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Research Article

Ensuring Photocatalyst Properties on Cellulosic Fabric by Using Citric Acid Modified with TiO_2 Degussa P25 Nanoparticles

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ABSTRACT

Citric acid, which is a type of polycarboxylic acid, is environmentally friendly, and non-harmful and it can be used as a cross-linker. Titanium dioxide (TiO_2) nanoparticle is a catalyst that provides many properties for textile products with its large surface area. Present study, a mixture was prepared with different concentrations of citric acid and commercial TiO_2 Degussa P25 nanopowder suspensions. Two different curing temperatures (120°C and 140°C) were applied to the cotton fabrics in the pad-dry-cure method. The adhesion of the chemicals to the fiber surface was confirmed by scanning electron microscopy (SEM) and Fourier transform infrared spectrophotometer (FT/IR) analysis. The yellowing effect caused by citric acid on cotton fabrics was eliminated with white TiO_2 nanoparticles. Methylene blue was used for staining the samples. Color analyses were performed with a spectrophotometer to determine photocatalytic properties of the samples. It was determined that the samples treated with a mixture of 30 g/L citric acid and TiO_2 suspensions were the most discolored samples after exposure to solar light. The photocatalyst properties of the samples were further improved by removing the aggregation of TiO_2 NPs on the fiber surface with the washing procedure.

1. Introduction

Nano-sized titanium dioxide (TiO_2 NP) particles have high chemical stability and they are frequently used in many areas due to their functional properties such as photocatalyst, UV blocker, antibacterial activity, etc. Photocatalysts are the substances that activate the catalyst by light exposure. In photocatalytic reactions, when a photocatalyst is exposed to photon light, it becomes active and generates highly active radicals [1]. The resulting radicals and ions interact with the organic molecule and break it down. As a result of this decomposition, carbon dioxide and water are formed. Titanium dioxide (TiO_2) is a good photocatalyst as a semiconductor with a band gap ranging from 3.0 to 3.2 eV. TiO_2 can be formed as anatase, rutile, and brookite phases, and these phases have different crystal forms and chemical stabilities. These structures of titanium dioxide can be found in nature [2]. There is also a commercial titanium dioxide nanoparticle called Degussa P25, which is a mixture of anatase and rutile forms in a 3:1 volumetric ratio [3]. TiO_2 NPs can be produced by different methods such as sol-gel, chemical vapor deposition, and uniform precipitation [4]. The most widely used method for the impregnation of TiO_2 NPs on textile surfaces is the pad-dry-cure method [5]. Citric acid (2-hydroxy-1,2,3-tricarboxylic acid) is one of the low-cost, easily accessible chemicals used to bind the functional substance to the textile surfaces. Citric acid is a polycarboxylic acid that can interact with the hydroxyl groups in the structure of TiO_2 nanoparticles and thus can be modified with applications [6]. In a study, the effect of the surface chemistry of citric acid on TiO_2 nanoparticles in anatase form was examined. It was emphasized that the acidic pH

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environment was important for adhesion and making a stable suspension but citric acid could cause an aggregation in an acidic pH environment [7]. In a study, TiO_2 NP anatase phase was impregnated in cotton-polyester blended fabrics by pad-dry-cure method using sodium hydrophosphite and citric acid mixtures in different concentrations [8].

In the results, it was determined that 30 g/L concentration of citric acid and 0.5% TiO_2 suspension were suitable mixture ratios and this mixture gave the material many properties such as self-cleaning and UV blocker. In another study, TiO_2 NPs were obtained by sol-gel method. In order to bind the produced TiO_2 NPs to cotton fabrics, citric acid solutions with different concentrations of 25, 30, 35, and 40 g/L (by also adding sodium hypophosphite) were prepared [9]. The prepared solutions were transferred to the fabrics by the pad-dry-cure method. The samples were then stained and exposed to UV light. Color differences before and after exposure were measured and calculated by a spectrophotometer. It was observed that TiO_2 NPs bonded with 25% citric acid solution provide the best self-cleaning feature on fabrics. In another study; TiO_2 was used as a catalyst and application was made to cotton fabrics at different concentrations, at different curing temperatures, at different times, and also at different citric acid concentrations [10]. The authors stated that the crease recovery of the fabric increased as the curing temperature, curing time, and citric acid concentration.

