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Photocatalysis-Assisted Process of Reusable PVA/TiO_2 Nanofibers

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Abstract

Photocatalysis-assisted PVA/TiO_2 nanofibers has become a prospective technology for water filtration applications. In line with this application, swelling behavior, photocatalytic activity and reusability are crucial considerations. This work presents the evaluation of swelling behavior and photocatalytic activity of PVA/TiO_2 nanofibers in harsh pH environment. By varying pH environment at pH = 1 - 12, we have successfully shown that pH = 7 is the best environment for the PVA/TiO_2 nanofibers-based water filtration. On this environment, the nanofibers has 92 % degradability and is able to resist Methylene Blue (MB) solution for up to 5 min. Likewise, it shows excellent reusability over 5 cycles usage. Moreover, the nanofibers is prospective for rapid filtration in harsh pH environment. This work is a step forward toward environmental-friendly water filtration in harsh pH environment.

Keywords: Harsh pH, Nanofibers, Photocatalysis-assisted, PVA, TiO_2

Introduction

Critical environmental conditions have pushed the boundaries of technology to overcome the continuous water shortage issue for the past decades. It demands technological breakthroughs by enabling liquid-waste-filtration technologies that are smaller, simpler, environment-friendly, highly efficient and highly resistant to harsh pH environments. Through the years, the amount and variety of chemical contaminants have increased as industrial activity has grown in various sectors. Those chemical contaminants are mostly in a strong acid or basic condition [1-4]. An effective and efficient water-filtration technology is required to degrade the chemical contaminants. For realizing green technology, photocatalysis is regarded as one of the most promising method to overcome the liquid waste issues. It degrades organic contaminants in liquid waste using photogenerated hydroxyl radicals [5]. It destroys pollutants with relatively safe oxidants. In addition, the organic pollutants are completely mineralized into carbon dioxide and water under ambient conditions [6]. More importantly, it is environment-friendly over other existing technologies [7].

Oxide semiconductors are widely utilized as catalytic materials which enable photocatalysis reactions. One-dimensional (1D) oxide semiconductor materials, particularly nanoparticles (NPs) TiO_2, are advisable since photocatalysis is a surface phenomenon where the degradation rate is strongly correlated to the surface area-to-volume ratio [8]. The NPs TiO_2 exhibit superb photocatalytic activity over methylene blue (MB) which is up to 80 % [9]. Therefore, NPs TiO_2 are effective catalytic materials for liquid waste treatment. Nevertheless, the NPs TiO_2 residues after photocatalysis are highlighted as the major drawback. The NPs TiO_2 have low reusability, low recyclability, and it is difficult to recover since it tends to create sedimentation after the treatment process [10,11]. Moreover, the NPs TiO_2 are likely to enter the aquatic system through liquid waste effluent [12]. To minimize the environmental risk, the NPs TiO_2 are immobilized in a polymer matrix by fabricating nanofibers. The TiO_2-based nanofibers have been proven to exhibit photocatalytic efficiency above 90 % in methylene blue [13,14] and methylene orange [15]. Likewise, the photocatalytic activity of TiO_2 is significantly affected by its design structures or morphologies. The evaluation over 7 different TiO_2 structures including solid microspheres (TSMS), mesoporous microspheres (TMMS), hollow spheres (THS), nanosheets (TNS), nanotubes (TNT), 3D sea urchin-like structure (TSU) and 3D hierarchically porous (THP), have shown that TNS exhibits the best methyl ethylene ketone (MEK) removal efficiency of 71.3 %. While TSMS exhibits the lowest removal efficiency of 31.8 % [16].

In particular, polyvinyl alcohol (PVA)-TiO_2 nanofiber are extensively used in water filtration, air filtration, paper coating, and textile industry owing to its excellent flexibility, chemical stability and thermal

stability [17-23]. PVA/TiO_2 nanofibers has been utilized for photocatalysis due to its flexibility, technological simplicity, high surface area-to-volume ratio and environment-friendly [18,24]. Nowadays, the photocatalytic performance of PVA/TiO_2 nanofibers is still an attractive topic to be investigated. A study of PVA/TiO_2 nanofiber's stability in harsh pH environments is necessary since most of the liquid waste is strongly acid/basic. Therefore, our aim is to study the photo-assisted process of reusable PVA/TiO_2 nanofibers.

