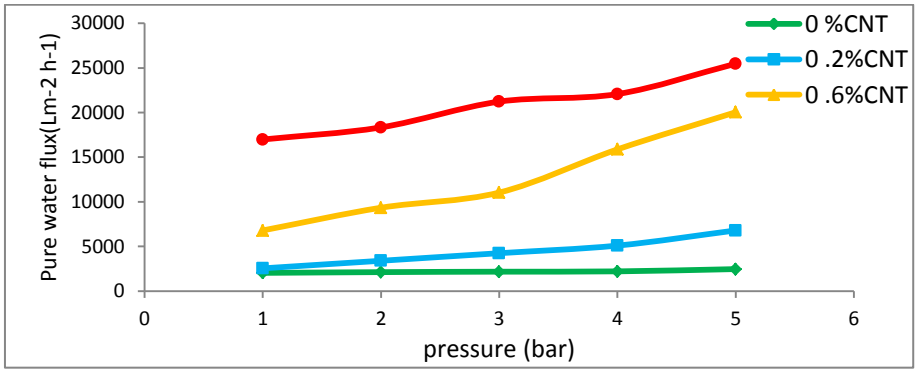


Figure (6)***:*** Effect of membrane pressure on the pure water permeation flux of the Nylon 6/MWCNT nanofiber membrane at room temperature and 50 min time.

Figure (7) shows the effect of carbon nanotube on salt rejection which increased with increasing concentration of carbon nanotube. The nanofibous membranes of Nylon 6 / MWCNTs shows a decrease in the average fiber diameter which leads to an increase in the reactive surface area of fibers and so works to capture the salt ions and increase the rejection ratio. Rejection ratio reached to 80.1 % for $Pb(NO_3)_2$ and 70.8 % for NaCl salts.

As relatively new adsorbents, CNTs have been proven to possess great potential for removing heavy metal ions such as lead, cadmium, chromium, copper and nickel from wastewater. The mechanisms by which the metal ions are adsorbed onto CNTs are very complicated and appear attributable to electrostatic attraction, sorption precipitation and chemical interaction between the metal ions and the surface functional groups of CNTs . The sorption capacities of metal ions by raw CNTs are very low but significantly increase after oxidized, this was agreed with (F. Fu, Q. Wang) [20].

The adsorption of (Pb (II)) using acidified (MWCNTs was reported by Wang et al. [21]). They found that the oxygenous functional groups on (MWCNTs) plays an important role in (Pb (II)) adsorption to form chemical complex adsorption which accounts for (75.3%) of all the (Pb (II)) adsorption capacity.

An efficient sorbent with both high capacity and fast rate adsorption should have the following two main characteristics: functional groups and large surface area [21]. From this point of view, the electrospun nanofiber provide the two factors of high specific surface area to volume aspect ratio and also the electrostic electrical force that formed in nanofiber during the electrospinning process which enhance the electrostatic attraction of the nanofiber membrane and improve the salt rejection.

Among the salts potassium sulphate showed more flux and rejection followed by Sodium chloride. This can explained with the help of ionic size and charge density. The high rejection of (K^+) ion

reaches the value (80%) for the membrane (PEI) and this is because of the higher ionic radius of (K^+) ion, which its value is (157 pm) compared with the value (116 pm) for (Na^+) [22]. This explained why high rejection of (Pb^{+2}) ion, which its value is (133 pm) and rejection ratio reached up to (80 %) and (Na^{+1}) ion (116 pm) up to (70 %). Nanofiber adsorption methods appear that nanofibers is the best to remove metal ions while have low pressure drops and high water fluxes.

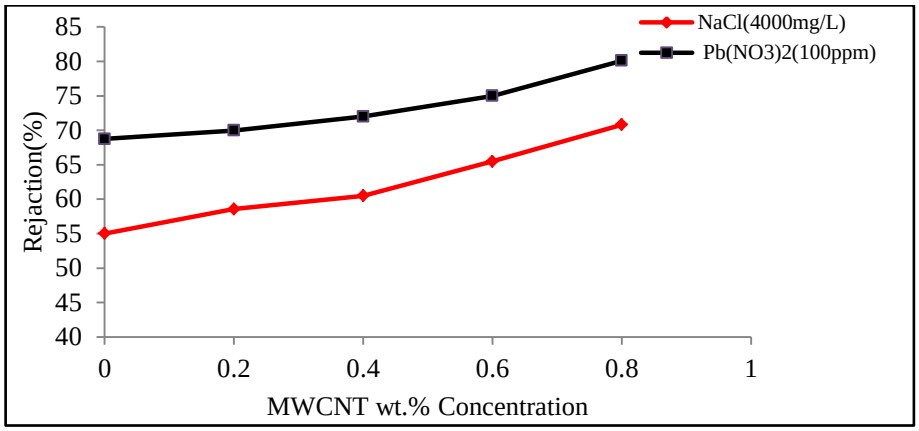


Figure (7): Effect of MWCNT/Nylon 6 ratio on rejection of Pb $(NO_3)_2$ salt and NaCl salt aqueous solutions with initial concentration 100 ppm and 4000mg/L respectively, at room temperature and 1 bar.

