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# APPLICATION OF POLYCARBOXYLIC ACIDS AS BINDERS FOR $TiO_2$ IMMOBILIZATION ON COTTON TEXTILES

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**Abstract** - Immobilizing the photocatalyst on a support is an alternative solution to a critical issue in photocatalysis, which is the need for unit operations to remove the photocatalyst from the effluent. In this work, $TiO_2$ was immobilized onto a cotton textile substrate by polycarboxylic acid binders (succinic and citric acids) using a solution deposition method, and the most appropriate conditions for pre-treatment and the relationship between variables were determined by an experimental design. Then, samples prepared at optimum conditions were exposed to UV for an extended period of time to evaluate the deactivation. The results showed an increase in photocatalytic activity and deposited mass by raising curing temperature, a statistically significant variable for tested binders. However, the increase in photocatalyst mass deposition is not always followed by an increase in photocatalytic activity, indicating that the photocatalyst distribution on the substrate is also important for photocatalytic efficiency. Both binders formed UV light active materials with sufficient displacement strength for photocatalysis use.

*Keywords*: Photocatalysis; Titanium compounds; Polycarboxylic acids; Immobilization; Textile substrates.

## INTRODUCTION

$TiO_2$-based photocatalysis has been widely studied in recent years due to the many advantages $TiO_2$ presents as a photocatalyst. Efforts have focused mainly on researching its most effective application in the degradation of organic pollutants in the liquid phase (Herrmann, 1999; Li et al., 2014; Padovan and Azevedo, 2015; Zangeneh et al., 2015; Abid et al., 2016; Tang et al., 2016; Grčić et al., 2017) and gas phase (Verbruggen, 2015), or as an antibacterial agent (Mccullagh et al., 2007). It is also being used as a component of self-cleaning materials in the construction industry, such as glasses, tiles, concretes and paints (Gupta e Tripathi, 2011; Liu et al., 2012), or in the textile industry (Gupta e Gulrajani, 2015; Stan et al., 2016).

The remarkable features of $TiO_2$ as a photocatalyst and the increasing concern over the effects of water and air quality on human health (Ren et al., 2017) have supported its application in wastewater and air treatment by heterogeneous photocatalysis. Moreover, heterogeneous photocatalysis has been extensively studied due to its potential in achieving high levels of degradation - or a complete mineralization - of organic pollutants within mild operation conditions (Ibhadon and Fitzpatrick, 2013; Umar and Aziz, 2013). This process has major advantages when compared to other technologies, such as low cost when solar or LED light is applied, low selectivity, low or no sewage formation and the need for small amounts of reagents.

In this sense, nano-titanium dioxide films deposited on solid supports present major benefits for these photocatalytic applications when compared to the commonly used powder morphologies. In a large-scale application, it is economically more advantageous to use photocatalysts immobilized on supports since

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the operation in a slurry system requires additional unit operations to remove the photocatalyst from the effluent.

In searching for suitable supports that can be applied in pollutant treatment by heterogeneous photocatalysis, it is highly desirable that they fit the equipment, maintain a satisfactory mass transfer, allow the passage of light and present a high affinity with the waste compound to be treated (Shan et al., 2010). In addition, immobilization procedures must preserve the physical and chemical properties presented by the original photocatalysts (Ibhadon e Fitzpatrick, 2013). A major challenge in the design of efficient photocatalytic coatings when compared to powders is the small amount of photocatalyst that can be stably deposited onto solid supports (Ivanova et al., 2015).

These requirements make textile-based materials potential support substrates: particularly cotton-based fabrics, due to their wide availability and ability to chemically bond with the photocatalyst through a cellulose pretreatment with crosslinking agents, extensively studied for other purposes in the textile industry (Harifi e Montazer, 2012; Dehabadi et al., 2013; Radetic, 2013). The cotton fiber is treated by crosslinking agents, mainly polycarboxylic acids, and phosphorus catalysts to improve wrinkle resistance. Further studies have shown that these agents could interact with $TiO_2$ nanoparticles and therefore be used as binders on immobilization processes (Dhananjeyan et al., 2001; Meilert et al., 2005). In that case, selecting polycarboxylic acids as binders for photocatalytic processes may be advantageous because it has been confirmed that these organic compounds are also resistant to radicals and oxidative species (Meilert et al., 2005).