Materials and methods

PVA/TiO_2 mixture was synthesized by dispersing Titanium (IV) oxide (anatase, < 25 nm particle size, 99.7 % trace metal basis, Sigma-Aldrich) in deionized water at 90 °C for 30 min. Simultaneously, Tetramethylammonium hydroxide (TMAH, Sigma-Aldrich) was added at TiO_2:TMAH = 10:1 which is further acts as a surfactant. Subsequently, the TiO_2 dispersion was sonicated at 40 °C for 1 h. Thereafter, Polyvinyl alcohol powder (PVA, Mw: 89.000 - 98.000 g/mol, Sigma-Aldrich) was added into the TiO_2 dispersion with a mass ratio of PVA:TIO_2 = 4:1, then stirred at 150 °C for 1 h. The PVA/TiO_2 mixture were sonicated at 40 °C for 3 h. The surfactant is added to prevent the agglomeration of TiO_2 nanoparticles. While the sonication was carried-out to improve the PVA/TiO_2 mixture homogeneity [9].

The as-prepared PVA/TiO_2 mixture was injected from a 10 mL syringe (0.25 mm needle's diameter). The tip-to-collector distance of 14 cm was set in the electrospinning equipment. A high-voltage of 15 kV was applied to induce the electrostatic force which further produce nanofibers [25]. Since the PVA/TiO_2 nanofibers has poor stability in water, the crosslinking method is carried-out to improve its stability. The PVA/TiO_2 nanofibers was dipped in the crosslinking agent (glutaraldehyde/GA from Sigma-Aldrich with 2.5 % (w/v) at GA:Acetone:HCl = 1:2:0.01). The dipping process was performed for 4 h at room temperature.

The morphology of PVA/TiO_2 nanofibers was evaluated through Scanning Electron Microscopy (SEM; FEI, Type: Inspect-S50). Whereas, the nanofiber's diameters are analyzed by utilizing ImageJ software. The elemental analysis was also performed to revealed the presence of TiO_2 nanoparticles in the PVA nanofibers by using Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX; FEI, Type: Inspect-S50). Finally, the ultraviolet - visible spectroscopy (UV-Vis; Shimadzu, UV-1700) is used to evaluated the absorption spectrum of methylene blue (MB) in various concentrations (ppm) as well as pH environments.

A 1.0×0.5 cm^2 of PVA/TiO_2 nanofibers was prepared for swelling evaluation in various pH environments (1, 2, 4, 7, 8, 9, 10, 11 and 12). The swelling of PVA/TiO_2 nanofibers is represented as the measured weight change from time to time for 60 min as follows [26]:

$$\%\text{swelling} = \frac{w_s - w_d}{w_d} \times 100\ \% \quad (1)$$

where w_d and w_s are weight of dried and wet samples, respectively. In general, the swelling index of each material tend to increased exponentially as depicted in the following equation [27]:

$$S_t = S_0 + A_1 e^{-\left(\frac{t}{\tau}\right)} \quad (2)$$

where S_t is the swelling index (swelling time = t), S_0 is the swelling index (swelling time = 0), A_1 is a constant, t is swelling time, and τ is saturated time where the swelling's curve has reached its saturated state ($t = \tau$).

To deeply study the swelling mechanism where the water was diffused into the PVA/TiO_2 nanofibers, the power law equation was used as follow [28]:

$$\frac{S_t}{S_\infty} = kt^n \quad (3)$$

where S_t is the swelling index (swelling time = t), S_∞ is the swelling index as swelling time approaches infinity, k is the intrinsic constant of polymer structure, t is time and n is the diffusional exponent.

The photocatalytic activities of PVA/TiO_2 nanofibers was evaluated by observing the color degradation of methylene blue (MB) under ultra-violet (UV) light. Six UV-light sources with wavelength

of 365 nm and total power of 60 W were utilized to evaluate the photocatalytic activity. A 1.5×1.5 cm^2 of PVA/TiO_2 nanofibers was prepared for evaluating the photocatalytic activity. The nanofibers was immersed into 10 mL MB solution (10 ppm). The degradation of MB was measured every 20 min for 2 h. The Beer-Lambert law was used to calculate the concentration of MB from time to time, as follow:

$$A = log\left(\frac{I_0}{I}\right) = acd \quad (4)$$

where A is absorbance, I_0 is initial light intensity, I is transmitted light intensity, a is absorbance constant, c is the concentration, and d is sample length. To deeply evaluate the degradation capability of PVA/TiO_2 nanofibers, the normalized value of C_0/C_1 was calculated. C_0 is the initial absorbance peak which obtained after calibrating the MB solution in various concentration (0 - 10 ppm). Whereas, C is the final absorbance peak which represent the concentration changes of MB as the function of time. Hence, the percentage of degradation was calculated using the following equation:

$$degradation\ \% = \frac{C_0 - C_1}{C_0} \times 100\ \% \quad (5)$$

Results and discussion

The PVA/TiO_2 mixture with considerable homogeneity was successfully obtained after 3 h of sonication. Combining the surfactant addition and the sonification time are significantly improve the NPs TiO_2 distribution on the PVA matrix. The surfactant prevents the agglomeration by encapsulating the NPs TiO_2. Whereas the sonification promotes NPs TiO_2 distribution throughout the nanofibers which is agrees with the previous reported work [9]. Nevertheless, prolonging the storage time of the sonicated PVA/TiO_2 mixture tends to create the NPs TiO_2 sediment which further degrade the homogeneity. As a consequence, the sonicated PVA/TiO_2 mixture is immediately injected to produce PVA/TiO_2 nanofibers.

An excellent smooth PVA/TiO_2 nanofibers was successfully obtained through electrospinning process as shown in **Figure 1(a)**. Likewise, a uniform PVA/TiO_2 nanofibers was obtained even after modified by Glutaraldehyde-crosslinking. The nanofibers show almost no beads, implying the minimum defect and maximum area per unit mass ratio which is confirmed by SEM evaluation. Nonetheless, the flexibility of PVA/TiO_2 nanofibers was slightly reduced after crosslinking by Glutaraldehyde. During the crosslinking, the hydroxyl group (PVA) binds to the aldehyde group (Glutaraldehyde), resulting in the acetal bridge which further strengthens PVA and improved its stability in water [29].

Moreover, SEM-EDX was utilized to evaluate the NPs TiO_2 distribution throughout the PVA matrix as displayed in Error! Reference source not found.**(b)**. Agglomeration of the NPs TiO_2 were observed in several areas which indicated by the bright green color in Error! Reference source not found.**(b)**. Nonetheless, after evaluating the wider membrane's areas, the NPs TiO_2 were uniformly distributed on the PVA matrix. It is likely due to the surfactant addition and sonication treatment during the PVA/TiO_2 synthesis as mentioned above. In addition, elemental analysis shows the atomic ratio of Ti (2.86 %) and O (34.48 %), indicating the presence of TiO_2. While the atomic ratio of C (62.65 %) is indicated to the polymer matrix (**Figure S1**).

Furthermore, image processing software (ImageJ) was used to analyzed the diameter of PVA/TiO_2 nanofibers. The captured image which is obtained from the SEM micrograph was analyzed by ImageJ software. Each nanofiber's diameter was measured and represented as Gaussian distribution as shown in Error! Reference source not found.**(c)**. The average diameters of PVA/TiO_2 nanofibers is about (138 ± 4) nm. While in the previous work, it was reported that the average's diameters of PVA nanofibers is about 355 nm [9]. Apparently, the addition of the NPs TiO_2 into PVA matrix tend to decrease the nanofiber's diameter [9].

The swelling evaluation of PVA/TiO_2 nanofibers was performed by immersing the nanofibers in 10 ppm of Methylene Blue (MB) solution at pH 1 - 12 for 60 min. The swelling ratio as a function of time can be obtained by using Eq. (1). As the pH was varying from 1 - 12, the swelling ratio of PVA/TiO_2 nanofibers is varied from 200 - 900 % (Error! Reference source not found.). The S_t specified the swelling ratio at the saturation state. It means that the swelling ratio is relatively constant after reaching the S_t. Interestingly, the PVA/TiO_2 nanofibers is extremely sensitive to acidic solution. A gradual increase of swelling ratio is severe at acidic solutions (pH 1 - 4). The hydroxyl group of PVA can easily interact with H^+ ions from acidic solutions creating ionic bonds. In terms of strong acid solutions, a high concentration of H^+ ions tend to increase the hydrophilicity.

In contrast, excess OH^- ions of alkaline solutions will bind with hydroxyl group of PVA creating covalent bonds which implies a decrease in the hydrophilicity of the nanofibers. Therefore, the S_t of acidic solutions are higher as compared to the alkaline solutions. In particular, the S_t was relatively stable at around 400 % for pH = 7 - 9. Likely, the amount of H^+ ions are compensated by the OH^- ions. Moreover, an excellent swelling ratio was observed for alkaline solution at pH = 12 with a S_t of 270 %. In other words, the nanofibers is only 3 times bigger after immersing after immersing in the alkaline solution. This characteristic is crucial since the lower swelling ratio is required for water filtration application.

