FUNCTIONALIZED TITANIUM DIOXIDE NANOPARTICLES - NYLON 6 NANOCOMPOSITE MEMBRANE FOR IMPROVED SALT REJECTION UNDER LOW PRESSURE WATER NANOFILTRATION

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ABSTRACT :-

In this paper, (Nylon-6) spider-net containing (dioxide titanium) nanoparticles were electro spun to produce nanofiber membrane with (TiO_2 NPs). Characterization of the nanofiber membrane containing (TiO_2 NPs) were done by (SEM) and (EDX) analyses. Pure (Nylon-6) nanofibers with an average diameter of (139 nm) were produced while (TiO_2) additive gives membrane (Nylon/TiO_2) with an average nanofibers diameter of (123 nm). (TiO_2 NPs) with small amounts in (Nylon-6) solution were found which improve the hydrophilicity (antifouling effect) with water contact angle (5.7^o), pure water flux (4800.45 $Lm^{-2}h^{-1}$) and mechanical strength (7.075 MPa). It was concluded that (Nylon-6/TiO_2) antimicrobial (spider-net) which considered as a composite membrane with antifouling effect can be used in water filter applications. An improvement in the produced membrane mechanical strength was reached, also, rejection test of salt was achieved with rejection percentage of (76) and (71) for ($Pb(NO_3)_2$) and (NaCl) respectively.

Key Words: Nylon-6, TiO_2, Electrospinning, Salt Rejection, Spider-net, Water Nanofiltration .

غشاء متراكب نانوي ثاني أكسيد التيتانيوم - نايلون 6 لتحسين طرد الاملاح تحت ضغط منخفض للترشيح النانوي للماء

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الخلاصة:

في البحث الحالي ، تم اجراء عملية برم كهربائي لمادة (نايلون6) الحاوية على (اوكيسد تيتانيوم النانوي) لتحضير غشاء ذو شبكة عنكبوتية من الالياف النانوية . تم توصيف الغشاء الحاوي على الالياف النانوية الناتج من عملية البرم الكهربائي (نايلون/ اوكسيد التيتانيوم النانوي) بواسطة (طيف الاشعه المتشتتة - EDX) و (المجهر الالكتروني الماسح - SEM) ، غشاء النايلون النقي اعطى الياف نانوية بمعدل قطر (139 نانومتر) بينما الغشاء (نايلون/ اوكسيد التيتانيوم) انتج الياف بمعدل قطر (123 نانومتر). كمية صغيرة من دقائق اوكسيد التيتانيوم النانوية في الاغشية حسنت قياس زاوية التماس الماء حيث انخفضت الى (5.7^o) وبذلك تحسنت خاصية البلل للغشاء كمرشح (hydrophilicity). معدل تدفق المياه النقية وصل الى (4800.045 لتر/ م^2 ساعة) . اظهرت الخواص الميكانيكية اجهاد شد وصل الى (7.075 ميجا باسكال). تم فحص خواص الغشاء المضاده للبكتريا وامكانية استخدامه في تنقية معالجة المياة. بلغت نسبة طرد الاملاح للغشاء (76% و 71%) لكل من نترات الرصاص وكلويد الصوديوم ، على التوالي .

الكلمات المفتاحية : البرم الكهربائي ، نسبة طرد الاملاح، الترشيح النانوي للماء.

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1- INTRODUCTION :-

Starting late, the blend and layout of organic – inorganic hybrid materials have made a mind boggling interest in the fields of materials sciences. Composite nanofiber materials formed by blending nanosized inorganic and common materials appealing with the true objective of making new materials with new or overhauled properties differentiated and single normal or inorganic materials. The incorporation of a small amount can upgrade the execution of the mechanical, thermal, electrical, optical antimicrobial, antifouling and catalytic properties of a polymer matrix [Jeffrey, et al., 2005, Damodar, et al., 2009]. This process makes fibers best rival in various applications, for instance, filtration [Damodar, et al., 2009, Akram, et al., 2015], tissue engineering [Yang, et al., 2009, Yang, et al., 2008], protective clothing [Jung, et al., 2009, Prasanth, et al., 2008], and sensor [Rajesh, et al., 2009]. Several processes like: (Sol-gel) processes, evaporation deposition and spin–coating were utilized to incorporate inorganic nanoparticles into a polymer matrix [Luca, et al., 2009, Venkat, et al., 2006]. Electrospinng is seemed to as a clear and adaptable strategy for this technique [Nasser, et al., 2010]. Moreover, polymeric fiber mats with (nano and submicron) fibers (spider-net like structure) in the same mats can finish new properties for formation of high aspect ratio nanofibers membrane. A couple of investigators have been investigated in the development of spider-net like structure nanofiber polymeric) mats [Dušan, et al., 2009, Bin, et al., 2006]. ANylon-6 polymer is a biodegradable and biocompatible. This polymer is broadly utilized as a part of numerous of modern fields in light of its low cost, unrivaled fiber forming ability, greater mechanical quality, and chemical and thermal stability [Akram, et al., 2016]. Electrospinning Nylon 6 mats have accounted for as an operation prompts produce compelling water filtration media [Aussawasathien, et al., 2008]. Likewise, it was accounted for that electospinning process which produce mats of Nylon 6 in the (spider- net like structure) with enhance hydrophilicity may be a potential possibility for such application.