There is no study examining the effect of Degussa P25, which is stated to be one of the best photocatalysts than other pure TiO_2 phases, on cotton fabrics together with citric acid in the literature [11]. Citric acid was preferred as a crosslinker due to its environmentally friendly and harmless to human health. It was intended to determine the effect of different citric acid concentrations and different temperatures in the applications on photocatalyst activities and optical properties of cotton fabrics and also to investigate washing durability of the treatments. It was determined that the use of TiO_2 nanoparticles increased the whiteness value of the samples despite citric acid, and photocatalytic properties were achieved with a mixture of 30 g/L citric acid and TiO_2 suspension.

2. Materials and Methods

2.1. Material

100% cotton, woven, and undyed fabric was used for the study, and the properties of the fabric are presented in Table 1. The chemicals used in the study; Degussa P25 titanium (IV) oxide (21 µm, ≥99.5%, Sigma Aldrich), citric acid ($HOC(COOH)(CH_2COOH)_2$≥%99.5), sodium hyroxide (NaOH, ≥ 97%, Tekkim), Ethanol (96%, Tekkim) methylene blue (AFG Bioscience).

Table 1. Properties of the cotton fabric

Fiber Type	100% Cotton
Weight in Grams	240,7 g/m^2
Warp Yarn - Density	Ne16 - 44 thread/cm
Weft Yarn - Density	Ne12,5 - 20 thread/cm
Pretreatment Processes	Bleached, Washed, Dried and Singed

2.2. Methods

2.2.1. Modifying TiO_2 NP suspension and the treatment process

TiO_2 NP was weighed at the rate of 10% according to the fabric weight and mixed with ethanol:water at 1:9 volumetric ratio which is the ideal mixing ratio for the stability of the suspension [12]. Then, citric acid mixtures at different concentrations (10, 20, and 30 g/L) were prepared in distilled water and added to TiO_2 NP suspensions. TiO_2 NP and citric acid suspensions were mixed in a 1:1 volumetric ratio. In order to homogenize these mixtures, the process was applied in an ultrasonic bath (J. P. Selecta) at a frequency of 20 kHz for an hour. The pH level of the different mixtures was measured between 3.3-3.7.

The cotton fabric samples were first treated with 1% NaOH solution and dried at 100 °C. Afterward, the samples were kept in a small vat containing TiO_2 NP and citric acid mixtures for 30 seconds and then they were passed between rollers with 90% pick-up. This process was repeated twice. After the process was completed, all samples were dried at 100 °C degree. For the

curing process; in order to see the effect of the applied temperature on the adhesion of the modified TiO_2 NP to the fibers, some of the samples were cured at 120 °C degrees and some of them were cured at 140 °C degrees for 2 min (Scheme 1).

2.2.2. Characterization

In the study, some characterization tests were carried out to verify the processes applied to the samples. In order to examine the fiber surface morphologies of the samples, images were obtained with x5000 magnification using scanning electron microscopy (Scanning Electronic Microscope, FEI Quanta 650 Field Emission). Fourier transform infrared spectroscopy (JASCO FT/IR 6800) analysis was applied for the characterization of the samples by chemical analytical method.

