JOURNAL OF KUFA–PHYSICS
www.uokufa.edu.iq/journals/index.php/jkp | ISSN: 2077–5830

Electrospinning Preparation of PAN/TiO_2 Nanofibers and Photocatalytic Regeneration Properties of Methylene Blue dye

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ARTICLE INF

Article history:
Received: 05 DEC, 2022
Revised: 01 JAN: 2023
Accepted: 08 JAN, 2023
Available Online: 12 FEB, 2023

Keywords:

Nanofibers
Electrospun
Polyacrylonitrile
photodegradation
methylene blue

ABSTRACT

The nanofiber membranes prepared by electrospinning method attracted the attention of researchers in the field of pollutant treatment due to their ease of manufacture, efficient performance and ease of removal. Some of these membranes lack the possibility of reuse due to low efficiency and high regeneration cost. In this paper, we were able to prepare nanofiber membranes from polyacrylonitrile (PAN) and PAN/TiO_2 by adding different ratios (5,10 and 15) wt% of TiO_2 respectively. The resultants nanofibers were characterized using Field Emission Scanning microscope (SEM), Fourier Transform Infrared spectroscopy (FTIR). This prepared membranes enable effective and complete degradation of MB dye in water using ultraviolet (UV) irradiation with the possibility of reuse and high efficiency after washing with distilled water. The efficiency is up to 98% when 15wt% TiO_2 was used, while the degradation reaches to 83% when reused the nanofibers composite (PAN/TiO_2). The work not only explains the possibility of using and reusing nanofiber films in the treatment of pollutants, but also gives a detailed of understanding the behavior of the membrane in dye degradation.

DOI: http://dx.doi.org/10.31257/2018/JKP/2022/140210

تحضير الياف نانوية PAN/TiO_2 بطريقة الغزل الكهربائي واستخدامها في التحلل الضوئي لإزالة صبغة الميثيلين الزرقاء

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الكلمات المفتاحية:

ألياف نانوية
مغزل كهربائي
بولي أكريلونايترايل

الـــخُـــلاصـــة

جذبت أغشية الألياف النانوية المحضرة بطريقة الغزل الكهربائي انتباه الباحثين في مجال

التحلل الضوئي لميثيلين الزرقاء

معالجـة الملوثـات نظـرًا لسـهولـة تصـنيعها وأدائهـا الفعـال وسـهولـة إزالتهـا. تفتقـر بعـض هـذه الأغشية إلـى إمكانيـة إعـادة الاستخدام بسبب انخفاض الكفـاءة وارتفـاع تكلفـة التجديـد. فـي هـذا البحث تمكنا من تحضير أغشية الألياف النانوية من *PAN* و *PAN/TiO₂* بإضافة نسب وزنية مختلفة من *TiO₂* *(15%,10%,5%)* على التوالي. تم تمييز الألياف النانوية الناتجـة باستخدام المجهر الإلكتروني الماسح *(SEM)* ، تحويل فورييه مطيافية الأشعة تحت الحمراء *(FTIR)*. تتيح الأغشية المحضرة إمكانية التحلل الفعال والكامل لصبغة بروميد الميثيل في الماء باستخدام الأشعة فوق البنفسجية مـع إمكانيـة إعـادة الاستخدام وكفاءة عاليـة بعد الغسيل بالمـاء المقطـر. كفاءة إعادة الاستخدام تصل إلـى ٩٨٪. لا يشـرح العمل فقط إمكانيـة استخدام وإعـادة استخدام أغشية ألياف النانو في معالجة الملوثات ، ولكنه يعطي فهمـاً مفصـلاً لسلوك الغشـاء فـي تـدهور الصبغة.

1. INTRODUCTION

The leakage of oil derivatives, the discharge of sewage, heavy metal, dyes and other pollutants into the water resources led to severe damages which negatively affects human health and lead to an environmental imbalance [1,2] . It is necessary to find out techniques that reduce the concentration of these pollutants and the percentage of its accumulation in the water [3] . These Techniques include filtration, adsorption, centrifugation, photocatalytic degradation , biological treatment, and self-cleanings material. Scientists have found that using energy for treatment of these pollutants causes an increase in the earth's temperature due to an increase in the proportion carbon dioxide in the atmosphere , and this known as global warming, [4].Therefore , it is necessary to find safe ways for the environment to get rid of these pollutants[5].One of these methods is photocatalysis, which is one of the most effective techniques for water pollution remediation[6] .There is a necessary need to find environmentally friendly materials, with good chemical stability, as an electron absorbent that acts as a catalyst[7].Titanium dioxide(TiO_2) as a semiconductor material is most widely used as a photocatalyst because of its non-toxic, easy and low cost of manufacture, its chemical stability, and it can react under normal conditions[8] . The TiO_2 is an n-type semiconductor that creates electron-hole pairs in the presence of ultraviolet radiation[9]. TiO_2 is successfully used as a catalyst for wastewater purification and decomposition of organic pollutants, but because of the high energy gap of TiO_2 (3.2 eV for anatase) only about 4% of the solar radiation can be used . The photocatalytic ability of TiO_2 depends on several variables such as surface area, phase structure, and interface[8,10]. Photo catalysis by using Nano fibrous membranes has attracted wide interest due to its easy of separation , large surface area and high porosity[11].The nanofiber membranes prepared by electrospinning polymer have attracted a lot of attention in the field of water pollution remediation[12] and these membrane serve as a carrier for the catalyst and other biological compounds . On the other hand, providing easy removal of pollutants and at low cost[7]. Lithifah et al at 2022 and his group worked on developing a photocatalytic film that combines a photo catalyst with polyacrylonitrile (PAN) and Titanium dioxide/ carbon nanotube (TiO_2/CNT) based fiber technology. To prevent the accumulation of pollutants on the membrane, thus increasing the life of the membrane and the efficiency in treating pollutants. The performance of the membrane on the hydrolysis of the dye methylene blue (MB) was studied. They concluded that the PAN/TiO_2/CNT membrane with a PAN concentration of 6.5% performed best in removing MB color by keeping the percentage of rejection (R%) at 90% for 240 minutes and the permeability at 750 LMH[13]. Z. Zhu et al in 2019, produced nanofibers by the electrospinning process of PAN/TiO_2, which is characterized by photocatalytic activity to reduce the effect of ethylene in the decomposition of vegetables and fruits during shipment and storage. The results showed that the ability of nanofibers by using low intensity irradiation of ultraviolet rays to preserve vegetables and fruits during shipment and storage, as the time for color change and softening of crops increased[14]. In this study, PAN nanofibers were used as a TiO_2 catalyst carrier in photocatalytic study. The aim was to develop nanofibers that degrade the methylene blue dye in a shorter time and more efficiency.