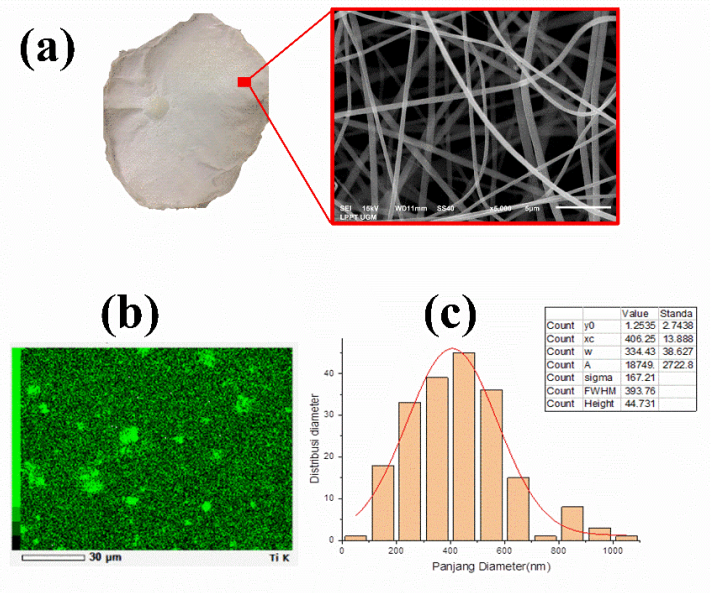

Figure 1 (a) SEM image of PVA/TiO_2 nanofibers, (b) SEM-EDX of TiO_2 nanoparticle's mapping, and (c) Gaussian distribution of nanofiber's diameters.

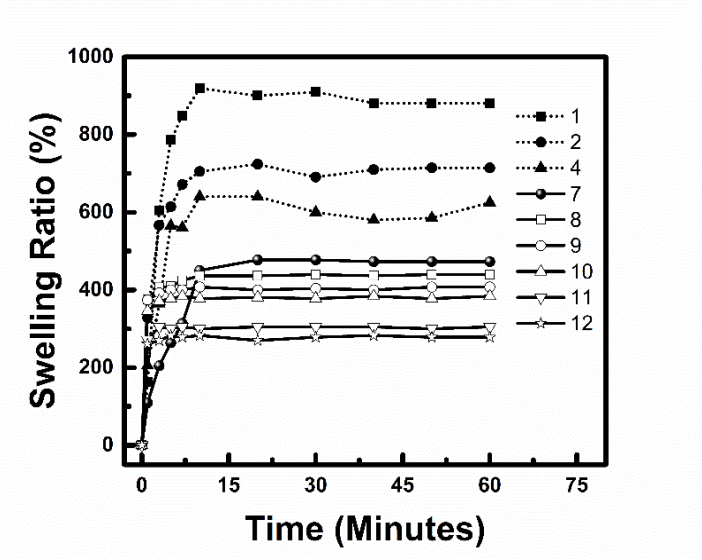

Figure 2 Effect of pH on the swelling index of PVA/TiO_2 nanofibers.

Afterwards, Eqs. (2) and (3) were used to calculate the swelling parameters including the saturated time (τ) and diffusional exponent (n) as summarized in Error! Reference source not found.. As the nanofibers is immersed in the MB solutions, the swelling ratio starts to increase gradually until it reaches a saturated state. The saturated state indicates the condition where the nanofibers is unable to absorb solvent anymore. The τ is the physical quantity of the swelling time at the saturated state ($t = \tau$). Likewise, it

indicates how fast the diffusion rate of MB solution is. A high τ implies better mechanical stability in the MB solution. Meaning, the nanofibers is strong enough to resist the MB solution from entering into the fibers at a certain time, resulting in a slower diffusion rate.

Apparently, the τ drastically decreased at pH > 7 owing to a high diffusion rate of MB solution. The nanofibers can only resist the MB solution for only less than 30 s. As the nanofibers is immersed, the MB solution immediately entered the nanofibers and degrades the mechanical stability. In consequence, the swelling ratio at t = 1 min is close to that at ($t = \tau$) counterparts (Error! Reference source not found.). There are no significant changes in the swelling ratio after immersing time of 1 min. In other words, the PVA/TiO_2 nanofibers has been probably damaged [3,4,30]. It loses the hydrophilicity so that the swelling rate become slow and eventually unable to absorb solvent anymore.

Table 1 Swelling parameters of PVA/TiO_2 nanofibers in various pH.