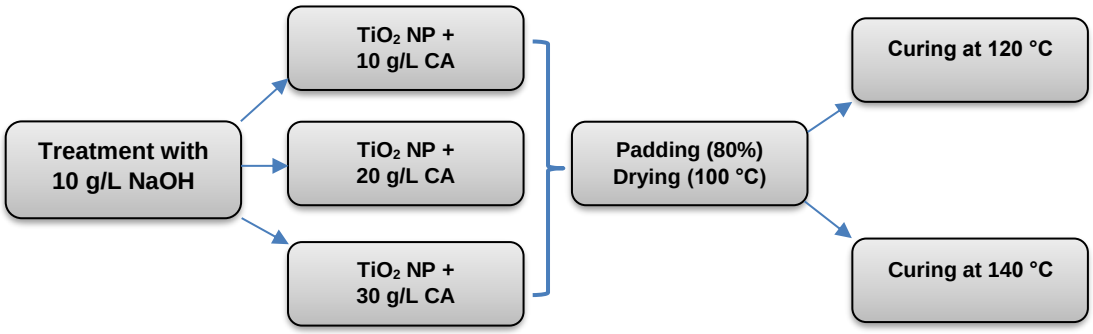
2.2.3. Washing durability

The permanence of the applied treatments after washing was determined by applying the ISO 105-C06:2010 standard. In accordance with the standard, the samples were washed in a washing machine at 40°C for 30 minutes by adding 4 g/L ECE detergent and 1 g/L sodium perborate into 150 mL of water in a tube. After washing, the samples were rinsed with distilled water (40 °C) and dried at room temperature. Treated samples were subjected to the performance tests after washing.

2.2.4. Photocatalytic and color measurements

Methylene blue (MB) is an aromatic heterocyclic basic dye and its chemical formula is $C_{16}H_{18}ClN_3S$ [13]. It can also be used in the treatment of many diseases [14]. In the study, the effect of functional finishing treatments applied to cotton samples on the degradation performance of this dye after light exposure was analyzed by color measurements. 0.02 g/L MB solution was prepared using distilled water to stain the samples with this dye. The cotton fabrics which were cut into small pieces were dipped in this solution for 30 sec.

Color measurements were carried out after the stained samples were dried. Color measurements were done with a spectrophotometer (Minolta CM 3600) at wavelengths between 400-700 nm, with an observer angle of 10°. Measurements were made in specular component included (SCI) mode, where the angle of reflection is equal to the angle of incidence of the light. Color analyses were performed with RealColor1.3® software. The effects of the chemical treatments on the whiteness (CIE W*) and yellowness (ASTM D1925-70 YI) values of the samples, and the color changes of the samples stained with methylene blue after exposure to solar light were calculated. Treated and untreated samples stained with methylene blue were exposed to solar light directly (between 9:30-11:30 am, May, Adana, Turkey) for periods of 2, 4, 6, and 8 hours.



Scheme 1. Chemical treatments applied to the samples

The average UV radiation energy was determined as 23.01 MJ/m^2 (Eppley, Adana) on the days when the samples were exposed to the sun. At the end of each period, color measurements were made and the total color difference (ΔE) (I) according to the initial color

of the samples and lightness (L*) values were calculated. These analyses were also applied to the washed samples and the washing durability of the process was determined.

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{½} \quad (1)$$

3. Results and Discussion

3.1. SEM and FT/IR analysis

The images of the untreated sample and the treated samples obtained by scanning electron microscope (SEM) with x5000 magnification and FT/IR graphs are presented in Figure 1. When the fiber surface morphology of the untreated sample is compared with the treated ones, it is determined that the applied treatment changed the fiber surface. The applied chemicals were deposited on the fiber's surface. It is seen that citric acid, which is a carboxylic acid, can be chemically bonded to cotton fibers [15]. As the citric acid concentration increased in the TiO_2 NP suspension, the fiber surface became rougher and aggregation occurred in some regions. Citric acid allowed TiO_2 nanoparticles to adhere to the fiber surface. It is observed that the samples treated with 20 and 30 g/L concentrations of citric acid and cured at 140°C degrees and regional tear-like structures were formed on the fiber surface. It can be claimed that the acidic environment and high temperature might have damaged the cellulosic fiber structure.

Fourier transform infrared spectra (FT/IR) are performed to determine characteristic functional groups. When the graphs are examined, it is seen that the absorption peaks of the samples were similar to each other. The peaks around 3328 cm^{-1} are thought to originate from the free hydroxyl groups resulting from the O-H stretching vibration and the O-H band of the carboxylic acid attached to the hydroxyl groups of the cellulosic fiber surface [16]. When compared with the untreated sample, citric acid, a type of carboxylic acid, did not significantly contribute to this absorption peak. 2893-2898 cm^{-1}, which is one of the major absorption peaks in the graphs, is from the C-H band stretch; 1624-1645 cm^{-1} peaks are due to the moisture-induced H2O in the structure of the fibers [17]. The most striking difference between the graphs was that some samples treated with citric acid with a concentration of 20 and 30 g/L showed absorption peaks around 1713-1714 cm^{-1}. This is due to the C=O and ester carbonyl stretching of the polycarboxylic acid [10]. In addition, it may also be caused by the attachment of C=O group of citric acid to hydroxyl group (O-H) of TiO_2 nanoparticles [6, 18]. It was concluded that the interactions (modification) occurred on the fiber surfaces by using citric acid at these concentrations (20 and 30 g/L) in the applications. The peaks between 1424-1105 cm^{-1} and 659-456 cm^{-1} are the fingerprint region, and there is no significant difference between the samples in this region.

