Influence of temperature on the photodegradation process using Ag-doped TiO₂ nanostructures: Negative impact with the nanofibers

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A B S T R A C T
In this study, the influence of the temperature on the photodegradation process using Ag-doped TiO₂ nanostructures was investigated. Two morphologies were used; nanoparticles and nanofibers. The nanofibers were synthesized by electrospinning of a sol–gel consisting of titanium isopropoxide, silver nitrate and poly(vinyl acetate). The silver nitrate amount was changed to produce nanofibers having different silver contents. Typically, sol–gels containing 0.5, 1.0, 1.5, 2.0 and 2.5 wt% silver nitrate were utilized. Calcination of the electrospun mats at 700 °C led to produce well morphology Ag-doped TiO₂ nanofibers for all formulations. The nanoparticles were prepared from the same sol–gels, however, instead of spinning the gels were dried, grinded and sintered at 700 °C. Photodegradation under UV irradiation for the rhodamine B at 5, 15, 25, 45 and 55 °C were performed. For the nanoparticles, increasing the temperature has positive impact as the best degradation was obtained at 55 °C. In contrast to the known influence of the temperature on the chemical reactions, in case of the nanofibrous morphology, the temperature has negative impact as the experimental work indicated that the optimum temperature is 25 °C. The observed strange effect of the temperature in case of the nanofibrous morphology indicates instant degradation of the dye molecules in the active zones surrounding the nanofibers. Therefore, the increase of temperature results in increase the kinetic energy of the dye molecules so the molecules escape from the active thin film surrounding the photocatalyst. Overall, this study shows that the nanofibrous morphology strongly enhances the surface activity of the photocatalyst which generates negative influence of the temperature.

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1. Introduction

Fast electrons/holes recombination is the main dilemma facing the semiconductors photocatalysts in general and titanium oxide in particular. Incorporation of noble metal nanoparticles (NPs) into the titania dielectric matrix is a recent strategy to overcome this problem and simultaneously improve the photocatalytic activity of titanium oxide [1,2]. Doping with foreign metal nanoparticles can produce high Schottky barrier that facilitates electron capture [3]. The capture of electrons postulate to produce a longer electron–hole pair separation lifetime, and therefore hinder the recombination of electron–hole pairs and enhance the transfer of holes and possibly electrons to O₂ adsorbed on the TiO₂ surface. Afterward, excited electrons migrate to the metal, where they become trapped and the electron–hole pair recombination is suppressed. Therefore, many investigations have reported the enhancement of photoactivities in both liquid and gas phases [4,5]. Moreover, this incorporation provides an absorption feature due to the surface plasmon resonance (SPR) occurring over the visible range of the spectrum [6]. Particularly, silver and gold nanoparticles are more familiar because of their color varieties in the visible region, which is attributed to oscillations of the electrons at the surface of the nanoparticles [7]. Silver is the most common metal used to modify titania, because its d–s band gap is in the UV region and does not damp out the plasmon mode as strongly as gold [8,9]. Titania-modified-silver particles have raised extensive interest due to their applications in photocatalytic degradation [10]. The researchers have intensively studied how silver provides titania distinct photocatalytic activity, the mechanism has been well explained in previous reports [11–13]. Moreover, some researchers have concluded that incorporation of silver in titanium dioxide leads to increases in the total surface area of the prepared titanium dioxide [14,15]. This can be considered an additional benefit of
utilizing silver-loaded titanium oxide in the field of photocatalytic degradation. Therefore, many researchers have practically demonstrated that the degradation rates of the dyes can be enhanced by the deposition of silver on titanium dioxide [16–18].

In the last decades, nanostructural materials have been intensively investigated because of their high surface area, which strongly affects their physiochemical properties. Different shapes have been introduced. Of the reported nanostructure shapes, special attention has been paid to one-dimensional forms such as nanorods, nanowires, and nanofibers. This is due to their potential applications in the nanodevices [19–21]. Nanofibers have received special consideration due to their high axial ratio, good mechanical properties, and their manageable and novel physical properties. Compared to nanoparticles, nanofibers have small surface area which might be considered a negative impact upon using as catalyst in the chemical reactions. Therefore, if the morphology has no impact, the nanofibers will have higher catalytic activity. Moreover, for the same surface activity, the temperature should have the same influence on both formulations. In most of the chemical reactions, positive effect of the temperature on the reaction rates is a prevailing impression. Temperature is a measure of the kinetic energy of a system, so higher temperature implies higher average kinetic energy of the molecules and more collisions per unit time. This hypothesis might be true in the normal cases, however, the nanostructures usually have unexpected behaviors compared to the bulk scales.