Nanoparticles of (TiO2) had several excellent properties like: hydrophilic properties, good stability, (UV) blocking ability and photocatalytic and antimicrobacterial ability [Amy, et al., 1995]. (TiO2 NPs) which is considered as photocatalytic degradation were highly investigated because it's high efficiently converting abundant (UV) visible light energy into chemical energy. Such ability is used to decompose harmful organic materials in air and water [Akira, et al., 1972, Mejia, et al., 2009]. (UV) illumination of (TiO_2) causes electrons to excite from the valence band to the conduction band which leaving holes in the valence band. The electrons then react with oxygen molecules which produce superoxide anions whereas the holes react with water to produce hydroxyl radicals. A variety of organic toxic materials were decomposing because of these two highly reactive species [Akira, et al., 1972]. Blending of these two materials at the nanoscale can form a remarkable and powerful multifunctional nanocomposite material. The (TiO_2) can form (spider-net like structure) fiber mats which can prompt an expansion in the quantity of reactive sites by comparing the change in hydrophilicity, photocataylitics and antimicrobial activity.

In this paper, it was centered around the planning of (Nylon/ TiO_2) organic-inorganic nanocomposite material as an electrospun mat containing two particular types of s (nano- sub micron-sized) stacked with TiO_2 NPs, prevalent mechanical quality high hydrophilicity and great antimicrobial and in addition UV- blocking capacity. This (spider-net like nano-structure) mat with antimicrobial and hydrophilic properties would have incredible potential water filtration applications.

2- MATERIALS AND METHODS :-

2.1 Materials

The raw materials used in this study are presented in Table (1).

2.2 Preparation of Nylon 6 /NANO TiO_2 solution

In this study, The Nylon 6 solutions containing Titania nanoparticles were prepared as follows: The nano- titania (TiO_2) (0.5, 1.0, 3.0, 5.0, and 7.0 wt. %) was dispersed in Nylon 6 solution, magnetic stirring and ultrasonicated at room temperature for (105 min) to disrupt possible agglomerates. Titania was added with respect to Nylon 6, the appropriate weight of Nylon 6 was used. TiO_2/Nylon 6 nanofibrous mats were produced by electrospinning of the prepared solution on a stainless steel / Millipore microfiltration fitter collector.

2.3 Electrospinning process

By using electrospinning device, type (by a Bio-electrospinning/ Electrospray system (ESB-200), provided by Nano NC, South Korea), the solution of composite Nylon 6 /TiO_2 is loaded into a syringe (10 ml) with a stainless steel needle (needle diameter 0.7 mm) and the distance between needle stage and dram type collector was (15cm). High voltage (25 KV) was supplied to the needle to create a potential difference between the needle and the collector, while the flow rate of the solution was (0.5 ml/hr) at room temperature.

2.4 Characterizations

Solution characterization: The conductivity of a solution was measured by (model (C and 7110 inolab)). Solution viscosity was measured by (Viscometer of type (DV-II- pro)) at room temperature. The Surface tension Surface was measured by (Tensiometer model (JYW-200A-laryee technology co)) by using platinum Ring during surface tension test.

Surface morphology: Nanofibers surface morphology were studied by using (scanning electron microscopy-(SEM) (Model: VEGA3 LM –TESCAN)), by mode of low variable pressure which must be enough and not need any more of sample gold ion sputtering coating to achieve conductivity surface for (SEM) test and (Energy Dispersive X-Ray Spectroscopy-(EDS)) .