IV. Antibacterial activity results

In case of plain Nylon 6 nanofiber, these zones were missing. The presence of additive in the nanofiber patch, may lead to kill the microorganism around the patch which results in formation of clear circular zones. Figures 8 and 9 show the effect of carbon nanotube on the formation inhibition zone, which has been increased with increasing the amount of carbon nanotube and conform its antibacterial activity against *E.Coli* bacteria. The inhibition zone reaches to about 5 mm at 0.8wt. % MWCNT.

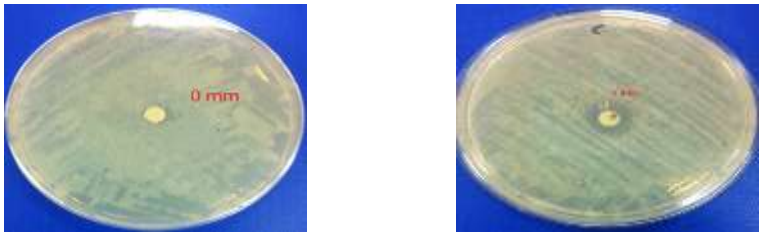


Figure (8): Shows the formation inhibition zone around the MWCNT/Nylon membrane, after 24 hrs. and 37ºC.

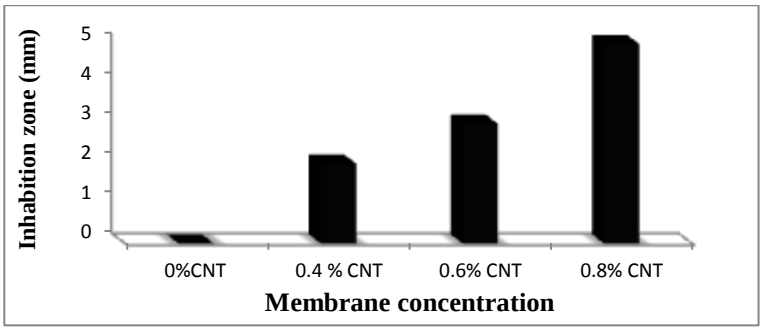


Figure (9): Effect of MWCNT /Nylon ratio in inhibition zone against (*E.coli.*) bacteria.

The antibacterial activity of treated Multiwall carbon nanotube toward the removal and inactivation of bacteria Gram negative (*E.coli*) has been studied by Mohammed et al. [23]. They found that reduction percent reached 90% . The antibacterial activity of carbon nanotube was inspected also, by the optical density measurement, before and after water filtration of water sample containing (1×10^8 (cell/ml) *E.coli*) bacteria. The recorded value of control sample was (0.312) at (450 nm). Furthermore, the optical density remarkable decreased after filtration by (Nylon 6/MWCNT) membrane because of small pore size and electrostatic force that formed in fiber during the electrospinning process. This work on capturing bacteria and prevent it from penetration with water. The increased amount of MWCNTs leads to decrease the average fiber diameter; also increased the amount of MWCNTs will increase the antibacterial activity as shown figure (10). Figure (11) shows how the nanofiber membranes capture and prevent bacteria from the penetration with water.

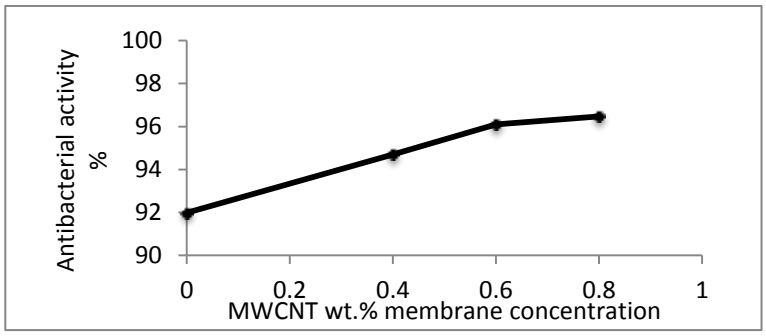


Figure (10): Effect of MWCNT addition in the antibacterial activity at room temperature.