3.2. Color measurements

3.2.1. Whiteness and yellowness index

The graphs of the whiteness and yellowness index values of the samples are illustrated in Figure 2. It is accepted that the surface reflected the light more and its whiteness increased as the CIE W value, which expresses the whiteness index, increased. In light of this information, it was observed that the whiteness degrees of all of the treated samples were higher than the untreated control sample. TiO_2 Degussa P25 suspensions containing different concentrations of citric acid increased the whiteness of the samples. This can be explained by the fact that TiO_2, a white pigment deposited on the cotton samples, caused them to reflect light more thus ensuring the sample to be perceived as whiter. The highest whiteness value belongs to the sample treated with 10 g/L citric acid-TiO_2 mixture and then cured at 120°C. The increase in the citric acid concentration applied to the treated samples also had a decrease in the whiteness values of the samples. In addition, when a comparison is made between the binary groups at the same concentration, it is noteworthy that the increase in the curing temperature caused the whiteness values of the samples to be lower. It is a result that has been also determined in a previous study that citric acid decreases the whiteness of cotton fabric with increasing curing temperature [19].

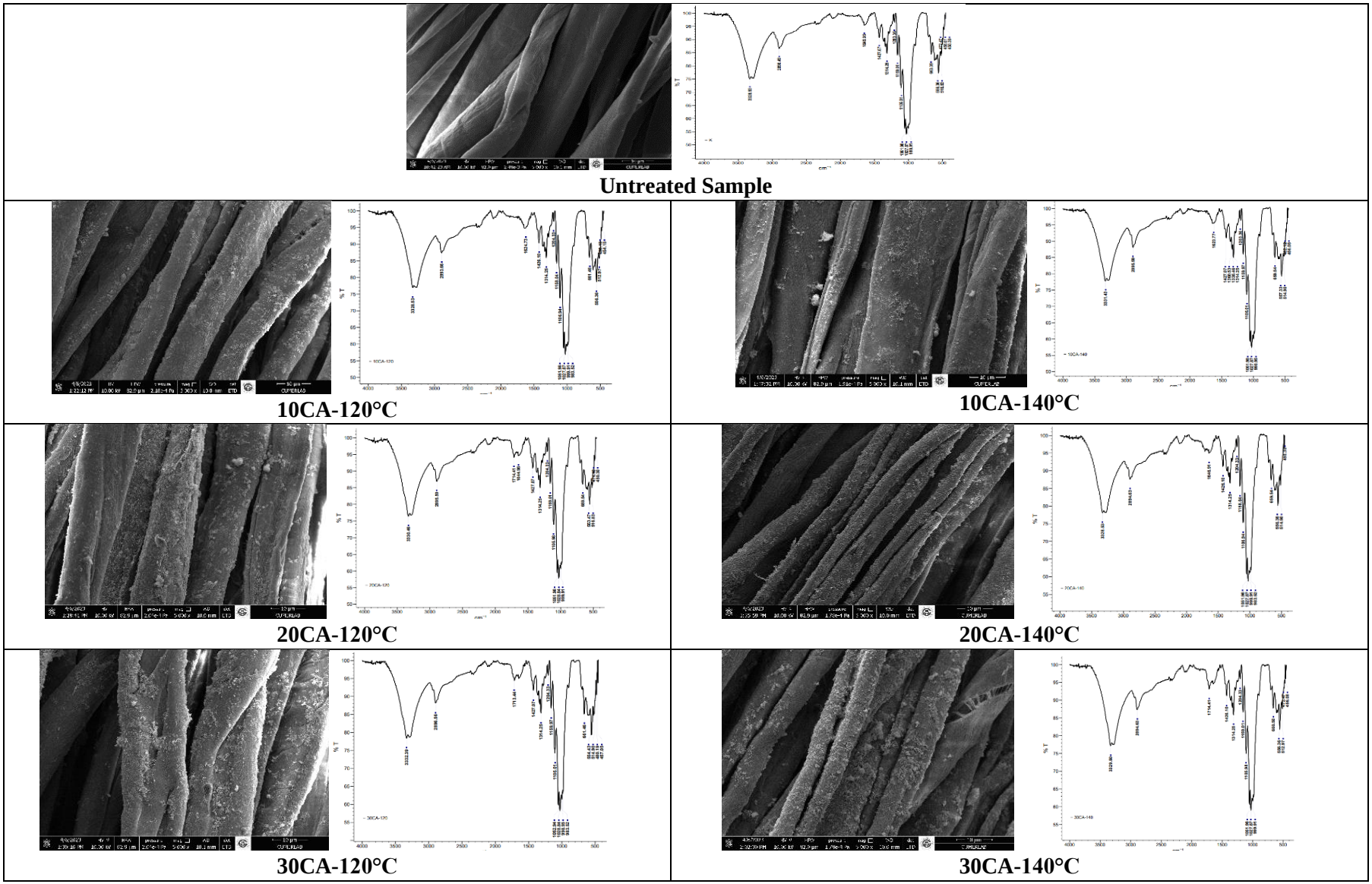


Figure 1. SEM images and FT/IR graphs of the cotton samples

The yellowness index value expresses the degree of shift towards yellow from the desired reference whiteness value. According to the ASTM D1925-70 YI results, the yellowness value of almost all samples decreased after chemical treatments. The yellowness index was lower in samples treated at 120°C, which is the lower curing temperature than in samples treated at 140°C. As the curing temperature increased, the whiteness of the samples decreased and the yellowness value increased. Unsaturated polycarboxylic acid structures of citric acid can cause yellowing [19, 20]. Titanium dioxide nanopowders applied to fabrics were able to eliminate this negative effect of citric acid causing yellowness in cotton fabrics. In