In this study, the aforementioned facts have been investigated for the Ag-doped TiO2 nanophotocatalyst. Two nano-formulations have been utilized; nanofibers and nanoparticles. Silver-grafted titanium oxide nanofibers have been synthesized using the electrospinning of silver nitrate/titanium isopropoxide/poly(vinyl acetate) sol–gel. However, the nanoparticulate form has been obtained by calcination of a ground powder prepared from the same electrosyn sol–gels. In contrast with the aforementioned known influences, compared to nanoparticles, the nanofibers showed better performance as a photocatalyst catalyzing the photodegradation of rhodamine B and methylene blue dyes. Moreover, negative effect of the temperature on the photocatalytic degradation of the rhodamine B dye was observed when the Ag-doped TiO2 nanofibers were utilized as photocatalyst.

2. Experimental

2.1. Materials

Silver nitrate (99.8 assay), methylene blue dihydrate dye (95.0 assay), N,N-dimethylformamide (DMF, 99.5 assay), and rhodamine B dye were obtained from Showa, Co., Japan. Titanium (1V) isopropoxide (Ti(Iso), 98.0 assay) was purchased from Junsei Co. Ltd., Japan. Poly (vinyl acetate) (PVAc, MW = 500,000 g/mol) was obtained from Aldrich, USA. These materials were used without any further purification.

2.2. Preparation of nanofibers and nanoparticles of Ag/TiO2 composite

2.2.1. Nanofibers (NFs)

The electrospinning process was utilized to prepare the silver-grafted titania NFs. Typically, a sol–gel was prepared by mixing titanium isopropoxide (Ti(Iso)) and poly(vinyl acetate) (PVAc, 14 wt% in DMF) with a weight ratio of 2:3, respectively, and then few drops of acetic acid were added until the solution became transparent. The mixing process was carried out at 25 °C using magnetic stirrer rotating at 150 rpm. To prepare sol–gels containing different contents of silver, silver nitrate solutions in DMF were mixed with proper quantities of the prepared Ti(Iso)/PVAc solution to prepare final solutions containing 0.5, 1.0, 1.5, 2.0 and 2.5 wt% AgNO3. Afterward, these solutions were homogeneously mixed under stirring conditions for 10 min at 25 °C and moderate stirring speed. A high voltage power supply (CPS-60 K02V1, Chungpa EMT Co., Republic of Korea) was used as the source of the electric field. The sol–gel was supplied through a plastic syringe attached to a capillary tip. A copper wire originating from the positive electrode (anode) connected with a graphite pin was inserted into the sol–gel and the negative electrode (cathode) was attached to a metallic collector covered with polyethylene sheet. Briefly, the solution was electrospun at 6 kV and 15 cm working distance (the distance between the needle tip and the collector). The electrospinning process was carried out at 25 °C in 40% relative humidity atmosphere. The formed nanofiber mats were initially dried for 24 h at 80 °C in a vacuum and then calcined in air atmosphere at 700 °C for 1 h with a heating rate of 5 °C/min.

2.2.2. Nanoparticles

Silver nitrate/Ti(Iso)/PVAc solutions having the aforementioned compositions and preparation procedure were utilized to prepare nanoparticles containing different silver contents. The process parameters (temperature and stirring) were not changed. Instead of spinning, the solution was vacuously dried at 80 °C for 48 h to completely remove the solvent. The obtained solid materials were finely ground and sintered in air at 700 °C for 1 h.

