

Antimicrobials Nano-Fiber PVA Pure and PVA: TiO₂ for Filtration Applications

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ABSTRACT

In this study, polyvinyl alcohol composite polymer membrane was successfully synthesized pure and at different TiO₂ concentrations (1%, 3%). The diameter of the PVA-TiO₂ fibers ranged from 100 to 200 nm. X-ray diffraction analysis indicated that the main crystal structure was amorphous and there are no any sign of Anatase or Rutile or Brookite when increased TiO₂ concentrations to 3%. Absorption properties of polymeric membranes doped absorb of increases compare with of the undoped membrane. PVA pure nano-fibers membrane less zone of inhibition than PVA : 0.1 TiO₂ nano-fibers membrane and PVA : 0.3 TiO₂ nano-fibers membrane against gram-negative (*Pseudomonas* and *Salmonella*) and gram-positive (*Staphylococcus aureus* (*S. aureus*)).

Keywords: nanofiber, polyvinyl alcohol, electrospinning

البولي فينيل الكحول النقي والمشوب بثاني اوكسيد التيتانيوم ضد المايكروبات لتطبيقات الفلاتر

الخلاصة:

في هذه الدراسة، تم تصنيع غشاء و بنجاح لبوليمر البولي فينيل الكحول النقي والمشوبه بتراكيز مختلفه (1%، 3%) لأكسيد التيتانيوم. قطر الفايبر لبولي فينول المشوب باوكسيد التيتانيوم يتراوح من 100 الى 200 نانو متر. اكدت نتائج حيود الاشعه السينيه ان معظم التراكيب البلوري كان عشوائي ولا توجد اي اشارة على وجود اي طور من اطوار اوكسيد التيتانيوم (Anatase و Rutile و Brookite) عندما ازداد تركيز الشوائب الى (3%). الخصائص البصريه للاغشيه البولمريه المشوبه اعلى امتصاص مقارنة مع الغير مشوبه. النانوفايبر النقي اقل منطقه تثبيط مقارنة المشوب (1%، 3%) باوكسيد التيتانيوم ضد نوعين من البكتريا السالبة (*Pseudomonas* and *Salmonella*) والموجبه (*Staphylococcus aureus* (*S. aureus*)).

INTRODUCTION:

Nanomaterials have become a research priority as biotechnology; defense and semiconductor industries in particular, are interested in potential applications of nanotechnology. Substantial amount of research on nano-scale fibers, for

instance, is being conducted due to their prospective application areas; such as tissue engineering, filters, microchips, micro air vehicles, and hydrophobic thin films

Electrospinning (also called electrostatic spinning) is one of the promising processes to produce nano-scale fibers from both synthetic and natural polymers. Electric forces are used to form fibers from material solutions or melts [1].

Poly(vinyl alcohol) (PVA) has great application potential in biomedical field because it is a water-soluble, fiber-processable, and biodegradable polymer. Recently, electrospun polymer nanofibers have attracted a great deal of attention for applications in medical and healthcare fields [2].

Among the polymeric nanofiber, polyvinyl alcohol (PVA) has extensive application in air filtration, textile industry and paper coating due to its flexibility and good chemical and thermal stability [2].

TiO₂ was selected as our target because of its important role in environmental cleaning and protection due to its ability to photocatalyse and decompose harmful organic compounds and low cost[3].

TiO₂ usually used as powder in solution, which high photocatalytic efficiency however, the catalysts should be separated from the purified water after treatment. To solve this problem, a photocatalytic membrane reactor has been developed using various membrane techniques [3]

For successful implementation of this ideal, metal-oxide nanoparticles must be well dispersed in the solvent and also compatible with the selected polymer to prevent phase separation.[4]

In this study, PVA nanofibers containing TiO₂ were electrospun from PVA solutions containing TiO₂. The PVA solutions were prepared by refluxing PVA/ TiO₂ aqueous solutions.

Experimental work:-

A-Materials.

PVA (99+% hydrolyzed, Mw=89,000–98,000) and TiO₂ (99.998%) were purchased from Fluka company.

i. Preparation of PVA/water Solutions Containing Ti Nanoparticles.