2.Materials and methods

2.1 Materials

Acrylonitrile monomer (AC) (99.34%, Fluka), N-dimethylformamide (DMF) (99.9%, BDH) were supplied from Fluka company, ammonium persulfate (ABS), methylene blue (MB), Served (S), deionized water, TiO_2 nanoparticle were supplied from Sigma Aldrich, with the following specification: [Color pure white, Particle size (23-25) nm], all material used without any purification .

2.2 Preparation of electrospun nanofibers of PAN and PAN/TiO_2 Nanocomposite

The electrospinning of the prepared PAN and PAN / TiO_2 nanofibers was carried out by dissolving 0.3g of the PAN in 9.7 ml DMF solvent, then the solution was stirred at room temperature for about 24 hrs. until homogenous clear of PAN-DMF solutions was obtained. Then the polymer solution was transferred into 5ml plastic syringe (24G), a high voltage (10 kV) was applied by copper electrode connected with syringe needle with a feed rate of 1 ml /hr., while the needle distance from target was 10 cm. the latter process was repeated again but with addition of TiO_2 with different weight percentages (5,10 and 15wt%) respectively to the PAN solution and treating it with sonication for 2 hours, . All the tests were conducted at ambient atmosphere. Figure (1), illustrates the electrospinning scheme,

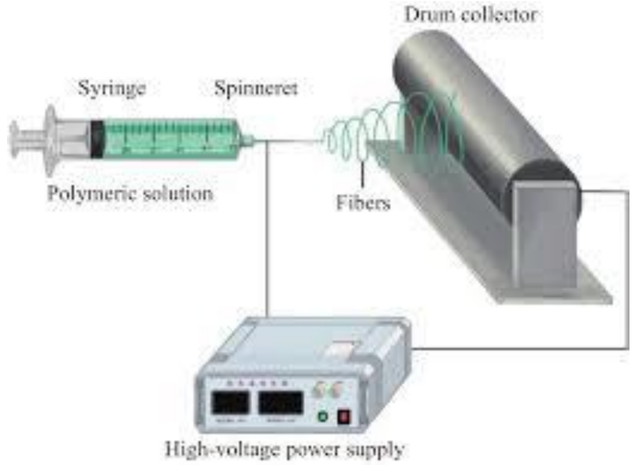


Figure 2: Electrospinning scheme

3. Characterization of PAN and PAN/TiO_2 Nanocomposite:

3.1. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR is an effective method to analyze the functional groups of the prepared polymer and composite. The FTIR spectrum of PAN can be shown shown in Figure (2),).It can be noted that observed characteristic band at 2245cm^{-1}, was due to the stretching vibration of C-N bond, a hydrocarbon back bond (C-H in CH_2 at 1365 cm^{-1} and CH in CH at 1361) [16,17]. The band at 1076 cm^{-1} is associated with PAN fingerprint region. In the case of PAN/ TiO_2 nanocomposite, the FTIR spectrum shown in Figure (3), it dictates the presence of nano TiO_2, as shown, new band at 456cm^{-1} which related to Ti-O band, while the band at (3629, 3537 cm^{-1}) due to the hydroxyl group in the TiO_2 which exist during their synthesis[17], as shown in Figure 4.

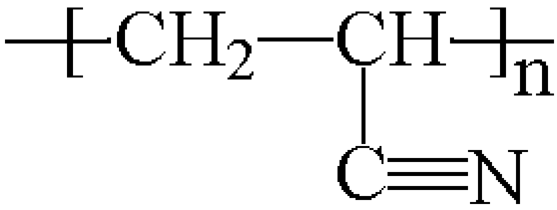


Figure 2: Chemical structure of PAN.