Contact angle measurement: Prepared electrospun membrane wettability was measured with deionized water contact angle measurements using a contact angle meter (CAM 110, Germany). Deionized water was automatically dropped onto the membrane. The measurement was carried out after (3) seconds **.** **Permeability Test:** Experiments were done at room temperature (23 ± 1^0C). In this test, high pressure cross flow filtration system was used. Membrane diameter was (30 mm). (Nylon-6/TiO_2) membranes were characterized by measuring the pure water flux and salt rejection. Each membrane was pressurized to (1 bar) for (50 min). Membranes were placed with a shim and a mesh structured spacer to eliminate pressure polarization. The membrane module was pressurized with a mechanical pump controlled by pressure regulators and then the pressure was decreased to the operating pressure (1-6 bars). Figure (1-a) shows pressure cross flow filtration system which is designed in this research especially to conduct the test. The permeable flux was calculated by eq. (1).

$$J = \frac{V}{A \times T} \quad (1)$$

Where (J) is the permeable flux (L/m^2 ×h), (V) is the volume of permeate (liter), (A) is the effective membrane surface area (m^2) and (T) is the time (hour.) .The salt rejection was determined using atomic absorption device (-AA-7000 atomic absorption spectrophotometer, Shimadzu). During the rejection test three membrane cells of the prepared electrospun nanofiber membrane that are used. The rejection of salts was obtained by:

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

Where (C_p) and (C_f) are ion concentration in permeate and feed, respectively, (R) is rejection as a percentage. Figure (1-b) shows a schematic diagram of the filtration system process.

Antimicrobial test:

a. Antibacterial activity test (Disc diffusion method): The bacteria were grown aerobically in nutrient broth at (37 ºC) for (12 hours). The cells were washed and suspended in distilled water, reaching the final concentration of 10^6 CFU/mL [Sukdeb, et al., 2007]. The antimicrobial susceptibility of (Nylon-6 nanofibers / TiO_2) was evaluated by 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. Experiments were carried out in the dark and under (UV) light with (20 W). Two forms of sterilized samples of nanofiber membrane (one containing TiO_2 and one without TiO_2, used as control) were cut into small standard circles (6 mm in diameter) for each circle. These samples were placed on the inoculated media surface. The plates were incubated at (37 ºC) for (24 hours). Following incubation plates were examined in order to identify zones of on growth (halos around the fragments) characteristic for antibacterial activity.

b. Measuring antibacterial activity by the optical density method: The antibacterial activity of electrospun nanofibers membrane was 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 of (0.85% NaCl) in (100 ml) distilled water. Water samples were then filtered through the membrane. After this step the optical density of the solution was measured by a (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:

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

Where (A) and (B) are the numbers of surviving cells in the control and test samples, respectively [Bokgi, et al., 2009].

3- RESULTS AND DISCUSSIONS:-

3.1 Electrospun mats morphology

The morphologies of the electrospun (Nylon-6) mats with different amounts of (TiO_2) are shown in Figures (2) and (3). From these images, it is clear that there is no any (spider-net like structure) in the pure (Nylon 6) membrane, in any case, (7 wt. % TiO_2) was a highly interconnected (spider net like structure) creation as found in (Figure (3-a)). The formation of the (spider-net like structure) is a direct result of the increasing of ionization of the polymer solution within the small amount of (TiO_2) through the electrospinning process. As known (Nylon-6) is polyelectrolyte, so its acidic solution will cause ionized in small (TiO_2) nanopartciles concentration, this also supported by conductivity data in table (1). The intermolecular hydrogen bond strength between polymeric species was decreased due to better dispersion of (TiO_2). This phenomenon will allow ions to freely move and led to increase conductivity and decrease viscosity. Nonetheless, opposite result was acquired above (5 wt. % TiO_2) solution, this is a direct result of begin aggregation of nanoparticles. Taking into account conductivity data said in (Table 1), the possible mechanism for (spider-net like structure) formation in low (TiO_2) nanocomposite membrane concentration was proposed, as found in figure (4). Table (1) shows that the conductivity increases up to (5%) and then slightly decreased while the viscosity is decreased due to the polymer content decreased. However, the surface tension of polymer solution wasn't significantly effect change.

3.2 Water contact angle measurement

Figure (6) shows the water contact angles of the different membranes after (3 sec) for (Nylon-6), (0.5, 1, 3, 5 and 7 wt. % TiO_2) in composite membrane, respectively. It shows that the (0.5, 1, 3, 5 and 7 wt. % TiO_2) membrane is more hydrophilic than the pure (Nylon-6) membrane. It is most likely due to the hydrophilicity (TiO_2 -nanoparticles) and the formation of a greater surface area to volume ratio of the nanofiber (spider net like structure) as well as the (TiO_2 NPs) distributed on them (low concentration of TiO_2). The decreased contact angle is an indication of increased hydrophilicity. This increased hydrophilicity can decrease the antifouling effect of filter membranes [Kiwi, et al., 2005]. Therefore, the presence of (TiO_2 NPs) in the (Nylon-6) membrane keeps it from fouling. Research results showed that small amounts of (TiO_2 NPs) in (Nylon-6) could give a (spider-net like structure) and simultaneously increase the hydrophobicity of the electrospun membrane. The presence of the (spider-net like structure) in the mat not only prevented the passage of the suspended Nano-impurities of water, but also increased the surface energy of the meat to make the membrane more hydrophilic. The increased hydrophilicity is charge of increasing the rate of filtration of water through the membrane as shows in figure (7) and (9).