2.3. Photocatalytic degradation

The photocatalytic degradation of two selected dyes; methylene blue and rhodamine B in the presence of Ag–TiO2 nanofibers and nanoparticles was carried out in a simple photo reactor. The reactor was made of glass (1000 ml capacity, 23 cm height and 15 cm diameter), covered with aluminum foil, and equipped with ultra-violet lamp emitting radiations at 365 nm. The initial dye solution and the photocatalyst were placed in the reactor and continuously stirred to ensure proper mixing during the photocatalytic reaction. Typically, 100 ml of dye solution (10 ppm, concentration) and 50 mg of catalyst were used. At specific time intervals, a 2 ml sample was withdrawn from the reactor and centrifuged to separate the residual catalyst, and then the absorbance intensity was measured at 664 and 554 nm for methylene blue and rhodamine B dyes, respectively.

2.4. Characterization

Surface morphology of nanofibers was studied by JEOL JSM-5900 scanning electron microscope (JEOL Ltd., Japan) and field-emission scanning electron microscope (FESEM, Hitachi S-7400, Japan). The phase and crystallinity were characterized by using Rigaku X-ray diffractometer (Rigaku Co., Japan) with Cu Kα (λ = 1.54056 Å) radiation over a range of 20 angles from 20° to 100°. High resolution image and selected area electron diffraction pattern were observed by JEOL JEM-2200FS transmission electron microscope (TEM) (JEOL Ltd., Japan). The concentration of the dyes during the photodegradation study was investigated by spectroscopic analysis using HP 8453 UV–visible spectroscopy system (Germany). The spectra obtained were analyzed by HP ChemiStation software 5890 series.

3. Results and discussion

3.1. The photocatalyst characterization

The polymer is an essential constituent in sol–gels to achieve the electrospinning process [19,22–24]. Metal alkoxides are the best candidates to form the gel structure due to their affinity to
hydrolysis and condensation in the polymer matrix. Because of the well polycondensation property [25,26], titanium isopropoxide is a famous precursor to prepare TiO2 nanofibers by using the electrospinning process and PVAc as a gelling polymer [27]. Addition of silver nitrate does not affect the nanofibrous morphology [5]. Fig. 1A displays the obtained PVAc/Ti(Iso)/AgNO3 (the later was 2.0 wt% in the electrospun solution) nanofibers. As shown, good morphology was obtained. It is noteworthy mentioning that all the formulations produced good morphology nanofibers; only slight decrease in the average fiber diameter with increasing the silver nitrate content was observed due to increase the electrical conductivity of the electrospun solutions. Calcination did not affect the nanofibrous morphology for all formulations. Fig. 1B represents the SEM image of the obtained powder from calcination of the electrospun mat containing 2.0 wt% silver nitrate. As shown, good nanofibers were obtained. Increase the roughness of the outer surface with increasing the silver nitrate content in the original electrospun sol–gel was a noticeable observation. Fig. 1C and D displays the FE SEM images of the pristine and Ag-containing (AgNO3 = 2.0 wt%) TiO2 nanofibers, respectively. Big difference between the surfaces of the investigated nanofibers can be observed. It is noteworthy mentioning that the surface roughness was dependent on the silver content, moreover increase the silver nitrate content more than the maximum value used in this study (i.e. 2.5 wt%) led to destroy the nanofibrous morphology and produce nanorods instead. Concerning the nanoparticulate shape, addition of silver nitrate improves the spherical morphology of the nanoparticles as shown in Fig. 1E and F which demonstrate the SEM images of the pristine and Ag-doped (2.0 wt%) TiO2 nanoparticles.

To properly investigate the effect of addition of silver nitrate on the surface of the silver-doped nanofibers, the surface area has been measured by using Brunauer–Emmett–Teller (BET) technique (Micromeritics, Norcross, GA). The obtained results indicated that the average surface area of the silver-free nanofibers was about 21.3102 ± 0.1351 m2/g, while, it was 38.8100 ± 0.1324 m2/g for the nanofibers obtained from calcination of silver nitrate (2 wt%) Ti(Iso)/PVAc electrospun nanofiber mats. As can be concluded from these results, the surface area of the silver containing nanofibers was duplicated compared to the pristine ones which strongly enhance the photocatalytic activity. For the nanoparticles, it is clear from the SEM images that addition of silver has negative influence on the surface area as the average diameter decreases with silver addition (Fig. 1E and F).