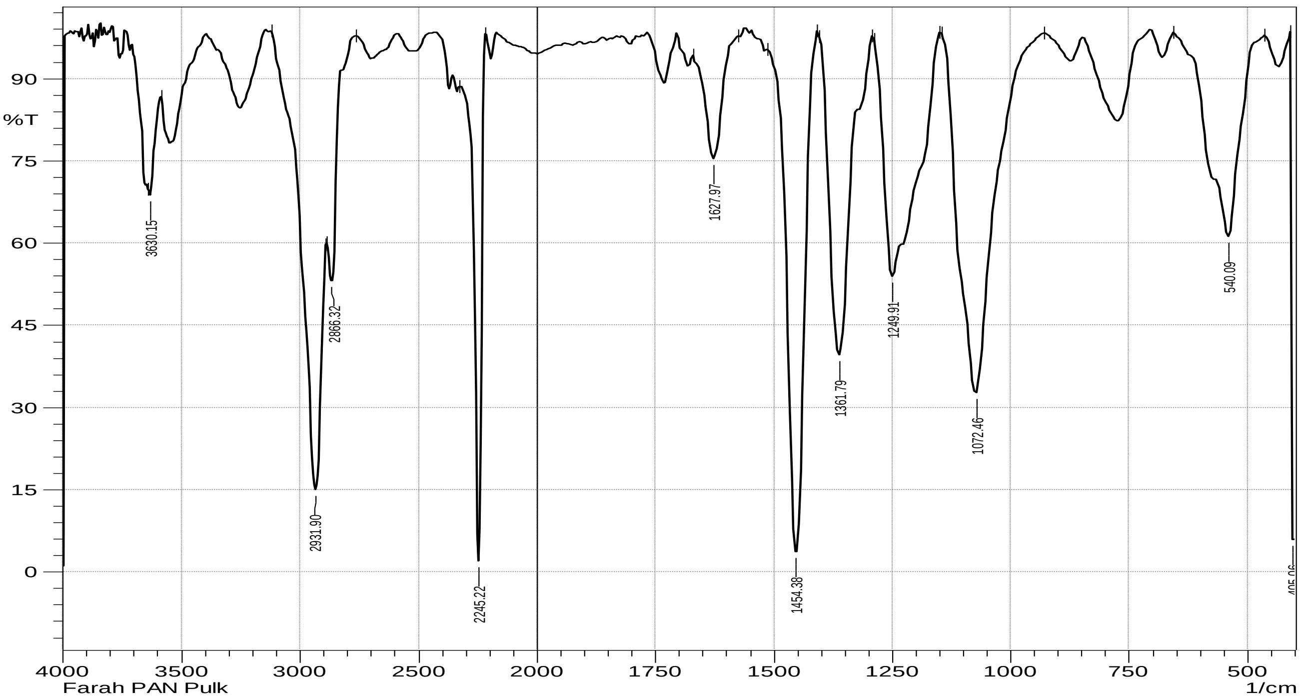


Figure 3: FTIR spectrum of PAN prepared in this study.

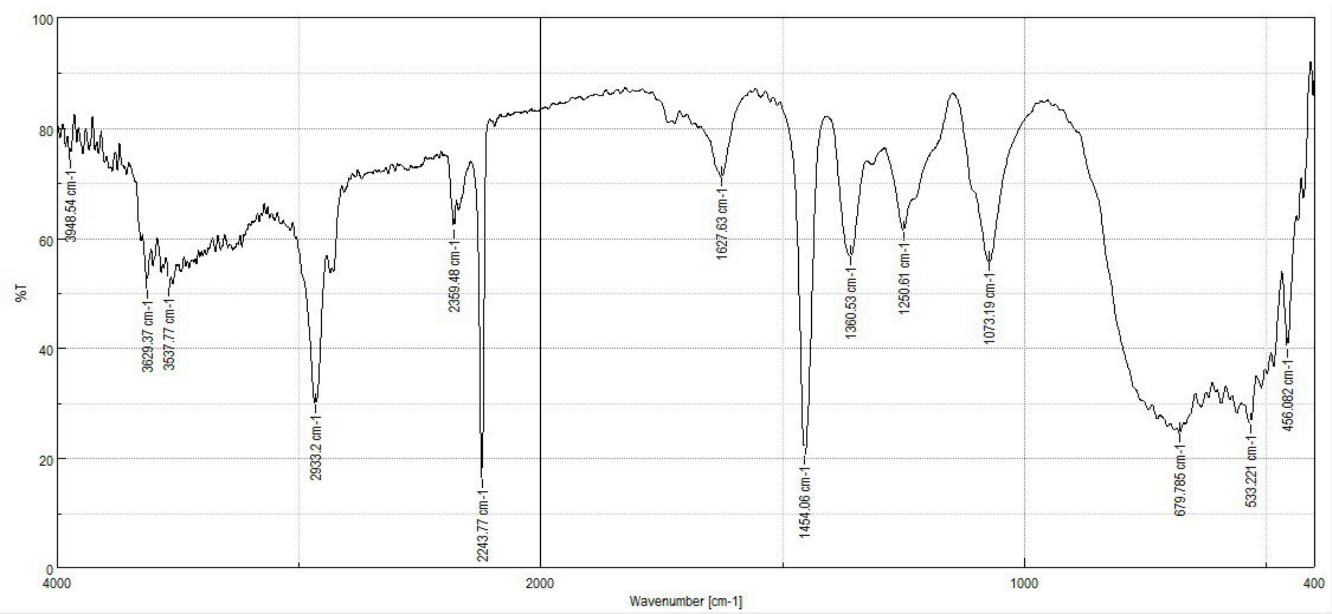


Figure 4: FTIR of (PAN/ TiO_2) 5 wt%.