another study, treatment with H_2O_2 solution was applied to reduce the yellowness effect of citric acid and the yellowness index could be reduced by breaking the C=C bond of the carboxylic acid [21]. It was also determined in another study that the increasing concentration of TiO_2 NP was directly proportional to the increase in the whiteness rate and the decrease in the yellowness degree in cotton fabrics [22].

3.2.2. Photocatalytic measurements

In Figure 3, the effect of different treatments on the total color difference (ΔE) values of the cotton samples according to changing solar light exposure time is presented. While evaluating; it is assumed that as the ΔE value decreased, the structure of MB (methylene blue) deteriorated and the samples came closer to the initial white color before staining. As expected, solar light caused a color change in all samples.

MB underwent oxidation after light exposure and the structure of the complex molecules was disrupted [13, 23]. All of the treated samples have a high tendency to return to their initial color after 2 hours of solar exposure, while this tendency is lower for the untreated control sample. In other words, TiO_2 NPs attached to the fibers with citric acid increased the rate of degradation of the dye. Degradation of MB is expected to be slow in visible light without a catalyst such as TiO_2 [13, 24]. Also, an acidic environment is a suitable condition for the photodegradation of MB by TiO_2 NP [25]. According to the color analysis made in this period, the applications of TiO_2 NP with 30 g/L citric acid at 140°C were the processes that brought the cotton samples closer to their initial color, the ΔE value of this sample is '3.32', while the sample treated at 120°C this value was '3.56'.

The ΔE values of the samples treated with 20 g/L citric acid at 120 and 140 °C were '3.88' and '3.47', respectively. These results are very close to each other. This can be explained by the fact that even though the adsorption of TiO_2 Degussa P25 nanoparticles to the fiber is increased with higher citric acid concentrations, the surface area decreases due to the aggregation of nanoparticles and the photocatalyst property is limited [8].