10 wt% aqueous PVA solutions with different amounts of TiO₂ were refluxed at various temperatures for 3 h in order to reduce the Ti⁺ ions into Ti nanoparticles. The weight percentage of TiO₂ in the solutions was calculated according to the weight of PVA.i

ii. Proceeding.

The PVA nanofibers containing TiO₂ were prepared by electrospinning the 10 wt% PVA/water solutions containing TiO₂.The electrospinning setup consisted of a syringe and a needle (ID=0.25 mm), an aluminum collecting plate, and a high-voltage supply (electrospinning system , model :ESP200,Nano Nc).

The syringe pump connected to the syringe was used to control the flow rate. The PVA solutions were electrospun at a positive voltage of 16 kV, a working distance of 12 cm (the distance between the needle tip and the collecting plate), and a solution flow rate of 0.2 mL/h. This stationary collection procedure results in non-woven fiber mats as seen in Figure (1)

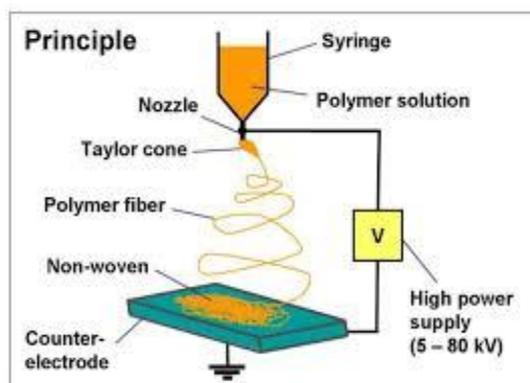


Figure (1) Electrospinning setup and its product: non-woven fiber mat.

B. Characterization techniques

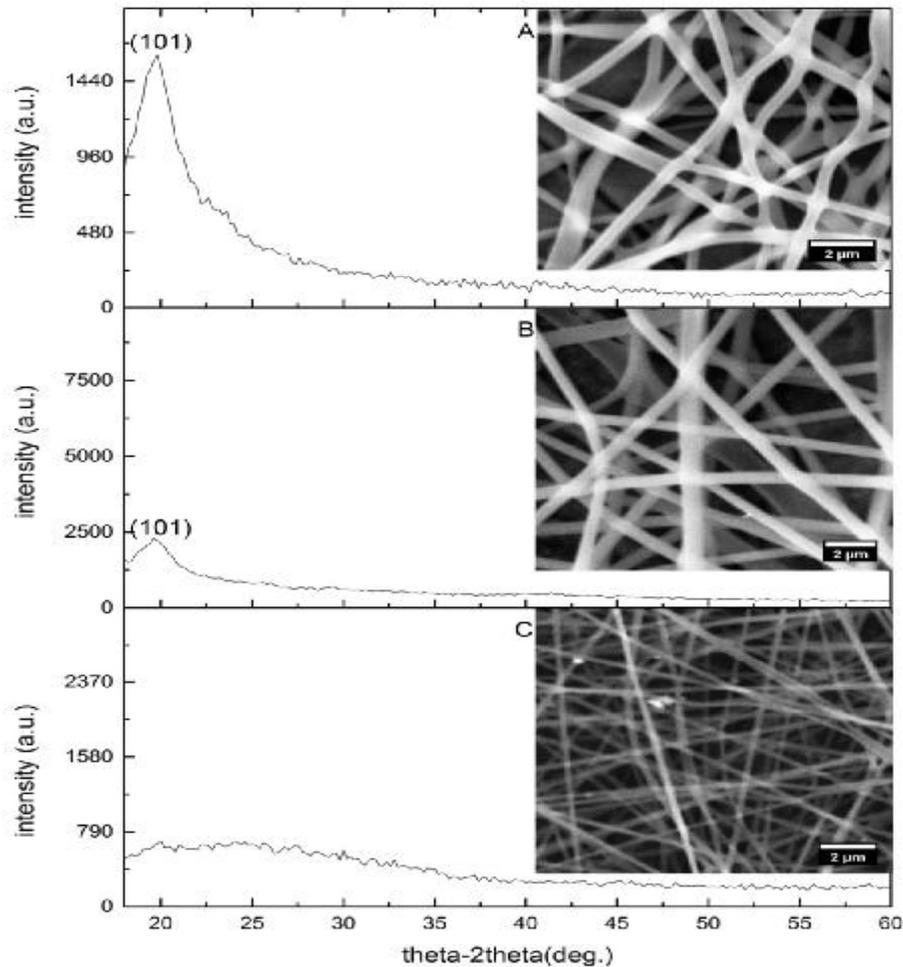
The crystalline structure of the powder has been determined by using X-ray diffraction (Philips PW 1050 X-ray diffract meter of 1.5°A from Cu-K α). Additionally. The surface morphology of nano fiber membrane was examined using Scanning Electron Microscopy (SEM ,the VEGA easy probe).The optical properties was examined using Optical absorption spectra of all the films were recorded using a UV-VIS spectrophotometer (Perkin Elemer Company).