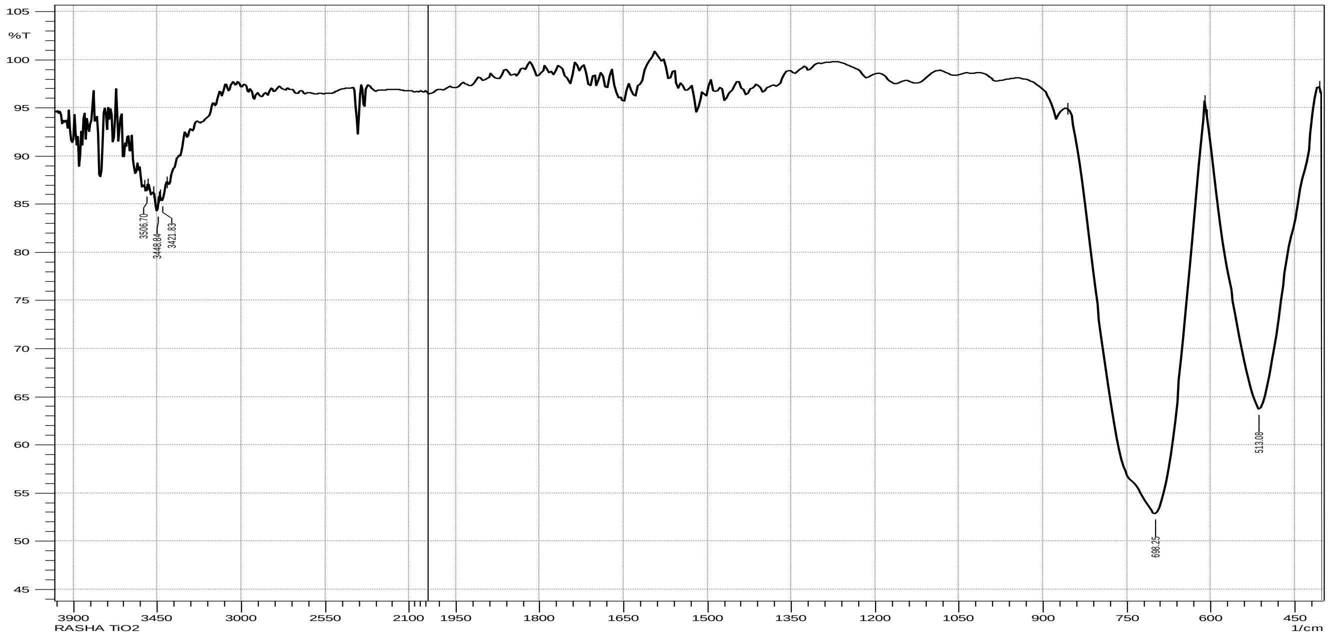


Figure 5: FTIR of TiO_2 Nano particle.

3.2. Scanning Electron Microscopy (SEM)

It can be seen from Figures 6 (a ,b, c, d) for PAN/TiO_2 nanofibers at weight ratio of (5%,10% and 15wt%)respectively, that the increase in collector rotation drive to more uniform and thinner fibers, this is potentially due to the higher stretching level imposed on them. .Statistical analyses showed that the increase in this variable provoked a change in fiber diameter which at the significance level of 1247rpm. .The rotating drum can be used, not only to control fiber alignment, but also to control fiber diameter. [3].The average diameter were 21.79nm for PAN nanofibers as shown in figure 6(a), while the average diameters in PAN/TiO_2 were 20nm, 13.86nm and 25.78nm for 5wt% ,10wt% and 15wt% as shown in figure 6 (b, c, d) respectively.