Solution	Swelling (%) at t = 1 min	Swelling (%) at t = 5 min	Swelling (%) at $t = \tau$	τ (s)	n
pH 1	162	786	900	420	0.147
pH 2	329	614	724	420	0.099
pH 4	205	565	640	300	0.123
pH 7	109	264	477	328	0.201
pH 8	376	409	436	29	0.275
pH 9	374	400	400	22	0.012
pH 10	345	377	381	24	0.013
pH 11	271	300	305	27	0.012
pH 12	260	282	270	22	0.008

In the case of pH < 7, the nanofibers has considerable mechanical stability in the MB solution for an immersing time of up to 1 min. Nonetheless, the swelling ratio was degraded as the immersing time was prolonged. Interestingly, the nanofibers has excellent mechanical stability at pH = 7 for an immersing time of 1 min. Likewise, good mechanical stability has been also shown for immersing time of 5 min.

To further elucidate the swelling mechanism, an empirical equation (Eq. (3)) was utilized to calculate the diffusion exponent (n). Where the n indicates the physical mechanism controlling the MB solution uptake. The calculations show that all samples have $n < 0.5$ which indicates the Pseudo-Fickian or Less Fickian diffusion [28]. The Pseudo-Fickian diffusion refers to a condition where the MB solution penetration rate in the nanofibers is less than the polymer chain relaxation rate [30]. The maximum n is found to be around 0.2 at pH = 7 and pH = 8.

The photocatalytic activity of PVA/TiO_2 nanofibers was evaluated through UV-Vis spectroscopy. The MB solution exhibits certain absorbance peaks spectra which are around 664.6 and 616 nm as displayed in Error! Reference source not found.. Furthermore, the main peak (664.6 nm) was used to analyze the photocatalytic activity. As the UV exposure time was prolonged, the peak intensity degraded owing to the degradation of the MB solution (**Figure S2**). Herein, a 3.39 eV UV light source (λ = 365 nm) was utilized to generate the photoinduced reaction of TiO_2 photocatalysis as explained by Schneider *et al.* [31]. As a result, the MB solution color changes from blue to transparent (**Figure S3**).

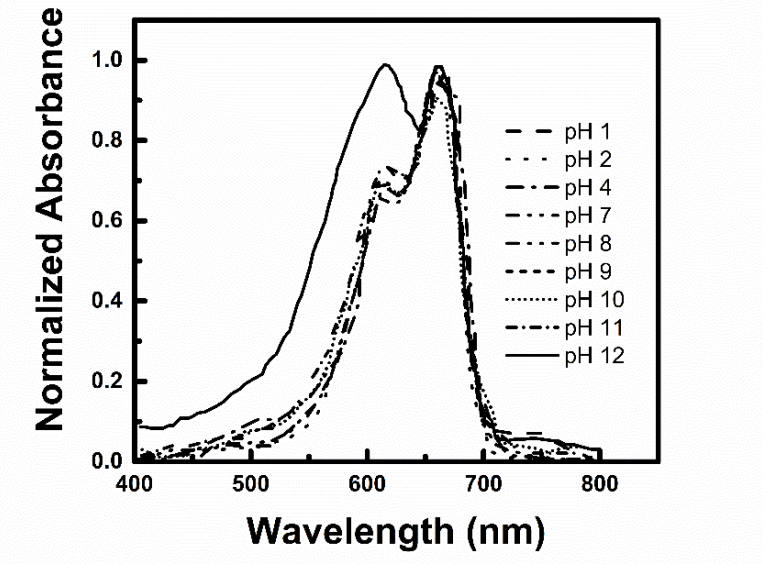

Figure 3 UV-Vis spectrum of the MB solution at various pH (t = 0 min).

The PVA/TiO_2 nanofibers significantly degraded the MB solution despite immersion in various pH environments (Error! Reference source not found.). After 120 min of photocatalysis, the MB solutions degraded by 22, 18 and 35 % in pH environments of 1, 2 and 4, respectively. Similar trend was observed for alkaline solution where the MB solutions degraded by 77, 85, 88 and 92 % in pH environments of 8, 9, 10 and 11. In the case of pH = 12, the degradability slightly decreased which is correlated to the absorbance peak shifting. As shown in Error! Reference source not found., a severe absorbance peak was observed at 664.6 nm for most of the samples. Nevertheless, the peak was shifted towards a shorter wavelength only for pH = 12 (**Figure S4**). The peak was shifted from 664.5 to 614 nm owing to deprotonation of the MB molecules [32]. Likewise, strong alkaline changes the MB structure and reduced the conjugated bonds [31]. Thus, the redshift of the absorbance peak has significantly decreased the degradability of the nanofibers. Regardless of those reasons, this sample shows excellent degradability of 82 %. In general, the alkaline solution shows a better degradation than the acidic solution which is agrees to the swelling behavior. In addition, it is likely due to the pH sensitive behavior of the NPs TiO_2. The best photocatalytic activity of NPs TiO_2 occurs in the alkaline condition [33]. Therefore, the combination of the NPs TiO_2 and PVA matrix have significantly exhibit excellent photocatalytic activity in the alkaline solution.