The most widely used polycarboxylic acid for wrinkle resistance improvement is 1,2,3,4-butanetetracarboxylic acid (BTCA)/$NaH_2PO_2$ due to its good washing resistance and reduced yellowing of textiles (Kim et al., 2000; Gupta e Gulrajani, 2015). However, some other possible compounds were also studied while searching for lower costs and more efficient routes. A short summary of these research findings is shown in Table 1, where 'SA' stands for succinic acid, 'PA' for 1,2,3-propanetricarboxylic acid and 'CA' for citric acid.

SA was studied by several researchers as a possible binder of $TiO_2$ and cellulose (Meilert et al., 2005; Karimi et al., 2010; Mirjalili e Karimi, 2011). The pioneering research in the area was carried out by Meilert, Laub and Kiwi (2005), mainly motivated by the development of better self-cleaning properties for cotton fabrics from $TiO_2$ immobilization with SA, PA and BTCA binders. An ester linkage between at least

**Table 1.** Summary of research findings on the $TiO_2$ immobilization in cotton using polycarboxylic acids.

| Catalyst | Binder | Relevant points of research | Authors |
|---|---|---|---|
| $TiO_2$ P25 | SA<br>PA<br>BTCA | Increasing the amount of carboxyl groups found on each binder had no influence on photocatalytic activity.<br>Higher cure temperature led to higher catalyst deposited mass, but no relation between these variables and photocatalytic activity was found. | Meilert et al. (2005) |
| $TiO_2$ P25 | BTCA | The use of the BTCA binder results in a larger deposited mass, but after 5wash cycles, the remaining mass is slightly higher than on the substrates without the binder. | Bonet et al. (2015) |
| $TiO_2$ P25 | BTCA | The formation of cyclic anhydrides is facilitated when a pH of 2.04 to 2.79 is used.<br>Proof of Ti-O-C bond formation by FTIR.<br>The use of BTCA increased the photocatalytic activity of the substrates. After 5 wash cycles, the activity of substrates without binders was dramatically reduced, while those with binders remained unchanged. | Galkina et al. (2012) |
| $TiO_2$ P25 | SA | Different concentrations of $TiO_2$ were tested and after 5 g $L^{-1}$, there was no increase in deposited mass or activity.<br>Lower deposited mass and photocatalytic activity were obtained in samples without SA. The increase in the activity for samples treated with AS is justified by the increase in deposited mass and the more homogeneous distribution of the particles in the matrix. | Karimi et al. (2010) |
| $TiO_2$ P25 | SA | The SA treated samples presented lower mass loss after ultrasonic bath than the samples without the treatment.<br>More homogeneous samples are obtained using the binder. | Mirjalili and Karimi (2011) |
| $TiO_2$ P25 | CA | $TiO_2$ is more active at pH <6.8. Results demonstrate efficient degradation of dye in aqueous medium, even in the presence of electrolytes, with CA-treated tissues.<br>The substrates treated with CA are stably active even after 5 cycles of sequenced reactions. | Montazer and Hashemikia (2012) |
| $TiO_2/SrTiO_3$ | CA | Acid pH provides better distribution of the particles in the matrix, resulting in higher activities.<br>The increase in the $TiO_2$ concentration increases the photocatalyticactivity until reaching approximately 0.4%wt, after which point, the activity remains stable. | Zohoori et al. (2014) |

one carboxylic group of the tested binders and the cellulose hydroxyl group was successfully obtained, as confirmed by IR spectroscopy. Furthermore, the higher molar ratio of carboxylic groups was not responsible for the higher catalyst mass deposited, which proves that not only the carboxylic group must be present for the esterification reaction to occur, but its availability on the surface to attract a catalyst is also indispensable (Meilert et al., 2005).