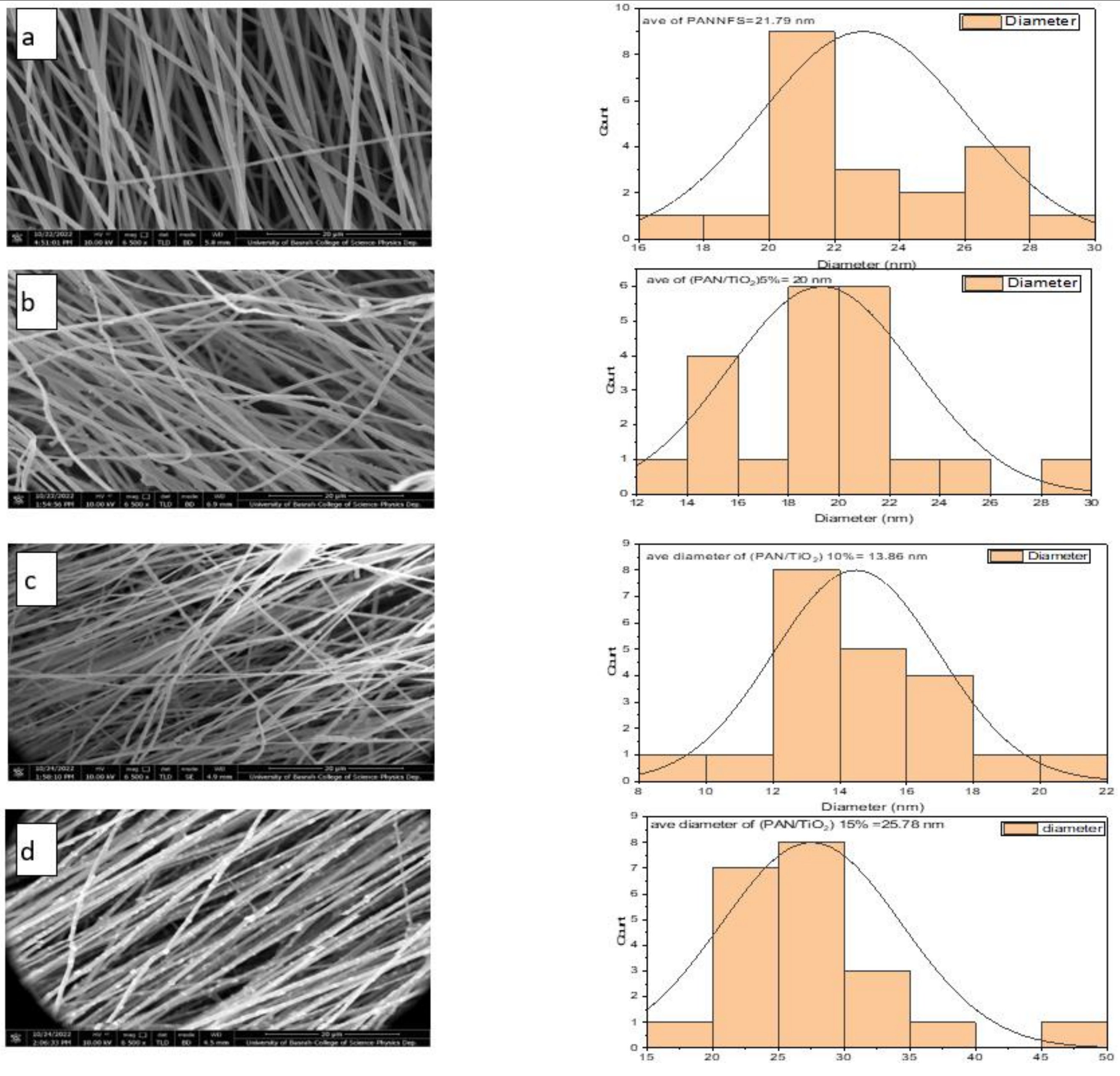


Figure 7 : SEM for (a) PAN nanofibers and PAN /TiO2 at different weight percentage (b) 5wt% (c) 10wt% (d) 15wt%.

4. Photocatalytic degradation of MB

MB dye was utilized as an investigative material to examine and evaluate the photocatalytic efficiency of PAN and PAN/ TiO_2 nanofiber. For supplying desired UV photon, UV-A(325-400nm wavelength) lamp of 300watt was executed and adjusted at the height of 5cm above the reaction vessel and irradiated perpendicularly to the surface of the solution .The Photocatalytic reaction was implemented at room temperature under the influence of 40 ml (10^{-5}M) of an aqueous solution of the MB dye was stirred to obtain the adsorption - desorption equilibrium prior to the radiation. The pH of MB aqueous solution was 7.13, then an adequate amount of the PAN fiber PAN/ TiO_2 fiber, with dimension (2.5x6.5) cm was immersed in the MB solution. Subsequent to the irradiation exposure time, 3.5 ml of the solution was taken and measured by UV-Visible spectroscopy. The MB degradation efficiency, in terms of the percentage of dye degradation efficiency, was calculated using the relationship [18].

$$\textbf{Degradation rate}(\%) = \left(\frac{\mathbf{A_o - A_t}}{\mathbf{A_o}}\right) \times \mathbf{100}\%$$

Where: A_o is the initial absorbance degradation of MB solution at time equal zero, while A_t the maximum absorbance of the MB (at 665 nm) at time t.

4.1 Photocatalytic degradation of methylene blue under UV irradiation:

The photocatalytic activity was evaluated by decomposition of MB under (UV) light. Figures (8) shows the behaviors of MB degradation under(a) PAN nanofiber and (b)PAN/ TiO_2 nanofiber (5%, 10% and 15wt%) respectively. The degradation of the prepared samples for methylene blue studied when there was no photocatalytic without light (Dark, no catalyst), the concentration of (MB) almost did not change; indicating that the properties of (MB) are stable. When catalysts were added, however, the concentration was decreased dramatically, indicating that the reduction in (MB) is photocatalytic path. It should be noted that the photocatalytic activity was evaluated without TiO_2 nano particles (only PAN), the result shown that the degradation percentage of (MB) was 54% after 120 min, but the best result was obtained in the case of PAN/ TiO_2 nanofiber (5, 10, and 15wt% TiO_2), also the result shown that the degradation of (MB) was increased by increasing (TiO_2) content in the prepared composites (i.e., 86, 98, and 97%) when the TiO_2 content was (5,10 and 15wt%) respectively, at 120 min. On the other hand, the absorption capacity increased rapidly in the first 100 min and then reached slow as a result of 15% TiO_2 composites. Exhibited the highest adsorption capacity and removal of MB compared with PAN with PAN alone (51% at 100 min).Tables (2,3,4) show the percentage rate and their efficiency degradation of (MB).