C. Test for antibacterial activity of PVA pure and PVA : TiO₂

The antibacterial susceptibility of PVA pure and PVA doped with TiO₂ was evaluated using the zone inhibition method. A 100 μ L sample of bacterial suspension should be equal to McFarland solution, and using as a control that equal to 10⁷ CFU/ml was then spread on a nutrient agar plate. The plates were then holed and supplemented with spherical of PVA pure and PVA doped with TiO₂ to determine the different antibacterial properties depending on sizes and shapes; the plates were then incubated further at 37 °C. The zones of inhibition were calculated after 24 h of incubation.

Result and Discussion

Figure (2) Show the XRD curve for various fibers samples. As shown in Figure 2a, Spectrum (a) of pure PVA shows an intense reflection peak at $2\theta = 19.8^\circ$ diffused in the hallow amorphous region and was assigned to a mixture of (101) and (10 $\bar{1}$) reflections .The appearance of sharp reflections and diffuse scattering is characteristic of crystalline and amorphous phases of conventional semi-crystalline polymers . when doped with 0.01TiO₂ intense reflection peak shifted at $2\theta = 19.6^\circ$. It is observed that the increasing of TiO₂ to 0.03 concentrations lead to decreases intensity of PVA peaks and convert to amorphous. However, intensity of peaks became more flat with the increasing of the content of TiO₂ .The broader peak in the hybrid fibers indicates that the hybrid fibers are amorphous and there are no any sign of Anatase or Rutile or Brookite. These results revealed that the crystallinity of PVA was largely influenced by the content of (TiO₂) in the hybrid fibers [6] ,[7],[8].



**Figure (2) XRD curve for fibers samples with different mass ratio. .a) PVA pure
b) PVA: 0.01TiO₂ pure c) PVA: 0.03 TiO₂**

The SEM images of hybrid fibers were displayed in Figure 3.(a,b and c) showed the smooth surface and uniform dimension of the fibers, with diameters of rang (100-200) nm .As a result, the PVA-3%TiO₂ membrane was suitable for use in filtration application. From the SEM images (Figure 3) it appeared that the distance between cross fibers ranged from (1 - 5) micrometer. This was because the non-woven distribution of the fibers gradually decreased the size of the membrane pore. This kind of microstructure would be highly important for air and water purification processes since it can effectively entrap micro and nano-sized dust particles, such as viruses and bacteria. [5]