CA has also been proposed as a binder in the $TiO_2$ immobilization on cotton textiles by Montazer and Hashemikia (2012). In that work, the use of textile as photocatalyst supports was successfully applied in the treatment of textile effluents (Montazer e Hashemikia, 2012).

The scheme of photocatalyst adhesion onto textile is shown in Fig. 1a for SA and in Fig. 1b for CA. As mentioned before, the esterification reaction occurs when the available hydroxyl groups in cellulose react with the binder's carboxylic group, forming an ester bond. The remaining carboxylic group can attract particles of $TiO_2$ by strong electrostatic attraction (Meilert et al., 2005; Montazer e Hashemikia, 2012).

It is worth mentioning that this cotton textile treatment with nanoparticles has several applications in the industry sector, not only for use in photoreactors, as proposed by this work, but also for specific functions in smart textiles, including hydrophobicity, antibacterial properties, conductivity, antiwrinkle properties, among others (Yetisen et al., 2016).

The most commonly used methodology to determine photocatalytic activity is performed in batches, where the samples to be analyzed are submerged in a liquid medium in which the test molecule, usually a dye, is dissolved. It is necessary to employ some sort of agitation, aeration and ultraviolet (UV) radiation or visible light source. This test application for photocatalysts immobilized on textiles is not only impractical, but it also results in small photocatalyst displacements, which cannot be easily measured, resulting in random effects on the results.

A more efficient method was proposed by Mills & Wells (2015) to determine the photoactivity of photocatalysts immobilized on glass, which has recently been acknowledged as a possible ISO standard (ISO/CD 21066). The proposed test is based on the use of inks as photoactivity indicators and involves a dye that when printed or deposited on photoactive film changes its coloration rapidly and irreversibly, within measurable rates, due to irradiation (Mills et al., 2005). The above mentioned method was adapted to be used with textiles, to avoid displacement errors and because of its more efficient and ecofriendly approach, since it provides a reduction in test time, reagent use and residues generation.

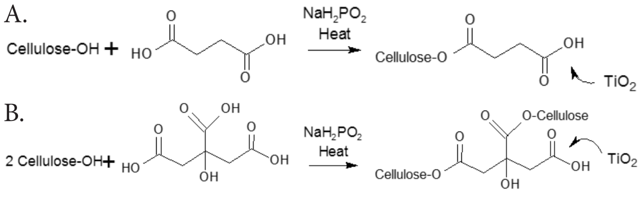

**Figure 1.** $TiO_2$ attachment onto cotton textile through pretreatment with SA (a) and CA (b).

Several formulations can be used, depending on the photocatalyst's operating range, but the most explored is resazurin/glycerol in the presence of hydroxyethyl cellulose in water. Unlike the other tests reported in the literature, this test does not focus on the occurrence of a photo-oxidative process, but rather on a photo-reductive one (Mills e Wells, 2015). The reaction scheme can be found in the above mentioned work.

In this context, the aim of the study was twofold: describe the best condition for $TiO_2$ immobilization onto cotton textiles under pretreatment with two different polycarboxylic acids, succinic and citric acid, statistically determined by experimental design, and compare the photocatalytic performance of the resulted materials.

## MATERIALS AND METHODS

The white 100% cotton textile was provided by Coats Corrente Ltda. (Brazil). The sodium hypophosphite, succinic acid (SA) and citric acid (CA) grade P.A. were provided by Sigma-Aldrich and used as received. The titanium dioxide (Aeroxide® P25) was supplied by Evonik (Brazil) with a particle size of 21 nm and a BET surface area of 50 $m^2\ g^{-1}$.