XRD is a reliable and widespread identification technique especially for crystalline materials. Fig. 2 represents the XRD pattern of the nanofibers obtained from two sol–gels, Ti(Iso)/PVAc and silver nitrate (2.0 wt%)/Ti(Iso)/PVAc. As shown in both spectra, the results confirm formation of pure anatase titanium dioxide. The
strong diffraction peaks at 2θ values of 25.09°, 37.65°, 38.44°, 47.89°, 53.89°, 55.07°, 62.40°, 68.70°, 70.04°, and 75.00° correspond to the crystal planes (1 0 1), (0 0 4), (1 1 2), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (2 2 0), (2 2 0), and (2 1 5), respectively indicate formation of anatase titanium dioxide [JCPDS card no. 21-1272]. In the case of the nanofibers obtained from calcination of silver nitrate/Ti(Iso)/PVAc mats (Fig. 2, spectra A), in addition to the titanium dioxide peaks, extra peaks at 2θ values of 38.11°, 44.29°, 64.43° and 77.48° corresponding to the crystal planes (1 1 1), (2 0 0), (2 2 0), and (3 1 1), respectively confirm presence of silver metal [JCPDS card no. 04-0783]. To make it easy, in Fig. 2, we have marked the peaks corresponding to titanium oxide and silver as A and S, respectively. It is noteworthy to mention that the morphology did not affect the XRD data (i.e. the same results have been obtained for the nanoparticles). Therefore, the XRD pattern of the nanoparticles was not added to simplify and clarify the figure.

Transmission electron microscope analysis is used to investigate the crystal structure. Fig. 3 shows the HR TEM of the obtained Ag-doped TiO₂ nanofibers (A) and nanoparticles (B). As shown in these figures, there are some black dots in both formulations which can be considered as the Ag nanoparticles as these dots have different crystal structures compared to the TiO₂ matrices. Both formulations have good crystallinity as shown in Fig. 3C and D which represents the SAED patterns of the Ag-doped TiO₂ nanofibers and nanoparticles, respectively. Moreover, the fast Fourier transform (FFT) images for both formulations reveal good crystallinity as shown in the corresponding insets.

3.2. Photodegradation of the organic dyes

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalyzed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis, the photocatalytic activity depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (hydroxyl radicals: *OH) able to undergo secondary reactions. Its comprehension has been made possible ever since the discovery of water electrolysis by means of the titanium dioxide.

Fig. 2. XRD results for the obtained powder after calcination of PVAc/Ti(Iso) and PVAc/Ti(Iso)/AgNO₃ (AgNO₃ = 0.2) electrosynon nanofibers in air at 700 °C.

Fig. 3. HR-TEM image of the Ag-doped TiO₂ nanofibers (A), nanoparticles (B) and SAED patterns of the marked areas (C) and (D). The insets show the FFT images of the marked areas.

Fig. 4. Effect of temperature on the degradation rate of rhodamine B dye using Ag-doped TiO₂ nanoparticles having 0.5 wt% AgNO₃ under UV irradiation.
Figs. 4–8 represent the photodegradation of rhodamine B using Ag-doped TiO$_2$ nanoparticles obtained from sol–gels contain 0.5, 1.0, 1.5, 2.0 and 2.5 wt% AgNO$_3$, respectively at different temperatures (5, 15, 25, 45 and 55 °C). As shown in these figures, increase the silver content in the doped nanoparticles enhances the photoactivity of the utilized photocatalyst. As it is known, increase the reaction temperature improves the photodegradation efficiency. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react (energy greater than activation energy $E > E_a$) is significantly higher. Accordingly, the dye photodegradation modified linearly with temperature increase. The best temperature was found to be 55 °C, at this temperature the maximum decolorization efficiencies at the utilized reaction time (3 h) were 65%, 74%, 84%, 86% and 100% for the photocatalyst obtained from sol–gels contain 0.5, 1.0, 1.5, 2.0 and 2.5 wt% AgNO$_3$, respectively. It is noteworthy mentioning that the investigated photocatalyst has good performance only under the UV irradiation as normal light has no impact as shown in Fig. 8.