3.3 Permeability and salt rejection measurement

The increased hydrophilicity is charge of increasing the rate of filtration of water through the membrane as shows in figure (7). It shows that when raise pressure the pure water flux is increased, because of flux directly proportional to the pressure drop across the membrane [Akram, et al., 2016], as shown in figure (8). Nanoparticles could offer advantages to the existing water and wastewater treatment processes [Anming, et al., 2014]. The electrospun nanofiber membrane was able to significantly reduce the content of toxic metals such as copper, zinc, and lead through adsorption process. An efficient sorbent with both high capacity and fast rate adsorption should have the following two main characteristics: functional groups and large surface area [Xiangtao, et al., 2012], from this point the electrospun nanofiber provide the tow factor of high specific surface area to volume aspect ratio and also the electrostic electrical force that formed in nanofiber during electrospinning process which enhance the electrostatic attraction of the nanofiber membrane and improve the salt rejection. Incorporation of (TiO_2) nanoparticles into nanofiber increased the surface area of fiber and surface reactivity of nanofiber this explanation may illustrate why the electrospun nanofiber reject salt from water. Figure (9) shows the rejection up to (71 %) for

(NaCl) salt and (76 %) rejection for ($Pb(NO_3)_2$) salt at (5 Wt % TiO_2) membrane and this ratio than decreased this may be due to the high porosity and large pore size, but its value remains other than that for pure (Nylon-6), with observed that the rejection for ($Pb(NO_3)_2$) salt have a high ratio in compared to (NaCl) salt, this can explained with the help of ionic size and charge density. The high rejection of (Pb^{+2} ion (133 pm)) and rejection ratio reached up to (76 %) and (Na^{+1} ion (116 pm)) up to (71 %).

3.4 Antibacterial performances result

The antimicrobial ability of the (Nylon-6/TiO_2) composite layer was inspected utilizing (*E.coli*) cell survival under (UV) light exposure. Figure (11) shows the antibacterial efficiency of (*E.coli*) on different (0-7% Nylon-6/TiO_2) composite membrane surfaces under (UV) light. The antibacterial activity (Nylon-6) was observed to be not as much as that on Nylon 6/TiO_2) under the same condition. It was found the antibacterial activity increased with increasing amount of (TiO_2) in the composite membrane. The comparative result in the (PVDF) membrane containing (TiO_2 NPs) was additionally reported by "Damodar et.al."[Damodar, et al., 2009]. Moreover, these outcome result indicates that (Nylon-6/TiO_2) nanocomposite membrane exposed to (UV) light were able to kill (E.coli) cells more efficiently than Nylon-6 membrane due to the photocatalytic bacterial effect of (TiO2-NPs). The presence of different reactive species such as ($HO^{\bullet}$), (H_2O_2) and ($O_2{}^{\bullet -}$), created by (TiO_2) and also the direct (UV) illumination of cell cause the bacterial ability of (UV/ TiO_2) [Kiwi, et al., 2004, Kiwi, et al., 2005]. Figure (11) shows the antibacterial activity efficiency which increased with increased the (TiO_2) concentration and reach to (99%) at (Nylon-6 /7 Wt.% TiO_2). Figure (10) shows the inhibition zone formed around membrane contained (TiO_2 NPs) where as missing these zones in pure (Nylon-6) membrane, the result showed inhibition zone have been increased with the increase in (TiO_2) concentration.

3.5 Mechanical strengths result:

The mechanical strength of (0.5 wt. % TiO_2 / Nylon-6) nanofiber membrane was observed to be greater than pure Nylon, this behavior proceeds up to (7 wt. % TiO_2). The enhanced mechanical properties may be because the good dispersion of nanoparticles all through the polymer solution and in addition development of highly interconnected (spider-net like structure). Besides, this increased mechanical effect can be attributed to an additional energy-dissipating mechanism introduced by nanoparticles in (Nylon-6) because of good dispersion all through the membrane. Dynamic studies were discussed this mechanism is a result of the mobility of the nanoparticles. During the deformation process the nanoparticles may orient and align under tensile stress, creating temporary crosslinks between polymer chains and thereby creating a local region of enhanced strength [Shah, et al., 2005]. Figure (12) shows the effect of (TiO_2) on Stress-strain curves.