### Photocatalyst Immobilization

Cotton textile stripes of 40 cm² were washed with colorless nonionic detergent 2 g $L^{-1}$ at 50 °C for 20 min, then rinsed with distilled water and dried in an oven at 100 °C for 1 h. The washed samples were immersed in an aqueous solution of succinic or citric acid in the presence of $NaH_2PO_2$ as a catalyst (4%wt) for 1 h, at a liquid to fabric weight ratio of 25:1. After wiping the samples on a manual press roll, the textiles were cured at different temperatures and time intervals, defined in the experimental design. The pre-treated samples were immersed in an aqueous solution of $TiO_2$ 5 g $L^{-1}$, previously sonicated for 30 min, for 1 h. After the photocatalyst deposition, the samples were dried in an oven for 1 h at 100 °C. The dried samples were then dipped into distilled and deionized water and sonicated for 5 min in order to remove the unbounded $TiO_2$.

### Photocatalytic Activity Evaluation

A resazurin solution was prepared by magnetic stirring of 50 g of hydroxyethyl cellulose (0.8%wt), 25 mg of resazurin dye, 4 mL of glycerol and 90 μL of polysorbate 20 for 12 h. The textile samples were cut and arranged in equally sized recipients of 18 $cm^2$. Then, 6 mL of solution were placed on the samples, and the support and samples were kept in an oven for 16 h at 50 °C. The dried samples were subsequently tested using two modified mercury vapor lamps of 125 W with 2.0 to 2.5 mW $cm^{-2}$ irradiation at 365nm in a holder to which the samples were attached.

Testing was monitored by taking pictures with a Sony Cybershot digital camera for further evaluation using Image J software. The method consists of capturing images at 2 min intervals and evaluating these images on software in order to obtain the red color fraction of the RGB (Red, Green, Blue) spectral colors for each of the observed times. Since resazurin (blue colored) reacts to resorufin (pink colored) as the reaction occurs, the relative value of red is incremented up to a maximum value. A comparison of the samples' activity was performed by evaluating the time it took to reach 90% of the total conversion (t90).

Each sample was tested in triplicate and the mean curve "relative red value versus time" was determined. From the points of this curve, the equation that best fit the experimental results was achieved (1). Then, y90 was obtained from equation (2) and replaced in (1), which determines t90, time to achieve 90% of conversion. This variable was used to compare each sample treatment.

$$y = A_1 \exp\left(-\frac{t}{A_2}\right) - A_3 \qquad (1)$$

$$y_{90} = y_{min} + 0.90 \cdot \left(y_{max} - y_{min}\right) \qquad (2)$$

in which $A_1$, $A_2$, $A_3$ are model parameters, $y_{min}$ is the initial red value fraction of the image's RGB composition, and $y_{max}$ is the maximum red value fraction of the image's RGB composition

## Gravimetric Analysis

The burning method was used to determine the $TiO_2$ mass deposited on the fabric's surface. Blank and treated samples of 36 cm² were placed in a porcelain crucible and kept in an oven at 600 °C for 140 min. The remaining weight of the blank sample was subtracted from the remaining weight of the treated samples, in order to obtain the mass (mc) of the deposited photocatalyst.

## Surface Response

The statistical model of a Circumscribed Central Composite Design (CCCD) was employed to investigate the influence of acid concentration, cure temperature and time on the photocatalytic activity (t90) and deposited photocatalyst mass (mc). This method was used to determine the best pre-treatment condition. The model consists of a 2k (k=3) experimental design, six star points and three central point replicates. The results were evaluated and validated at a 95% confidence interval by Statistica 10 software.

## SEM Analysis

The surface of the samples was characterized by scanning electron microscope (JSM 6060). The accelerating voltage was 10 kV. The analysis was performed to verify $TiO_2$ presence and its morphology in the treated samples.

## Deactivation

A test was conducted in a labyrinth reactor to compare the weight loss resistance of the photocatalyst, attached to the textile, achieved by using each of the binders, as well as to evaluate the remaining photocatalytic activity after several hours. A schematic representation of the deactivation test reactor is presented in Figure 2. A water volumetric flow of 200 L min-1 with bubbling air and UV irradiation was applied for up to 24 h.