Table 2: Degradation of MB dye as a function of time using photocatalyst PAN and PAN/TiO_2 nanofibers at different weight percentage.

Time (min)	**Photocatalyst system PAN/ TiO_2 nanofiber**			
	Degradation percent			
	PAN nanofiber	**5wt% TiO_2**	**10wt% TiO_2**	**15wt% TiO_2**
0	0	0	0	0
20	8.68	25.98	31.60	41.37
40	28.40	51.97	44.28	69.64
60	33.33	72.76	60.49	88.14
80	34.74	79.62	78.17	92.93
100	51.87	86.90	٩٠٤٣	97.50
120	53.99	95.63	98.54	98.33

Table 3: Efficiency Degradation of MB dye as a function of time using photocatalyst PAN and PAN/TiO_2 nanofibers at different weight percentage.

Time (min)	**Photocatalyst system PAN/ TiO_2 nanofiber**			
	ln (A_o\\A_t)			
	PAN nanofiber	**5wt% TiO_2**	**10wt% TiO_2**	**15wt% TiO_2**
٠	0	٠	٠	٠
20	0.29	٠.٣٠	٠.٣٧	٠.٥٣
40	0.95	٠.٤٢	٠.٥٨٤	١.١٩
60	1.89	٠.٧٣	٠.٩٢	٢.١٣
80	2.41	٠.٧٨	١.٥٢	٢.٦٤
100	3.45	١.٥٩	٢.٣٤	٣.٦٩
120	3.86	٢.٠٣	٤.٢٢	٤.٠٩

Figure 9. show the degradation rate of MB blue dye increased with increasing the weight ratio of TiO_2 at different of illumination time and it is good result compared by the published literature[11,18]. Dye degradation is happening by photo catalysts when a photon with energy higher than the energy gap illuminates the catalyst leading to excite electrons from valance band (VB) to conduction band (CB) leaving holes. High oxidation potential of holes in CB allows direct oxidation of dye in the reaction medium followed by the degradation process. Dye decay is caused by its interaction with free

radicals of hydroxyl (HO·) and superoxide($O_2^{\cdot}$) that produce by the catalyst according to the interaction that shown by equations below [19]:

$$TiO_2 + h\nu \longrightarrow e^-_{cb} + h^+_{vb}$$

$$h^+_{vb} + H_2O \longrightarrow H^+ + HO^{\cdot}$$

$$e^-_{cb} + O_2 \longrightarrow O_2^{\cdot}$$

$$O_2^{\cdot} + H^+ \longrightarrow HO_2^{\cdot}$$

$$HO_2^{\cdot} + HO_2^{\cdot} \longrightarrow H_2O_2 + O_2$$

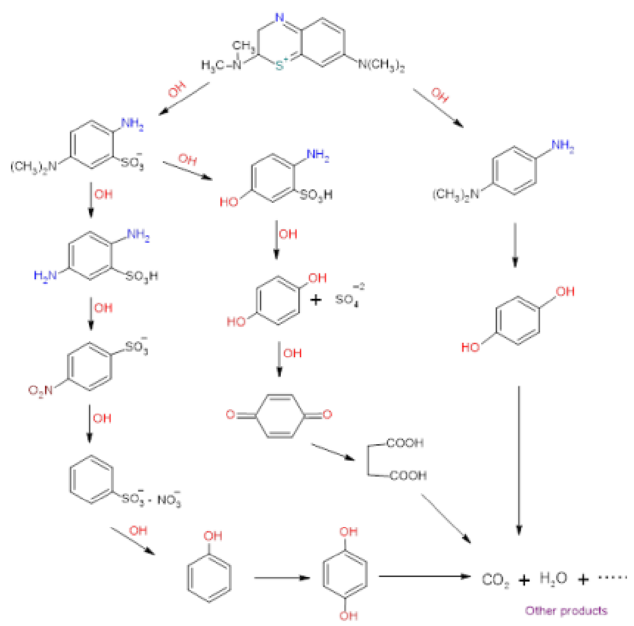
$$H_2O_2 + e^-_{cb} \longrightarrow HO^{\cdot} + HO^-$$

$$H_2O_2 + h\nu \longrightarrow 2\,HO^{\cdot}$$

$$R + HO^{\cdot} \longrightarrow CO_2 + H_2O$$

Where R means the MB dye.

while the mechanism of MB degradation was shown in scheme 1



Scheme 1: MB mechanism degradation[20]

Table 4. Rate degradation of MB dye as a function of time using photocatalyst PAN and PAN/TiO_2 nanofibers at different weight percentage.