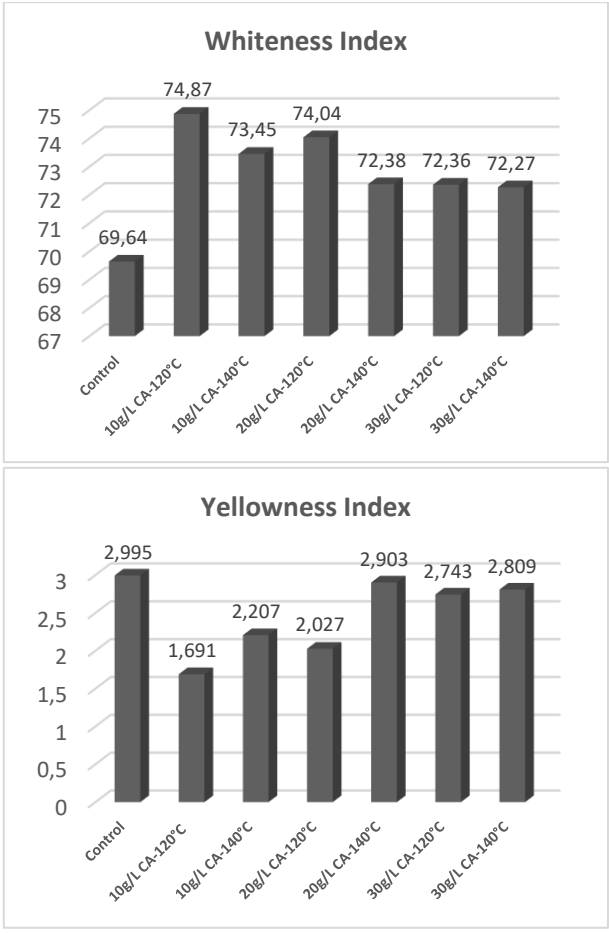


Figure 2. Whiteness and Yellowness Index of the untreated and treated samples

Besides, it was determined that the increase of twenty degrees of curing temperature did not have a significant effect on the photocatalyst properties of the samples.

In another study, it was also determined that the curing temperature did not affect the photocatalyst properties of the cotton samples,

using TiO_2 (in an undetermined phase) together with citric acid [26]. As the curing temperature increases, carboxylic acids are consummated and their esterification with cellulose is accelerated [27]. As the temperature increases, the reaction approaches the equilibrium state. The effect of the higher curing temperature, and the acceleration of the displacement reaction of the -OH groups in the structure of the carboxylic acid with the -OR group did not have a great effect on the photocatalyst activity of TiO_2 NPs. However, it is possible to observe this more clearly by working with a higher curing temperature. In Figure 4, the lightness (L*) values of the samples are presented after staining with MB and after 2, 4, 6, and 8-hour periods, respectively. As expected, the color of the samples became lighter as the exposure time to light increased. The effect of the applied treatments is remarkable even after the measurements at the end of the 2nd hour. The variation of the lightness values occurring in the colors of the samples according to time shows differences in each of them. The lightness values that change according to the solar exposure show a parallel change with the ΔE values in Figure 2. This shows that the increase in the L* value of the samples made it closer to the initial color values of the samples and increased the total color difference (ΔE) according to the formula (I).

In the measurements made at the end of the eighth hour, it is seen that the color lightness of the samples increased as the citric acid concentration increased and the lightness value of the control samples was the lowest. However, the L* values of the samples treated with 20 and 30 g/L citric acid are very close to each other. Different curing temperatures applied in the same citric acid concentration groups had almost no significant effect on the L* values of the samples.

3.2.3. Washing durability

Figure 5 shows the total color difference values (ΔE) between the unstained treated sample and the treated, washed, stained samples that were exposed to solar light for eight hours.