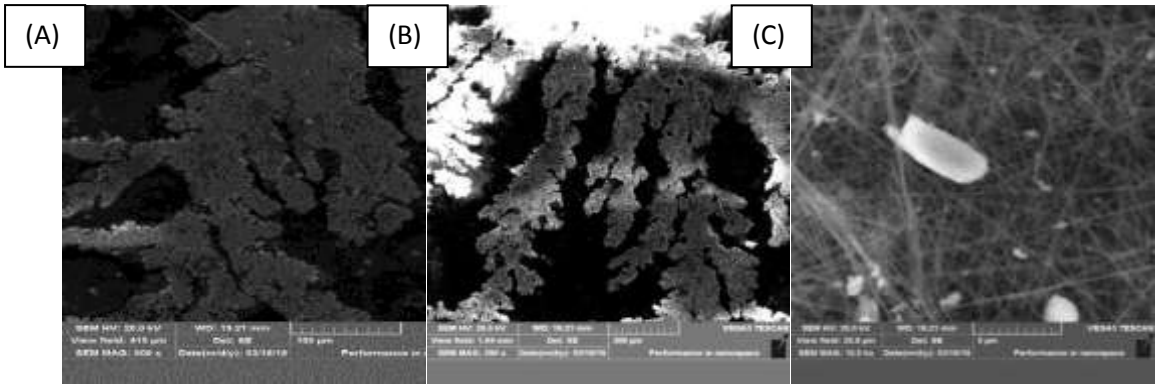


Figure (11): SEM of membrane after exposing to bacteria, where the bacteria cluster: (A) on the membrane surface as a dendritic shape colony, (B) and (C) shows how fiber capture the bacteria.

V. Mechanical test results: The results of stress-strain curves for Nylon 6 membrane of different compositions (Pure Nylon, Nylon / MWCNT) have been studied to show the effect of MWCNTs in the mechanical behavior of the membrane. Figure (12) explains the effect of MWCNTs on mechanical behavior of Nylon 6. MWCNTs has high tensile strength; addition of MWCNTs forms a membrane with high mechanical strength (4.158MPa) of Nylon/ 0.8 wt. % MWCNT.

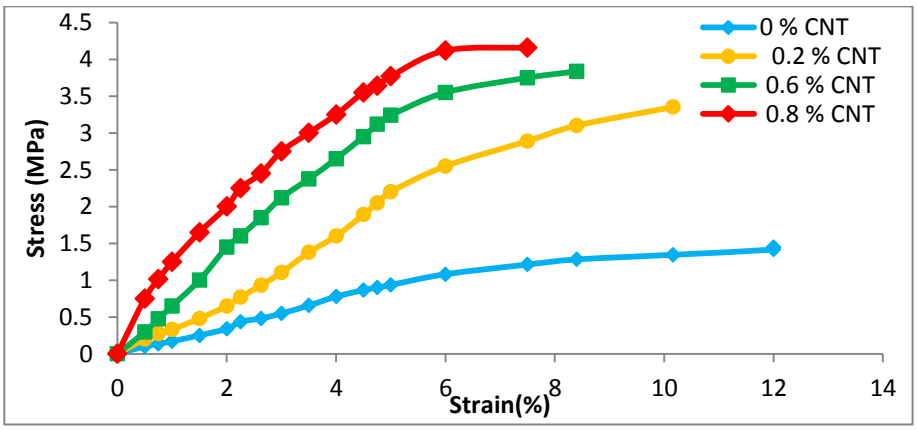


Figure (12): Stress – Strain curve of MWCNT /Nylon 6 with various ratios.

Conclusion

MWCNT/ Nylon 6 nanofiber membrane were prepared via electrospinning by mixing different amounts of (functionalized Multiwall carbon nanotube) with (Nylon 6). The addition of (modified carbon nanotube) improves the hydrophilicity and mechanical strength of (Nylon 6) nanofiber membrane. The enhanced hydrophilicity of the nanofiber membrane can decrease fouling to make the mat a potential candidate for water filtration and improve the performance of membrane at low pressures. The (MWCNT) blended with (Nylon 6) membranes showed better antibactericidal ability as compared to the neat (Nylon 6) membranes. Water filter media with a high rejection ratio against heavy metal ions reached (80%) at (0.8 wt. % MWCNT) membrane.

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