Time (min)	Photocatalyst system PAN/ TiO_2 nanofiber			
	$A_t \backslash A_o$			
	PAN nanofiber	5wt % TiO_2	10wt % TiO_2	15wt% TiO_2
0	1	1	1	1
20	0.74	0.74	0.68	0.58
40	0.38	0.65	0.55	0.30
60	0.15	0.48	0.39	0.11
80	0.08	0.45	0.21	0.07
100	0.03	0.20	0.09	0.02
120	0.02	0.13	0.01	0.01

Table 5: Degradation percent of MB dye as a function of time using reused photocatalyst PAN/ TiO_2 nanofibers at different weight percentage

Time (min)	Photocatalyst system PAN/ TiO_2 nanofiber			
	Degradation percent			
	PAN nanofiber	5wt% TiO_2	10wt% TiO_2	15wt% TiO_2
0	0	0	0	0
20	13.14	25.98	35.96	27.65
40	13.61	34.71	51.35	71.72
60	17.37	66.52	58.41	74.22
80	22.53	75.46	70.47	76.09
100	24.17	84.82	80.66	79.20
120	48.59	87.73	83.57	85.44

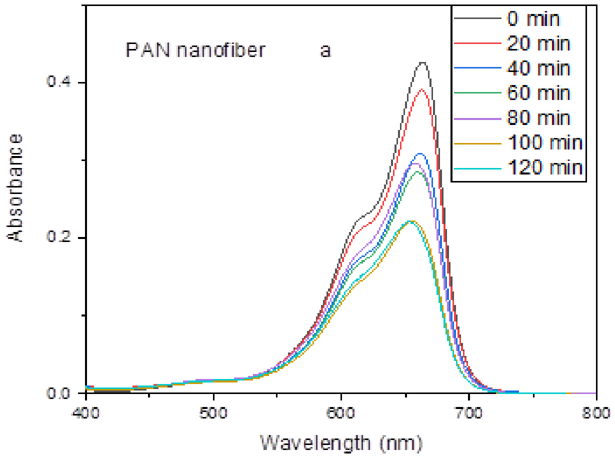
Table 6. Efficiency Degradation of MB dye as a function of time using reused photocatalyst PAN/TiO_2 at different weight percentage.

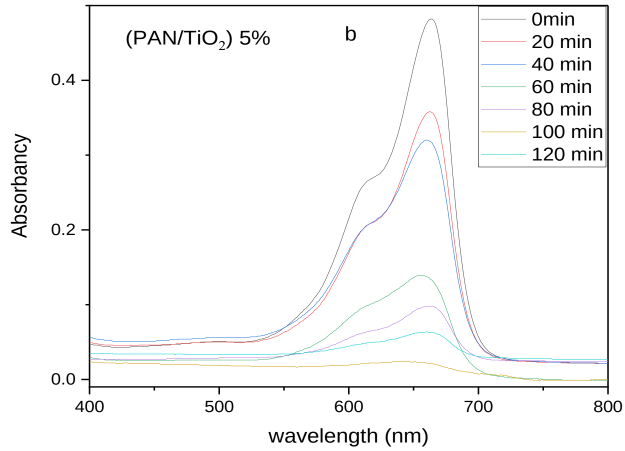
Time (min)	Photocatalyst system PAN/ TiO_2 nanofiber			
	ln (Ao\At)			
	PAN nanofiber	5wt% TiO_2	10wt% TiO_2	15wt% TiO_2
0	0	0	0	0
20	0.14	0.30	0.44	0.32
40	0.14	0.42	0.72	1.26
60	0.19	1.09	0.87	1.35
80	0.25	1.40	1.22	1.43

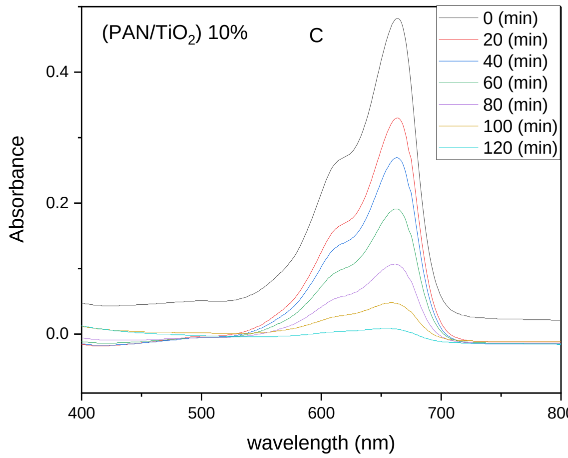
100	0.27	1.88	1.64	1.57
120	0.66	2.09	1.80	1.92

Table7. Rate degradation of MB as a function of time using reused photo catalysis NFPAN and PAN/TiO_2 nanofiber at different weight percentage.

Time (min)	Photocatalyst system PAN/ TiO_2 nanofiber ($A_t\backslash A_0$)			
	PAN nanofibe r	5wt% TiO_2	10wt% TiO_2	15wt% TiO_2
٠	1	1	1	1
20	0.86	0.47	0.46	0.79
40	0.86	0.65	0.48	0.53
60	0.82	0.33	0.41	0.09
80	0.77	0.24	0.29	0.07
100	0.08	0.15	0.19	0.04
120	0.51	0.12	0.16	0.03







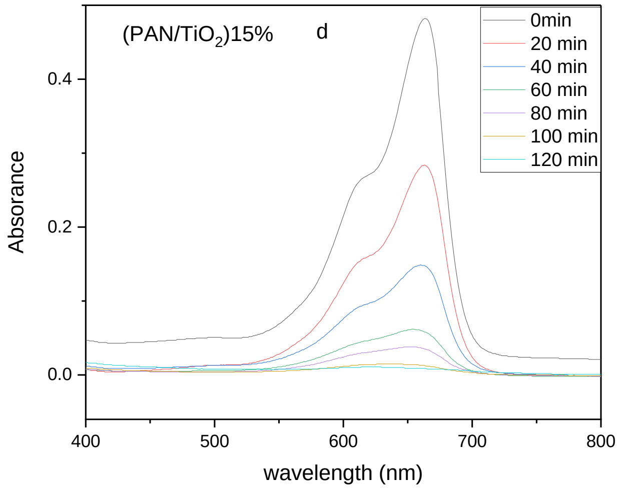


Figure 7: UV-VIS spectra of MB dye photocatalytic by (a) PAN nanofibers and (PAN/TiO_2) nanofiber (b) 5wt% (c) 10wt% (d) 15wt%.