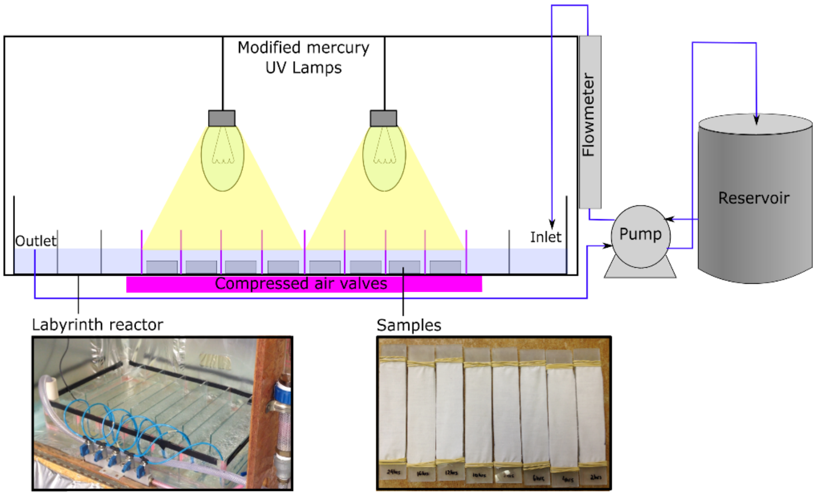

**Figure 2.** Schematic representation of the deactivation test reactor.

Samples were collected at 2, 4, 6, 8, 10, 12, 16 and 24 h periods, and then the photocatalytic activity (t90) and deposited photocatalyst mass (mc) were evaluated for each sample.

## RESULTS AND DISCUSSION

### Surface Response Evaluation

The calculated values for ‘t90’ and ‘mc’ at each point of the experimental design, using SA and CA binders, are shown in Table 2. The numbers in brackets represent coded variables. It should be pointed out, since it is not usual, that the lowest values of t90 indicate the most active samples. Also worth mentioning is that blank samples without treatment were tested under the same conditions as the CCCD samples. In this case, no change in ink color was observed.

The statistically significant variables for photocatalytic activity, common to both binders, were: concentration, curing temperature and their interaction (Fig. 3). Furthermore, for SA, the curing time and the interaction between concentration and curing time were also significant.

Additionally, the variable that exerts the greatest influence on the photocatalyst deposited mass response was the cure temperature (Fig. 4). For binders, the higher the cure temperature within the range studied, the greater the amount of photocatalyst deposited. As expected, higher curing temperatures provide a higher degree of advancement of the cellulose esterification reaction and, therefore, it is possible to obtain greater polycarboxylic acid adhesion to the fabric surface (Dhananjeyan et al., 2001; Harifi e Montazer, 2012; Ivanova et al., 2015). Not only should a larger acid amount adhere to the textile, but a larger amount of carboxyl groups should be available on the surface to attract the catalyst particles, which is then confirmed by the increase in deposited mass.