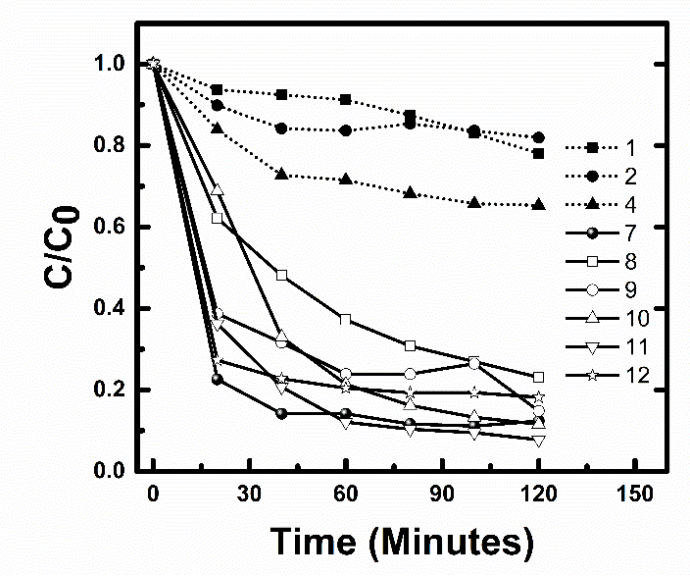

Figure 4 Degradation of methylene blue by PVA/TiO_2 nanofibers in various pH.

Interestingly, pH = 7 shows superb degradability of 88 % only for 80 min of photocatalysis. More importantly, it has 85 % degradability at early 20 min of photocatalysis (Error! Reference source not found.). Considering both swelling behavior and photocatalytic activity, it can be inferred that pH = 7 is the best environment for PVA/TiO_2 nanofiber-based water filtration. Whereas in the case of pH < 7 and pH > 7, the PVA/TiO_2 nanofibers is still considered as a prospective material for rapid filtration in acidic and alkaline environments. Nonetheless, an enhancement of the swelling stability and photocatalytic activity is necessary for prolonged filtration time.

Table 2 Summary of PVA/TiO2 nanofibers degradability in various pH.

Solution	*t* = 20 min		*t* = 120 min	
	MB degraded (%)	MB remained (%)	MB degraded (%)	MB remained (%)
pH 1	6	94	22	78
pH 2	10	90	18	82
pH 4	16	84	35	65
pH 7	77	23	88	12
pH 8	38	62	77	23
pH 9	61	39	85	15
pH 10	31	69	88	12
pH 11	64	36	92	8
pH 12	73	27	82	18

Aside from the swelling behavior and photocatalytic activity, the reusability of the nanofiber-based filtration is a critical consideration. Other than that, the reusability of nanofibers technology is in line with the environmental sustainability issue. Therefore, this work presented the reusability evaluation of PVA/TiO_2 nanofibers in degrading the MB-solution over 5 cycles of usage. Each cycle is conducted by performing a photocatalysis process for 120 min. The 2nd cycle is carried out subsequently after the 1st cycle by using the same nanofibers sample. In total, 600-minute-photocatalysis process for a 1.5×1.5 cm^2 of PVA/TiO_2 nanofibers was demonstrated consecutively.

Interestingly, an excellent degradability in all experimental conditions were observed with a degradation level of > 70 % (Error! Reference source not found.). PVA/TiO_2 nanofibers has successfully degraded the MB solutions by 92, 79, 74, 79 and 80 % at the 1st - 5th usage respectively. On the 2nd usage, the degradability decreased by 13 % owing to the breakdown of the glutaraldehyde-crosslinker. The crosslinker acts to improve the nanofiber's stability in a liquid medium by encapsulating the active surface of nanofibers. On the longer time usage, the crosslinker has slightly vanished allowing MB solution penetration into the nanofibers. Thus, the degradability is reduced.