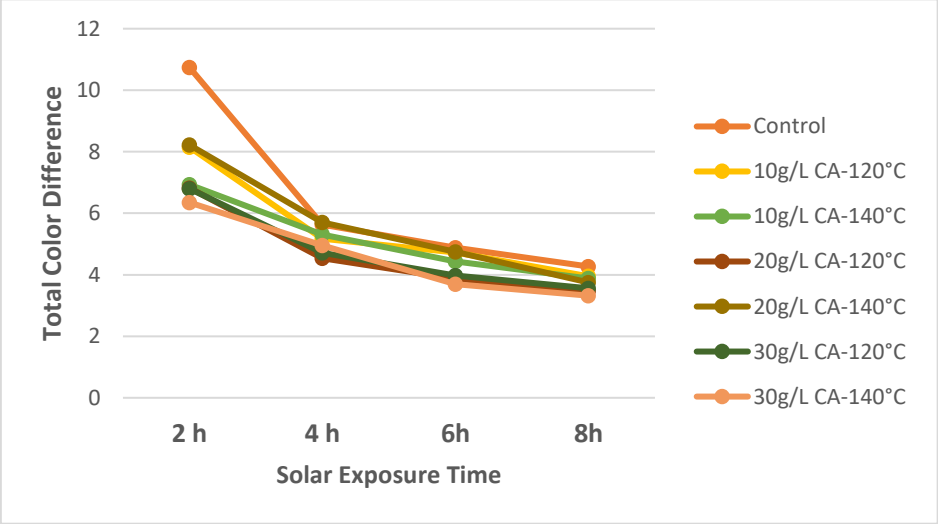


Figure 3. Effect of solar exposure time on the total color difference of the untreated and treated samples

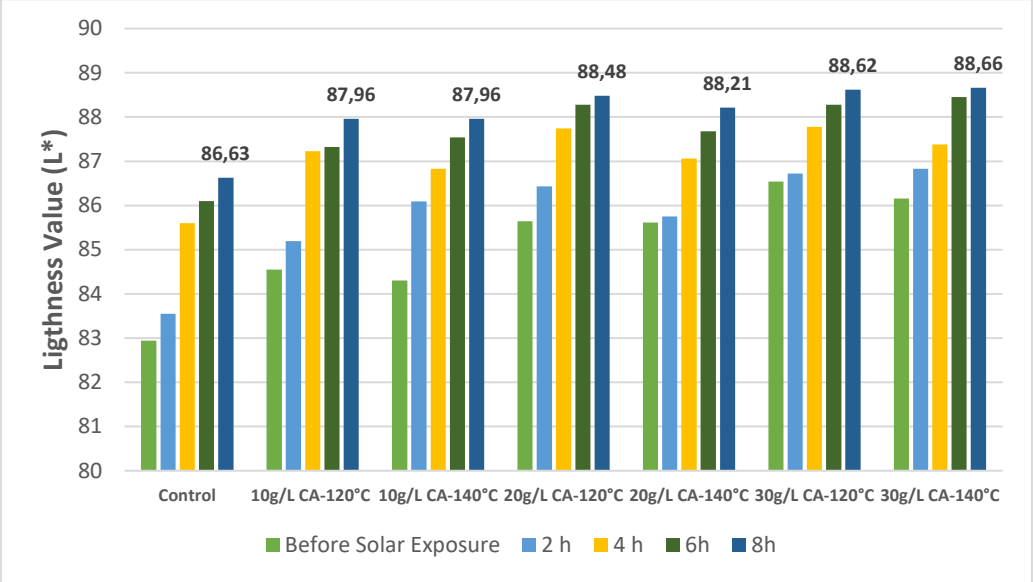


Figure 4. The lightness values of the samples before and after solar exposure at different periods