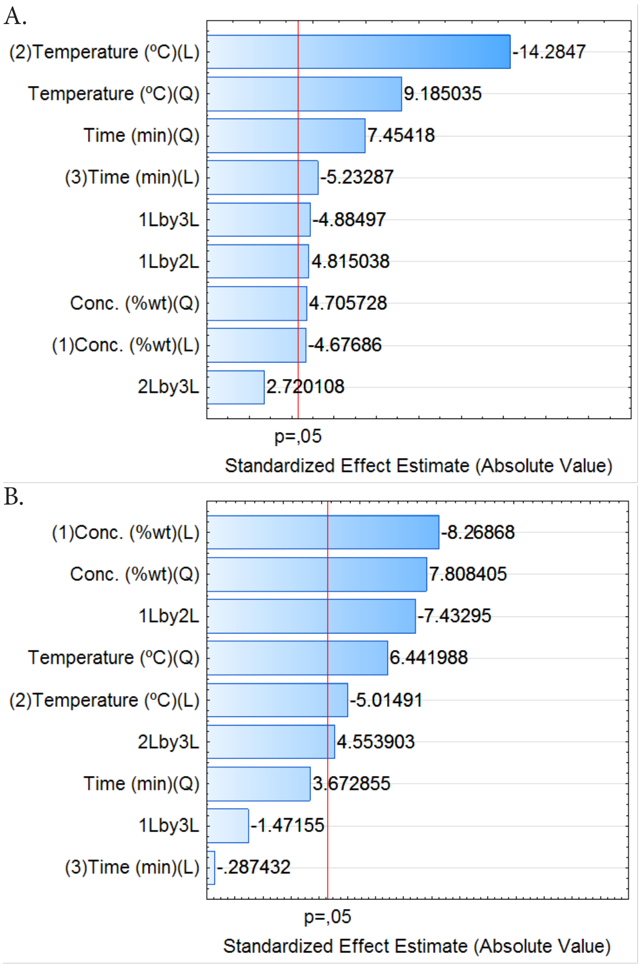

**Figure 3.** Pareto chart of effects for t90 by (a) SA and (b) CA pretreatment.

**Table 2.** Experimental design results (adjusted R² of ca. 0.7-0.8).

| Exp. | Binder concentration (%wt) | Curing temperature (°C) | Curing time (min) | Succinic acid | | Citric acid | |
|---|---|---|---|---|---|---|---|
| | | | | t90 (min) | mc (mg) | t90 (min) | mc (Mg) |
| 1 | 3 (-1) | 110 (-1) | 3 (-1) | 12.1 | 9.9 | 13.4 | 2.9 |
| 2 | 9 (+1) | 110 (-1) | 3 (-1) | 14.1 | 5.7 | 16.6 | 2.1 |
| 3 | 3 (-1) | 210 (+1) | 3 (-1) | 3.6 | 13.0 | 8.6 | 5.4 |
| 4 | 9 (+1) | 210 (+1) | 3 (-1) | 3.8 | 10.9 | 2.9 | 8.9 |
| 5 | 3 (-1) | 110 (-1) | 10 (+1) | 15.7 | 8.2 | 10.1 | 2.6 |
| 6 | 9 (+1) | 110 (-1) | 10 (+1) | 6.4 | 10.9 | 13.3 | 3.7 |
| 7 | 3 (-1) | 210 (+1) | 10 (+1) | 3.3 | 9.6 | 14.3 | 1.9 |
| 8 | 9 (+1) | 210 (+1) | 10 (+1) | 5.2 | 15.1 | 4.2 | 9.9 |
| 9 | 11.04 (+1.68) | 160 (0) | 6.5 (0) | 3.0 | 8.7 | 1.6 | 6.0 |
| 10 | 0.96 (-1.68) | 160 (0) | 6.5 (0) | 7.2 | 10.4 | 15.3 | 8.8 |
| 11 | 6 (0) | 244 (+1.68) | 6.5 (0) | 6.5 | 13.8 | 8.3 | 11.9 |
| 12 | 6 (0) | 76 (-1.68) | 6.5 (0) | 9.0 | 10.1 | 6.1 | 4.8 |
| 13 | 6 (0) | 160 (0) | 12.38 (+1.68) | 3.6 | 11.9 | 4.3 | 6.3 |
| 14 | 6 (0) | 160 (0) | 0.62 (-1.68) | 9.8 | 10.4 | 5.2 | 2.3 |
| 15 | 6 (0) | 160 (0) | 6.5 (0) | 2.4 | 15.1 | 4.7 | 4.9 |
| 16 | 6 (0) | 160 (0) | 6.5 (0) | 3.7 | 13.0 | 2.6 | 5.6 |
| 17 | 6 (0) | 160 (0) | 6.5 (0) | 3.4 | 10.8 | 3.6 | 5.1 |