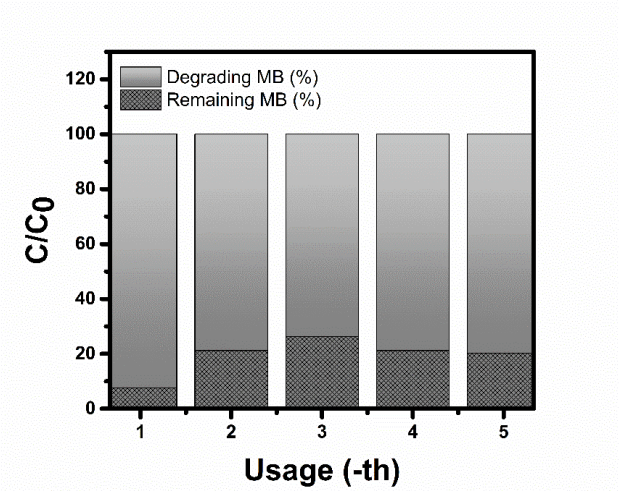

Figure 5 Reusability of PVA/TiO_2 nanofibers.

Conclusions

This work demonstrates the evaluation of swelling behavior and photocatalytic activity of PVA/TiO_2 nanofibers in harsh pH environment. Our result suggests that pH = 7 is the best environment for the PVA/TiO_2 nanofibers-based water filtration. The nanofibers exhibit up to 92 % degradation of MB solution at pH = 7. Likewise, it has an excellent swelling index for an immersing time of 5 min. More importantly, this sample shows superb reusability over 5 cycles of usage. Furthermore, our result suggests that the PVA/TiO_2 nanofibers is also prospective for rapid filtration in acidic and alkaline environments. This result will be beneficial for future realization of an environmental-friendly water filtration technology in harsh pH environment.

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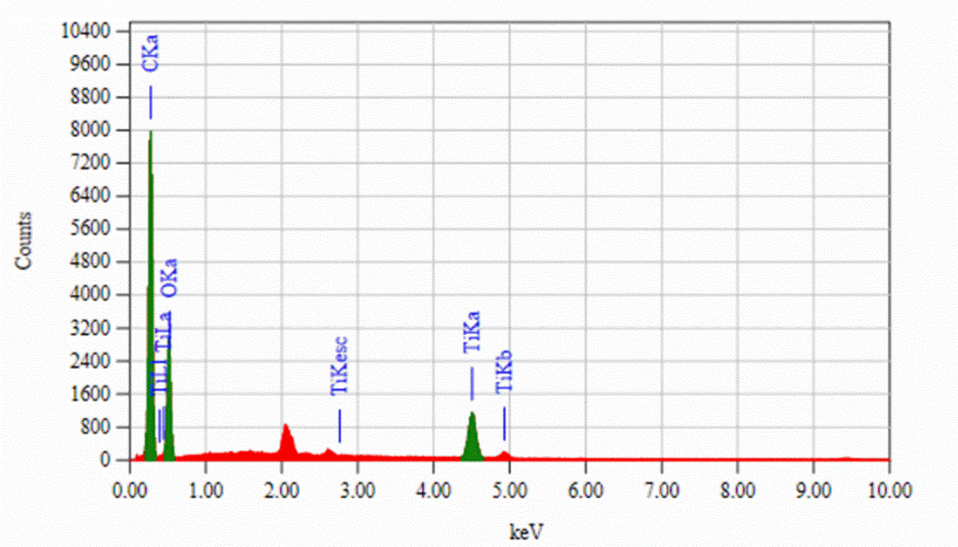
Supplementary



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.0846

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
C K	0.277	52.21	0.02	62.65				54.8797
O K	0.525	38.28	0.10	34.48				31.2757
Ti K	4.508	9.51	0.05	2.86				13.8446
Total		100.00		100.00				

Figure S1 SEM-EDX of PVA/TiO_2 nanofibers.