4- CONCLUSIONS :-

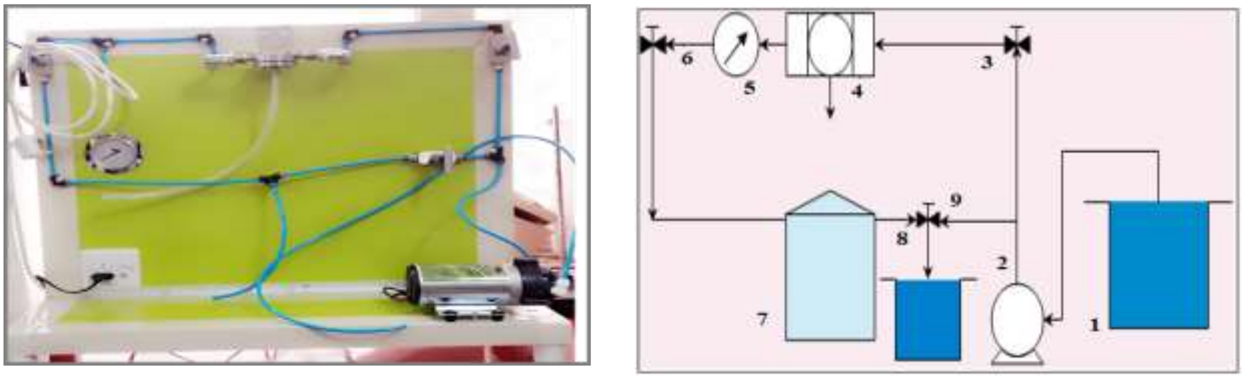
Composite nanofiber mats of (Nylon-6/TiO_2) were produced by electrospinning through mixing different amounts of (TiO_2 NPs) with (Nylon-6) solution. Adding small amounts of (TiO_2 NPs) improves the hydrophilicity and mechanical strength of (Nylon-6) nanofiber membrane. Hydrophilicity of the (spider-net like structure) enhanced and causes to decrease the antifouling effect to make the mat a potential candidate for water filtration and improve the performance of membrane at low pressures. The (TiO_2) entrapped (Nylon-6) membranes showed better bactericidal ability as compared to the pure (Nylon-6) mat under (UV) light. The produced high aspect ratio nanofiber membrane (due to the spider-net like structure) can be potentially applicable in a wide variety of filter applications, water filter media with high rejection ratio against heavy metal ions reached to (76%) .

Table (1) the raw materials used .

Raw materials	Formulation	Molecular weight (g/mol)	Purity %	Physical state	Origin manufacturing
Nylon 6	$(C_6H_{11}NO)_n$	113.16	---	Solid	USA
Formic acid	(CH_2O_2)	46.03	88	Liquid	USA
Titanium oxide nanoparticles	TiO_2	79.87	99.5	Solid	USA
Lead nitrate	$Pb(NO_3)_2$	331.2	99	Solid	Germany
Sodium chloride	NaCl	58.44	99	Solid	India
Millipore glass filter with binder (technical micro Filter)	AP25	----	---	---	---

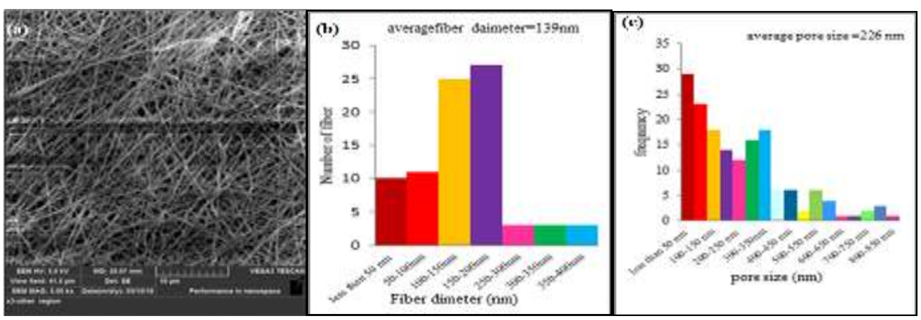
Table (2): Conductivity, viscosity, and surface tension of electrospinning polymeric (Nylon-6 /TiO_2) solution.