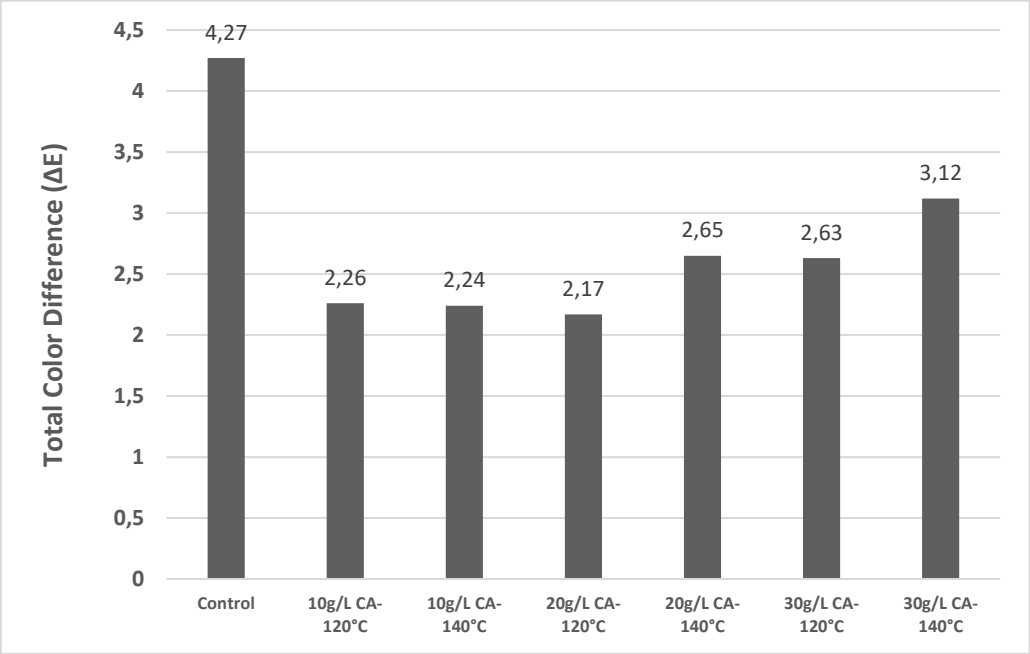


Figure 5. Total color difference values of untreated and washed treated samples according to their first color before and after eight hours

For comparison, the ΔE values measured at the eighth hour of the untreated sample are also included in the graph. It can be clearly seen that all of the treated samples were closer to their initial color than the untreated sample. It can be stated that TiO_2 Degussa P25 NPs attached to the fiber surface with citric acid showed their permanence against washing conditions. In other previous studies, it has been observed that citric acid adheres tightly to cotton surfaces and maintains its permanence even after repeated washing [28]. In fact, after this washing process, the ability of the samples to return to their original colors with solar light increased even more (compared to the Figure 3 results). This revealed the necessity of a post-washing process for cotton products after the binding of TiO_2 NPs to the fibers by using carboxylic acid as a cross-linker. In addition, the aggregation formed by TiO_2 nanoparticles formed in the acidic environment may have reduced the amount of radiation absorbed and its functionality by reducing the surface area [8]. It is thought that these agglomerations decreased with the washing process, the TiO_2 surface area increased further, and the photocatalyst performance of the samples

increased. While the tendency of the samples treated with 10 and 20 g/L citric acid concentrations to return to their initial colors is close to each other and the best, the difference is higher than the first color of the samples treated with 30 g/L citric acid.

It is thought that this is due to the result that as the citric acid concentration increases, the nanoparticles adhere more tightly to the fiber and some aggregations that have formed cannot be removed by washing.

4. Conclusion

Citric acid is a polycarboxylic acid that is low-cost and harmless to the environment and human health. TiO_2 nanoparticle is an important semiconductor that plays a role in the degradation of organic pollutants by irradiation. Within the scope of the study, a commercial TiO_2 Degussa P25 nanopowder, which is a mixture of anatase/rutile phases, was mixed with citric acid which was used as a cross-linker to ensure the bonding of nanoparticles to the cellulosic fiber. SEM analysis showed that a higher number of TiO_2 nanoparticles adhered to the fiber surface at high citric acid concentrations. On account of TiO_2 Degussa P25 nanoparticles, yellowing caused by citric acid on cotton products was prevented and the samples became whiter.
The samples stained with methylene blue were exposed to sunlight directly at different times and the color measurements of the samples were performed with a spectrophotometer. Accordingly, treatments with citric acid doped with TiO_2 Degussa P25 NP suspension provided accelerated degradation of MB that penetrated the cotton fabric. After 8 hours of irradiation, the color of the samples treated with TiO_2 Degussa P25 NP added 30 g/L citric acid solutions were closest to its initial color. Different curing temperatures did not have a significant effect on the photocatalyst property of the sample. The washing durability of the treatments was high, and even the photocatalyst properties of all samples treated at the end of the washing process increased even more. In future studies, the effect of different catalysts and mixtures of citric acid in varying proportion on self-cleaning performances of textile products can be evaluated.

Article Information Form

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This study does not require ethics committee permission or any special permission.

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