Table 1 shows the rate of the rhodamine B photodegradation (mg/min) at different temperatures and silver contents. As shown in the table, the maximum rate is not always obtained at the maximum temperature; it depends on the silver content. At the lowest silver content (i.e., 0.5 wt%), the highest rate was obtained at 15 °C. Increasing the silver content shifts the maximum rate to be at 25 °C for the samples obtained from sol–gels having 1.0 and 1.5 wt% silver nitrate. However, at the higher silver contents the best rate was obtained at 45 °C. Overall, the maximum degradation rate is corresponding to the samples obtained from the sol–gels having 1.0 and 1.5 wt% silver nitrate at the room temperature (0.0356 mg/min). As aforementioned, besides enhancing the activation energy, increase the temperature leads to increase the kinetic energy of the dyes molecules which modifies the collisions with the catalyst surface. If the catalyst surface is very active so numerous free radicals will be present in the thin film surrounding the catalyst nanoparticles, so fast cracking reactions of the dye molecules will take place, otherwise the molecules will escape without degradation. Therefore, for the low silver content NPs, the surface is not so active so relatively low temperature (15 °C) is preferred to provide suitable time for dye molecules to react with the available $OH$ radicals. Increase the temperature leads to escape the molecules. More increase in the silver content results in more activation of the NPs surfaces, so low contact time is enough to degrade the dye molecules in the thin layer surrounding the catalyst NPs. Accordingly, the maximum degradation rates were obtained at 45 °C for the samples having high silver contents (last two columns in Table 1). At 55 °C, the kinetic energy is high enough to liberate the dye molecules from
the active zones before degradation so low degradation rate was obtained. However, the number of the degraded dye molecules is high in the beginning of the reaction (the first 10 min) which makes the quantitative degradation is more at 55 °C. For instance after 10 min, at 55 °C, the eliminated dyes were 35%, 38% and 55% for the nanoparticles obtained from sol–gels containing 0.5, 1.5, and 2.5 wt% silver nitrate, respectively. It is noteworthy to mention that the fast initial degradation in the first 10 min (Figs. 4–8) made the total elimination of the dyes linearly dependent on the temperature. However, after this initial declination, the photodegradation rate becomes temperature independent as shown in Table 1.

In contrast to the nanoparticles, influence of temperature was different in case of Ag-doped TiO2 nanofibers. Figs. 9–13 represent the photodegradation of rhodamine B using Ag-doped TiO2 nanofibers obtained from electrospun nanofiber mats contain 0.5, 1.0, 1.5, 2.0 and 2.5 wt% AgNO3, respectively at different temperatures. As shown in these figures, contrary to the nanoparticulate morphology, the photodegradation efficiency was temperature-dependent only at low silver content (0.5 wt%, Fig. 9) as the best degradation was obtained at the highest temperature. Moreover, the amount of the eliminated dyes was gradually and regularly increases with the temperature increase. For the nanofibers obtained from electrospun mats having 1.0 wt% silver nitrate, the optimum reaction temperature was 45 °C as shown in Fig. 10. However, for the remaining formulations the optimum temperature was 25 °C; Figs. 11–13. For all formulations, 5 °C reaction temperature is the worst conditions as the lowest degradation was

### Table 1

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<th>Temperature (°C)</th>
<th>AgNO3 content (wt%)</th>
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<th>1.5</th>
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<td>1885.29</td>
<td>1989.64</td>
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Fig. 9. Effect of temperature on the degradation rate of rhodamine B dye using Ag-doped TiO2 nanoparticles having 0.5 wt% AgNO3 under UV irradiation.

Fig. 10. Effect of temperature on the degradation rate of rhodamine B dye using Ag-doped TiO2 nanoparticles having 1.0 wt% AgNO3 under UV irradiation.

Fig. 11. Effect of temperature on the degradation rate of rhodamine B dye using Ag-doped TiO2 nanoparticles having 1.5 wt% AgNO3 under UV irradiation.

Fig. 12. Effect of temperature on the degradation rate of rhodamine B dye using Ag-doped TiO2 nanoparticles having 2.0 wt% AgNO3 under UV irradiation.
obtained at this temperature. Moreover, contrary to the nanoparticulate morphology, starting from silver nitrate content of 1.0 wt% in the electrospun nanofibers mats, the photodegradation cannot be mathematically correlated with the reaction temperatures as shown in Figs. 10–13. These obtained results can be explained by the higher activity of the nanofibrous Ag-doped TiO$_2$ compared to the nanoparticulate morphology especially at high silver contents. Beside the desorption process and kinetic energy, it is possible also that the temperature affects the e–h pairs transfer and lifetime.