Nylon-6/wt.%TiO_2 Concentration	Electrical conductivity(mS/cm)	Viscosity (cP)	Surface tension (mN/m)
0	4	692	34.43
0.5	4.05	555	34.41
1	4.09	475	34.38
3	4.18	378	34.31
5	4.18	347	34.25
7	4.16	329	34.2

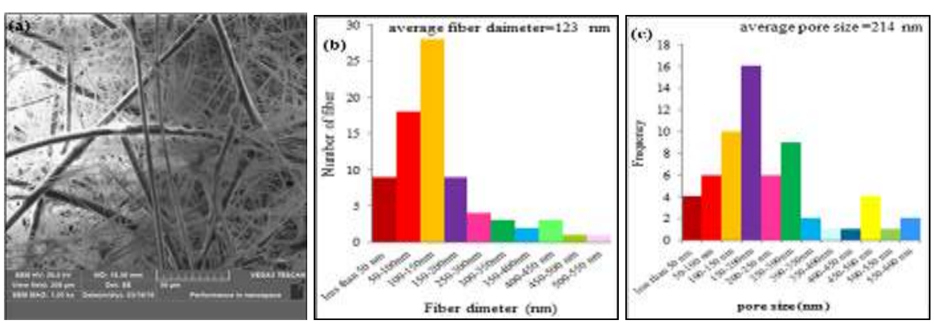


(A) **(B)**

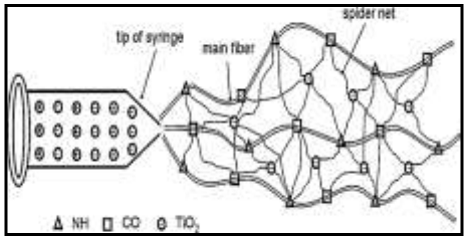
(Fig. 1): Pressure cross flow (A) image of filtration system (B) Schematic diagram of the filtration system process. Where **1.** Tank for water sample test. **2.** Pump. **3.** Valve entry. **4.** Filter / Module. **5.** Pressure gage. **6.** Valve out. **7.** Open tank for permeate water sample. **8.** Tank of rejected water sample. **9.** Recycle valve **.**



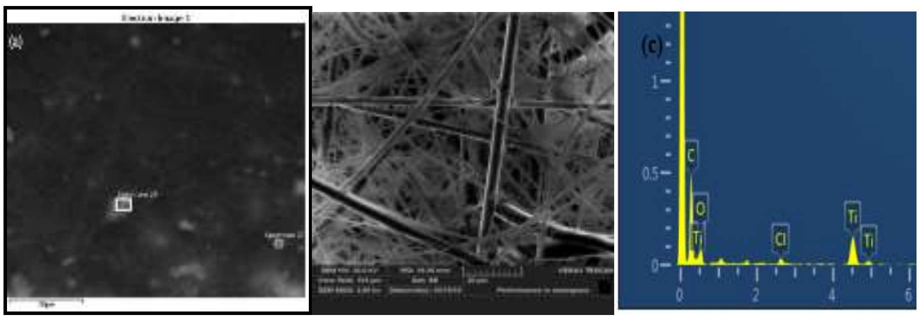
(Fig. 2): **(a)** SEM image of pure (Nylon-6) nanofibers membrane, **(b)** diameter distribution and **(c)** pore size distribution **.**



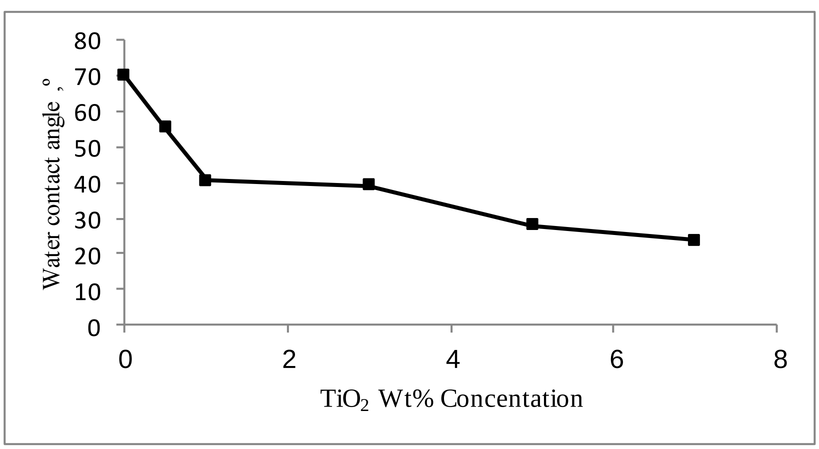
(Fig. 3): **(a)** SEM image of (7% TiO_2) nanofibers membrane, **(b)** diameter distribution and **(c)** pore size distribution.