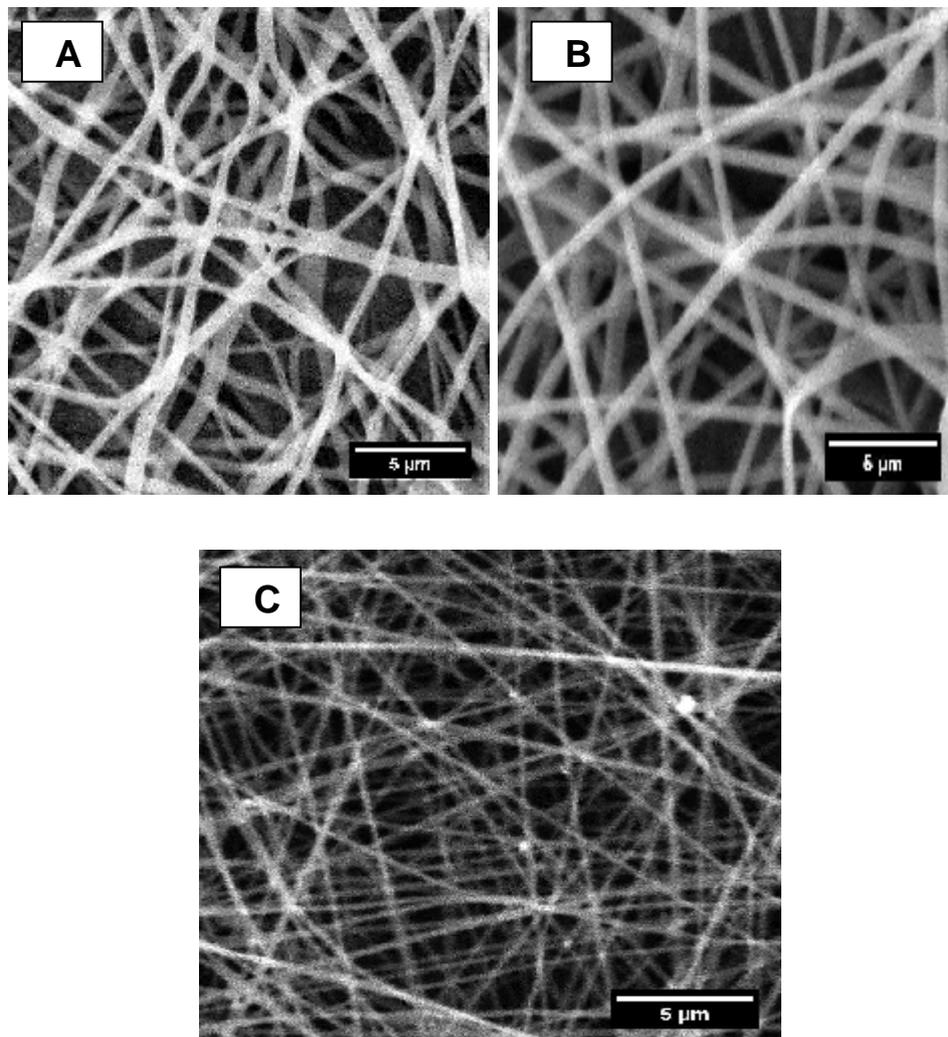


Figure (3) SEM images of (a) electrospun PVA nano-fibers membrane, (b) electrospun PVA-1%TiO₂ membrane, (c) electrospun PVA- 3%TiO₂ membrane,

The UV- Vis optical properties in the range from 300nm to 1100nm at various doping concentration, shows that the absorbance depends stronger on doping concentration as shown in Figure 4. At 1% concentration the absorption spectrum is very few modified. As the concentration of TiO₂ increases to 3% concentration, the absorption peak is amplitude increases compare with of the (PVA) undoped membrane, This behavior shows clearly the enhancement of absorption properties after addition of TiO₂. [9],[10].