The importance of using polymeric nanofibers is the ease of use and the possibility of repeating the fibers several times, and this leads to cost reduction. The tables (5,6,7) show the results of degradation using NFPAN and PAN/TiO_2 nanocomposite again, as it is noted from the results obtained for polymer that they reach 53.99%, while they reach the greatest value of dye degradation to be about at ٩٥.٦٣% at 5wt% of TiO_2 fibers.

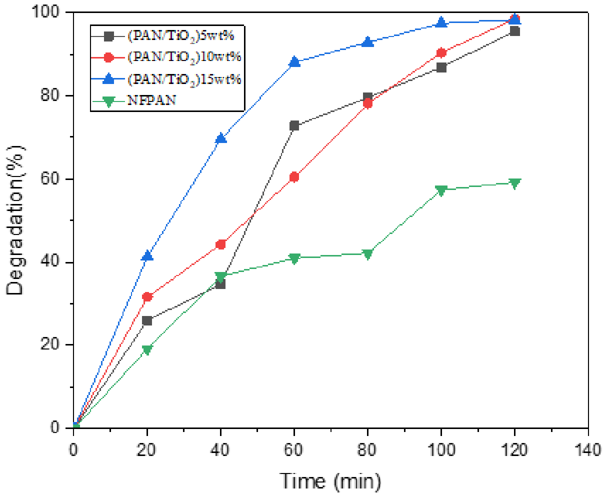


Figure 8: Photocatalytic degradation percent of MB as a function of time using($PAN/xTiO_2$) as photocatalyst.

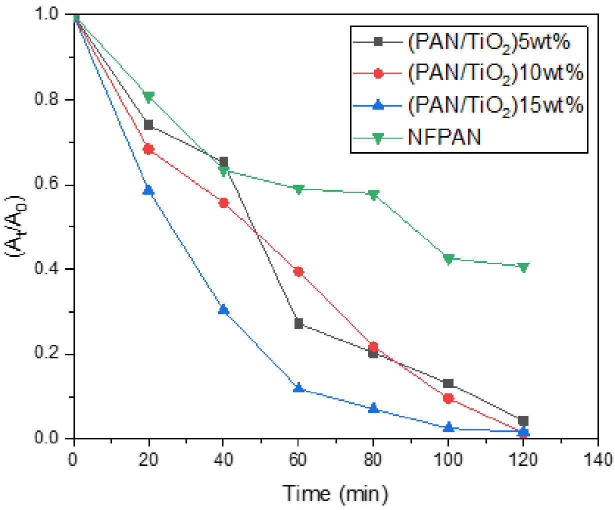


Figure 9: Photocatalytic degradation rate of MB as a function of time using ($PAN/xTiO_2$)as photocatalyst.

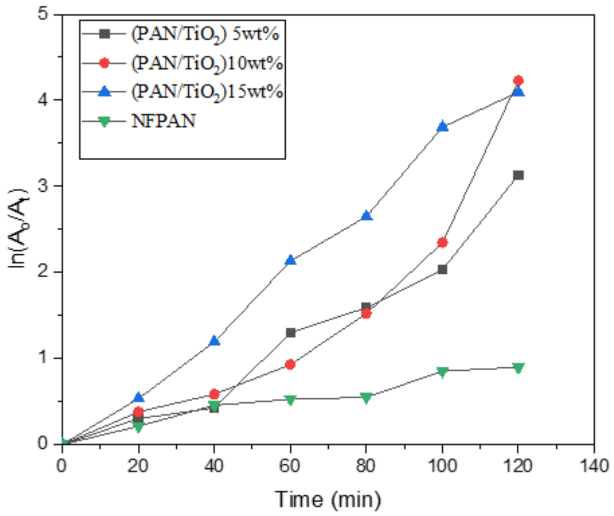


Figure 10: Photocatalytic degradation efficiency of MB as a function of time using ($PAN/xTiO_2$) as photocatalyst.

Conclusion:

In this work, polyacrylonitrile (PAN) was prepared via free radical polymerization. Then PAN and PAN/TiO_2 nanofiber membrane were successfully fabricated by the electrospinning method. FTIR study indicate polymerization of the acrylonitrile, then this polymer and composite used as photocatalysis against degradation of MB dye using different percentages of TiO_2 . The results proved that the deterioration of MB dye increase by increasing the irradiation time. The TiO_2 has an active role in electron transfer and photoexcitation when irradiated with ultraviolet (UV) ray. Possible reasons for the increased degradation of the dye by increasing the irradiation time is the increased production of free hydroxyl radicals (OH) and superoxide radicals, which are strong oxidants that degrade the dye, also the pH has affected the degradation process of MB and the result indicate that in the basic medium, the degradation increased due to increase in the hydroxyl radicals which lead to decompose of the dye. results indicate the increase in the degradation of MB.

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