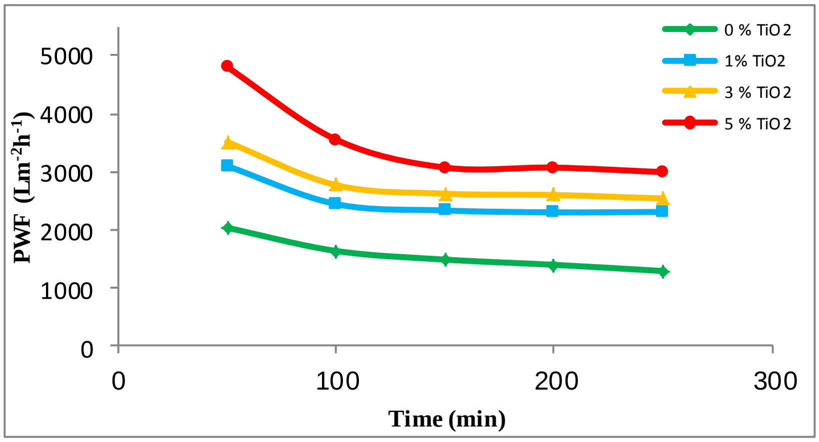
(Fig. 4): Schematic illustration showing the mechanism of (spider-net like structure) formation during electrospinning .



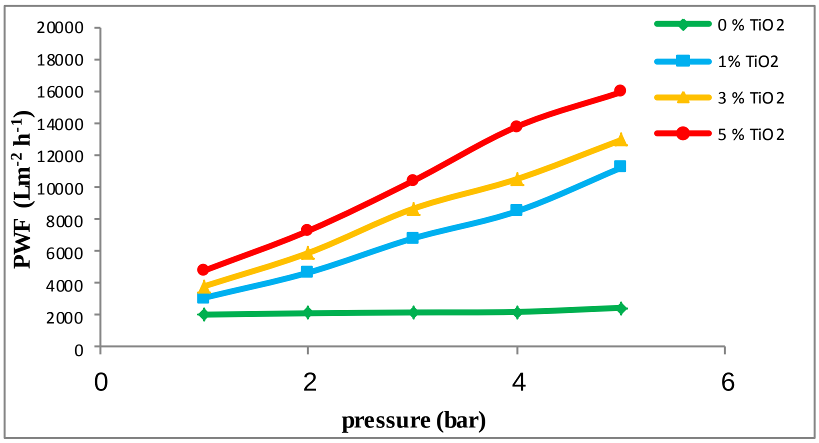
(Fig. 5): (a) Section selected from SEM image **(b)** SEM Image **(c)** EDX of (7% TiO_2 / Nylon-6) nanofiber membrane .



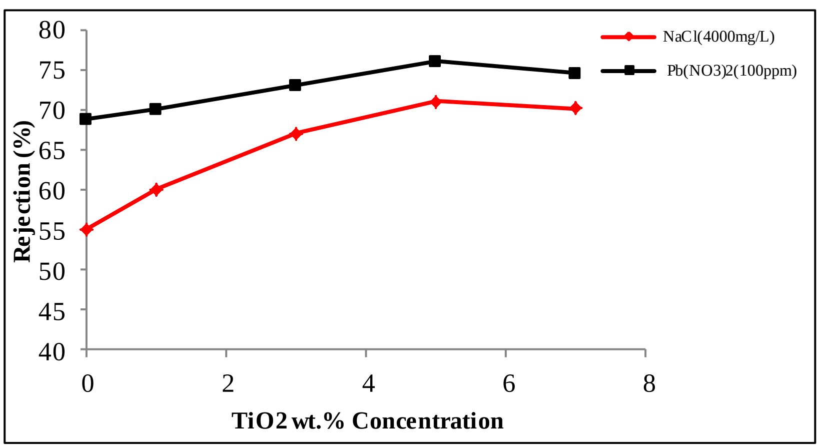
(Fig. 6): Effect of (TiO_2) addition on water contact angle of electrospun nanofiber membrane.