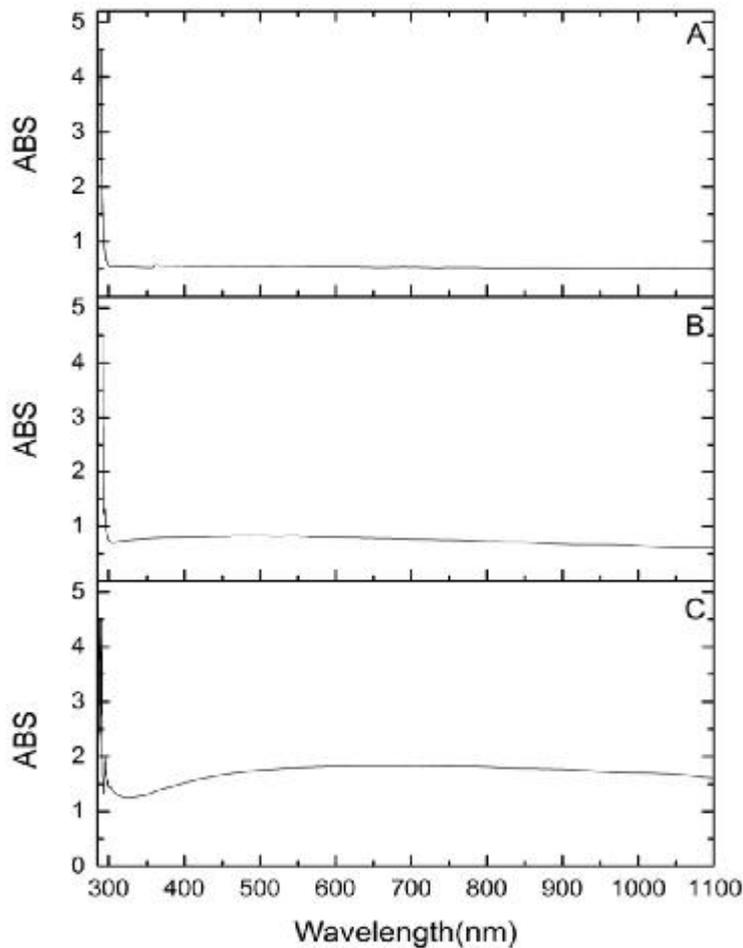


Figure (4) show absorption properties of polymeric membranes pure and doped with different concentrations of TiO₂.

Antibacterial checking by zone of inhibition (well diffusion assay) was carried out to qualitatively determine the level of inhibition using PVA nano-fibers membrane and PVA : 0.01 TiO₂ nano-fibers membrane and PVA : 0.03 TiO₂ nano-fibers membrane against gram-negative(*Pseudomonas* and *Salmonella*) and gram-positive (*Staphylococcus aureus* (*S. aureus*))bacterial systems Figure 6, shows the inhibitory effect PVA nano-fibers membrane and PVA doping with TiO₂and, can be observed as shown in Table 1 .

Table (1). The antimicrobial test results of treated PVA nano-fibers membrane and PVA : 0.01 TiO₂ nano-fibers membrane and PVA : 0.03 TiO₂ nano-fibers membrane .

BACTERIA Material	Staph	Pseudomonas	Salmonella
PVA pure	5	8	8
PVA:0.01 TiO ₂	14	16	16
PVA:0.03 TiO ₂	15	17	18

From this table can be noticed PVA pure nano-fibers membrane less zone of inhibition than PVA: 0.01 TiO₂ nano-fibers membrane and PVA: 0.03 TiO₂ nano-fibers membrane against gram-negative(Pseudomonas and Salmonella) and gram-positive (Staphylococcus aureus (S. aureus))bacterial systems and PVA :(0.03, 0.01)TiO₂ membrane against gram-negative more zone of inhibition than gram-positive (Staphylococcus aureus (S. aureus)).