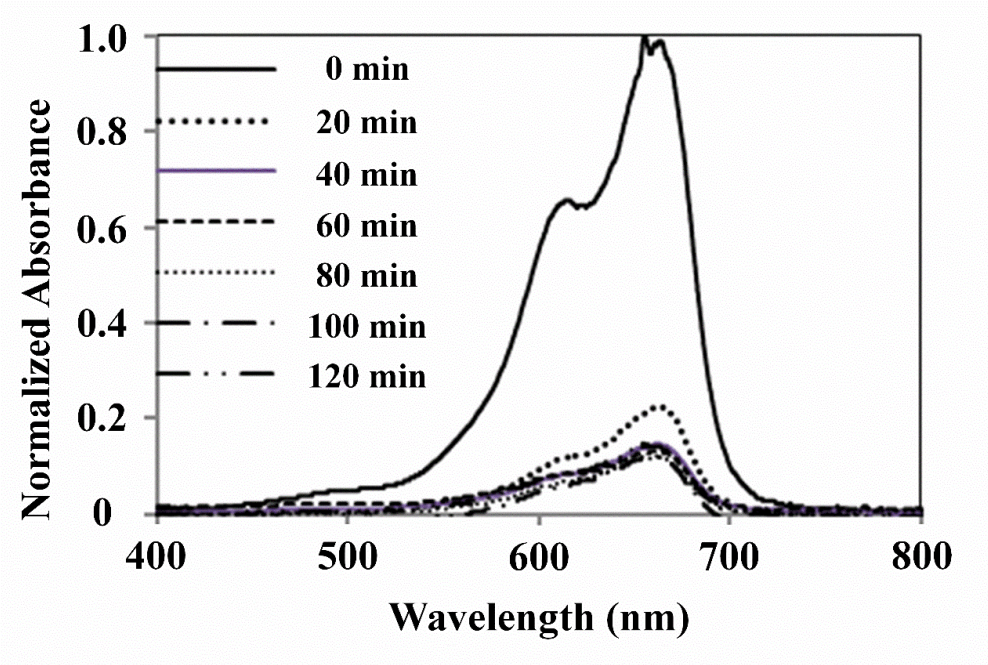


Figure S2 Absorbance spectra of MB solution at pH = 7.

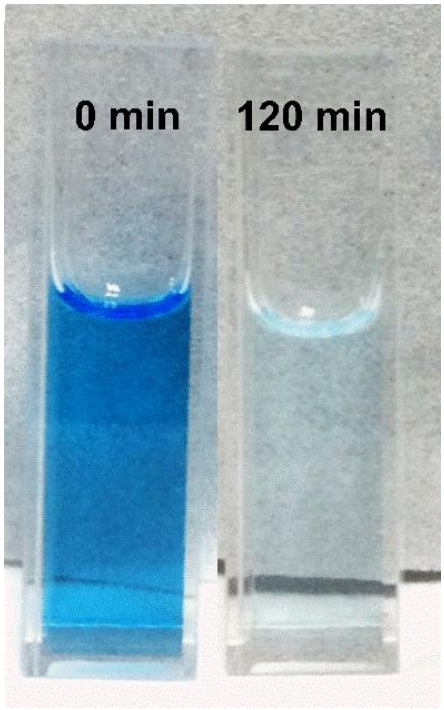


Figure S3 Color changes in MB solution after 120 min photocatalysis.

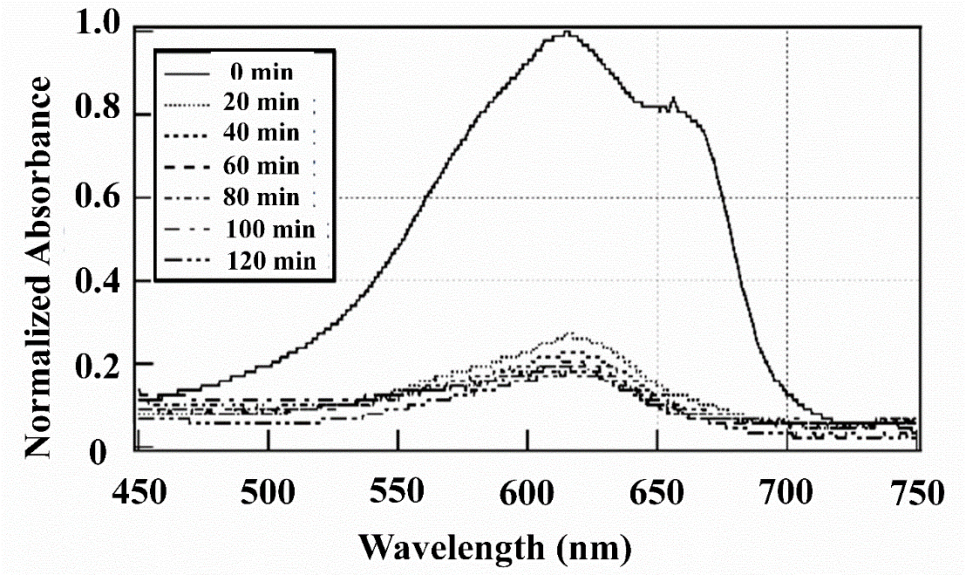


Figure S4 Absorbance spectra of MB solution at pH = 12.