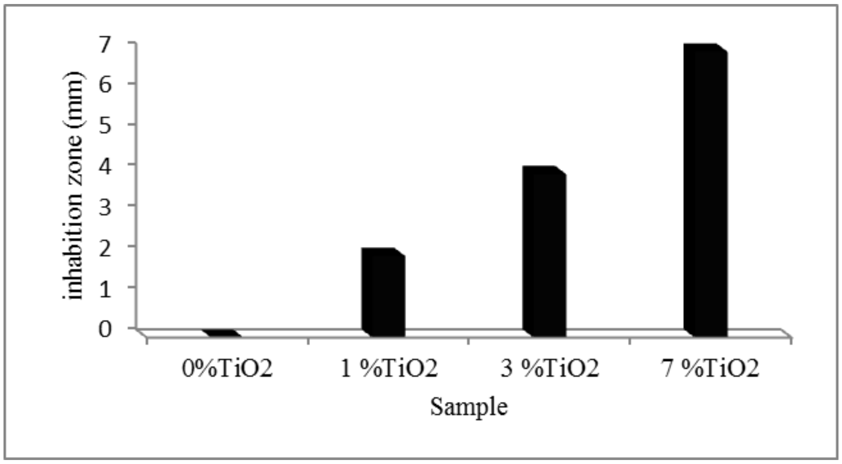
(Fig. 7) : Pure water permeation flux with time of (Nylon-6/ TiO_2) nanofiber membrane at room temperature and (1 bar) pressure.



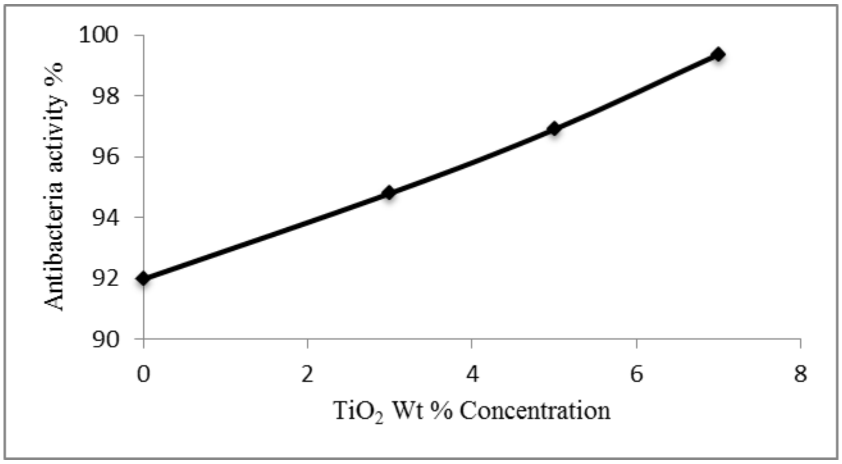
(Fig. 8) : Effect of membrane pressure on the pure water permeation flux of the (Nylon-6 / TiO_2) nanofiber membrane.



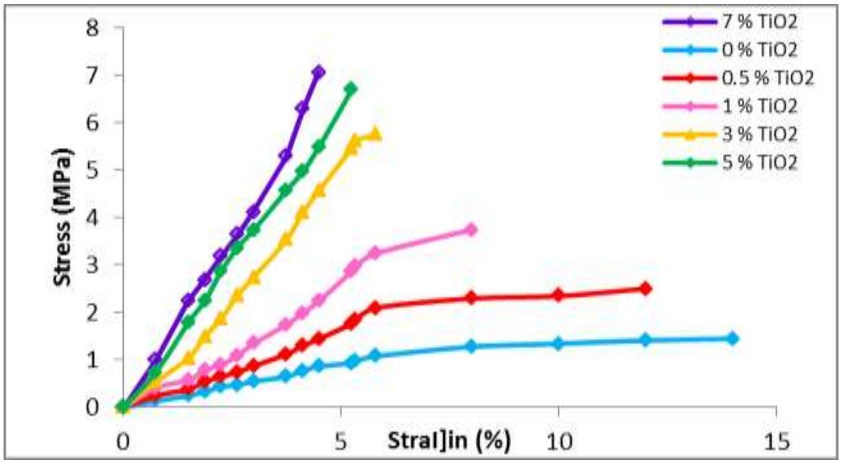
(Fig.9) : Effect of (Nylon /TiO_2) ratio on rejection of ($Pb(NO_3)_2$) salt and (NaCl) Salt aqueous solutions with initial concentration (100 ppm) and (4000mg/L) respectively, at room temperature and (1 bar) Pressure.



(Fig. 10): Effect of (TiO_2 /Nylon-6) ratio on the inhibition zone against (E.coli) bacteria.



(Fig. 11): Effect of (TiO_2) on the antibacterial activity against (*E.coli*) bacteria.



(Fig. 12): Stress-strain curve of (TiO_2 /Nylon-6) with various concentrations.

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