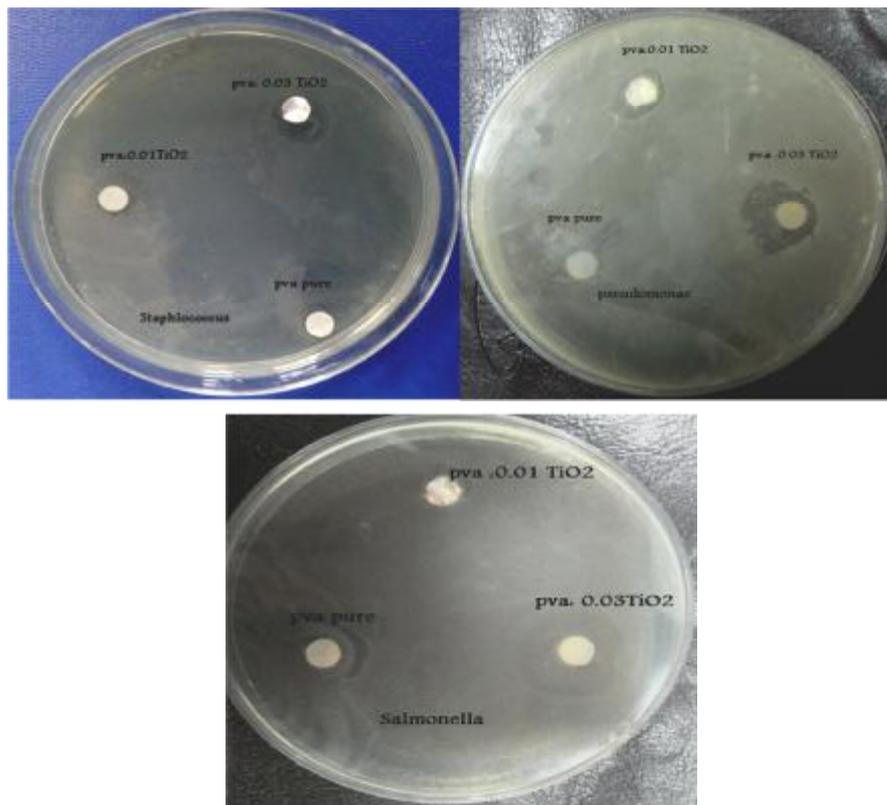


Figure (5) Antimicrobial activity of PVA nano-fibers membrane and PVA : 0.01 TiO₂ nano-fibers membrane and PVA : 0.03 TiO₂ nano-fibers membrane against Pseudomonas ,Salmonella and Staphylococcus aureus (S. aureus) shows the inhibition of growth after 24 hours of incubation.

CONCLUSION:

The surface morphology of of hybrid fibers have been studied by using scanning electron microscope showed the smooth surface and uniform dimension of the fibers, with diameters of rang hundred-two hundred nm and the pore size ranged one-five micrometer. UV-VIS absorption measurements have shown that the absorption peak is amplitude increases compare with of the (PVA) undoped membrane.

The study showed that PVA pure and doped fatal for both gram-negative and positive types of bacteria.

This kind of microstructure would be highly important for air and water purification processes since it can effectively entrap micro and nano-sized dust particles, such as

REFERENCES :-

- [1] A., K., Simsek, E., Ow-Yang, C., Menciloglu, Y. Z. "Tunable, Superhydrophobically Stable Polymeric Surfaces by Electrospinning," *Angewandte Chemie International Edition*, VOL.43, NO.39,PP. 5210-5213, (2004) .
- [2]K. Hwa Hong, J.Park, , J Youk* and T.Jin Kang " Preparation of antimicrobial poly(vinyl alcohol) nanofibers containing silver nanoparticles " *Journal of Polymer Science Part B: Polymer Physics*,VOL. 44, NO. 17, PP. 2468–2474, (2006).
- [3]N.Thuy ,B. Linh, B.Taek andT. Lee"Fabrication of photocatalytic PVA-TiO₂ nano-fibrous hybrid membrane using the electro-spinning method" *Journal of Materials Science*,VOL.46,NO.17,(2011).
- [4] S. Mandal , R. Sharma,and M. Katiyar"A Hybrid Dielectric Ink Consisting of up to 50 wt% of TiO₂ Nanoparticles in Polyvinyl Alcohol (PVA)" *J. Chem. Chem. Eng.*VOL. 6 ,PP.625-630 ,(2012) .
- [5]S. Homaeigohar , and M. Elbahri"Nanocomposite Electrospun Nanofiber Membranes for Environm ental Remediation" *Materials*,VOL. 7, PP.1017-1045,(2014).
- [6]G. Attial and M.F.H. Abd El-kader,"Structural, Optical and Thermal Characterization of PVA/2HEC Polyblend Films" *International Journal of Electrochemical science*, VOL.8 ,PP. 5672 - 5687 ,(2013) .
- [7] N. T. Ba Linh, K. H. Lee and B.T. Lee" A Novel Photoactive Nano-Filtration Module Composed of a TiO₂Loaded PVA Nano-Fibrous Membrane on Sponge Al₂O₃ Scaffolds and Al₂O₃-(m-ZrO₂)/t-ZrO₂ Composites" *Materials Transactions*, VOL. 52, NO. 7, PP. 1452 to 1456 (2011).
- [8]H. Ma, T. Shi and Q. Song"Synthesis and Characterization of Novel PVA/SiO₂-TiO₂Hybrid Fibers" *Fibers*, VOL.2, PP.275-284,(2014)
- [9]. S. Mallakpour and A. Barati, "Efficient preparation of hybrid nanocomposite coatingsbased on poly(vinyl alcohol) and silane coupling agent modified TiO₂ nanoparticles",*Progress in Organic Coatings*,VOL. 71,NO. 391 ,(2011).
- [10]R. Venckatesh, K. Balachandaranand R. Sivaraj "Synthesis and characterization of nano TiO₂-SiO₂:PVA composite - anovel route". *International Nano Letters*, VOL.2, NO.15, (2012).