Fig. 14 represents a conceptual illustration to explain the influence of the temperature on the photodegradation of the rhodamine B molecules using Ag-doped TiO$_2$ nanoparticles and nanofibers. In case of nanoparticles, the surface activity is not high so increase the temperature has the normal impact on the chemical reactions and enhances the degradation process in general by modifying the activation energy. However, in case of the nanofibers having high silver content, the surface is very active so instant degradation for the dye molecules takes place at the thin film surrounding the nanofibers. Therefore, increase the temperature which leads to increase the molecules kinetic energy has positive impact in the beginning as it helps to move the molecules to the active zones. However, more increase in the temperature leads to produce kinetic energy able to move away the dye molecules from the active zones before achieving the degradation process. Therefore, for the nanofibers obtained from electrospun mats having silver nitrate more than 1.5 wt% the optimum temperature is 25 °C followed by 45 °C and then 55 °C which means inverse relationship between the photodegradation and the temperature due to increase the kinetic energy of the molecules. In summary, in case of nanofibers, the temperature affects the photodegradation process from the kinetic energy point of view. However, in case of nanoparticles, beside the kinetic energy, temperature can enhance the activation energy which improves the photodegradation process.

Based on the introduced hypothesis; the initial rate should show a positive temperature effect over the nanofibers with high silver content. However, some results (Fig. 13) do not match this expected behavior because the experimental plan was established to detect the first concentration after 10 min. Because the surface is very active, it is believed that if the first samples, in case of nanofibers, were drawn after very short time (e.g. 2 min) the initial rate will be found temperature dependent.

Fig. 15 displays the photodegradation of the methylene blue dye using Ag-doped nanoparticles (A) and nanofibers (B) at the optimum temperatures (i.e. 55 and 25 °C, respectively). As shown in the figure, the nanofibers have distinct performance compared with the nanoparticles at all silver contents. As shown in the figure, 92% from the dye was degraded in 10 min when Ag-doped TiO$_2$ nanofibers obtained from electrospun mats containing 2.0 wt% silver nitrate were used as photocatalyst. As aforementioned in the introduction section, silver-doping is a known strategy to enhance
the photocatalytic activity of the titanium oxide nanostructure. Therefore, the photocatalytic activity of the both utilized formulations was strongly enhanced upon silver addition as shown in all the obtained results.

The results obtained in Fig. 15 supports the aforementioned hypothesis about the strong activity of the nanoparticles surfaces compared to the nanoparticles. Therefore, for the same silver content, distinct difference in the photodegradation performance was obtained as shown in all results. A proposed explanation for this finding can be as follow: as the photodegradation process mainly bases on electrons transfer through the photocatalyst so the structure providing high surface to volume ratio is expected to have better performance because it supplies good electron mobility. Mathematically, it is known that the particulate shape (sphere) has the lowest surface to volume ratio. Therefore, the nanofibrous shape provides more space for the electrons which reflects higher activity compared to the nanoparticles.

4. Conclusion

Ag-doped TiO₂ nanofibers can be prepared by calcination of electrosprun nanofiber mats obtained from electrospinning of titanium isoproxide, silver nitrate and poly(vinyl acetate) sol–gels. Also, drying, grinding and calcination of the same sol–gels lead to produce Ag-doped TiO₂ nanoparticles. The temperature has positive impact on the photodegradation when the photocatalyst is exploited in the form of nanoparticles due to modification of the kinetic and the activation energies. However, in case of the nanofibrous morphology, the temperature has negative impact due to the super activity of the surface compared to the nanoparticles. Increase the temperature leads to enhance the kinetic energy of the dyes molecules which leads to escape the molecules from the active zones surrounding the nanoparticles. Overall, this study strongly recommends utilizing using the photocatalyst in the form of nanofibers at room temperature as the maximum degradation can be obtained at these conditions.

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