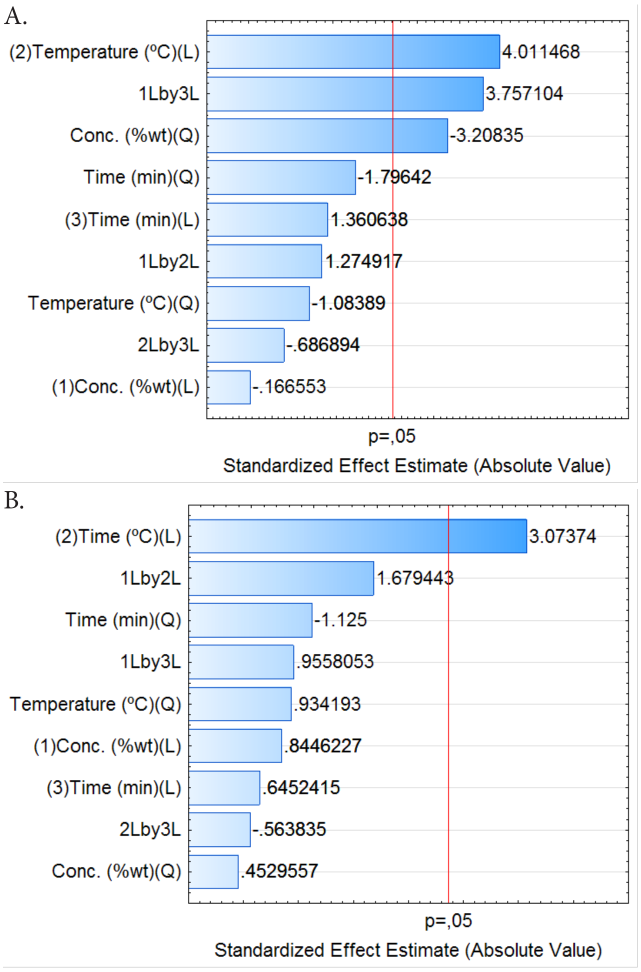

**Figure 4.** Pareto chart of effects for mc by (a) SA and (b) CA pretreatment.

Therefore, the increase in photoactivity at higher temperatures, for both binders, is justified by the increase in deposited photocatalyst mass. However, regarding temperature, unlike the behavior seen for mc, there is a slight photoactivity reduction starting at about 200 °C, possibly caused by cluster formation or an uneven $TiO_2$ particle distribution (Meilert et al., 2005; Montazer e Hashemikia, 2012).

For samples treated with SA, it was observed that concentrations above the critical value (Table 3) cause solution saturation, which may explain the decrease in activity starting at 7.5%wt. The reduction in activity is also explained by a decrease in the deposited mass, since for this binder, the quadratic concentration term was also significant, indicating maximum deposition for that concentration, which also resulted in the sample's higher photoactivity.

**Table 3.** Critical values.

| Variables | Concentration (%wt) | Temperature (°C) | Time (min) |
|---|---|---|---|
| SA | 7.5 | 190 | 7 |
| CA | 10 | 240 | 4 |

The interaction between binder concentration and curing temperature was significant for both SA and CA. In Fig. 5 and 6, it can be seen that the increase in concentration at low temperatures is more important for photoactivity than at higher temperatures. When the reaction rate is higher, at greater temperatures, the available acid amount on the surface is less significant, as long as it is sufficient, i.e., it approaches a limit of bonded molecules regardless of the concentration used. Moreover, when the reaction time is not sufficiently high, increasing the acid concentration on the fabric surface may not result in more ester bonds with cellulose, and unreacted molecules may potentially remain on the surface.

A second-order empirical model equation (3 and 4) was obtained for t90 of SA and CA treatment, respectively, as a function of statistically significant parameters ($p<0.05$).

$$\begin{aligned} t_{90} &= 3.09+0.88x_1+0.98x_1^2-2.69x_2+1.91x_2^2- \\ &- 0.99x_3+1.55x_3^2+1.18x_1x_2-1.2x_1x_3 \end{aligned} \tag{3}$$

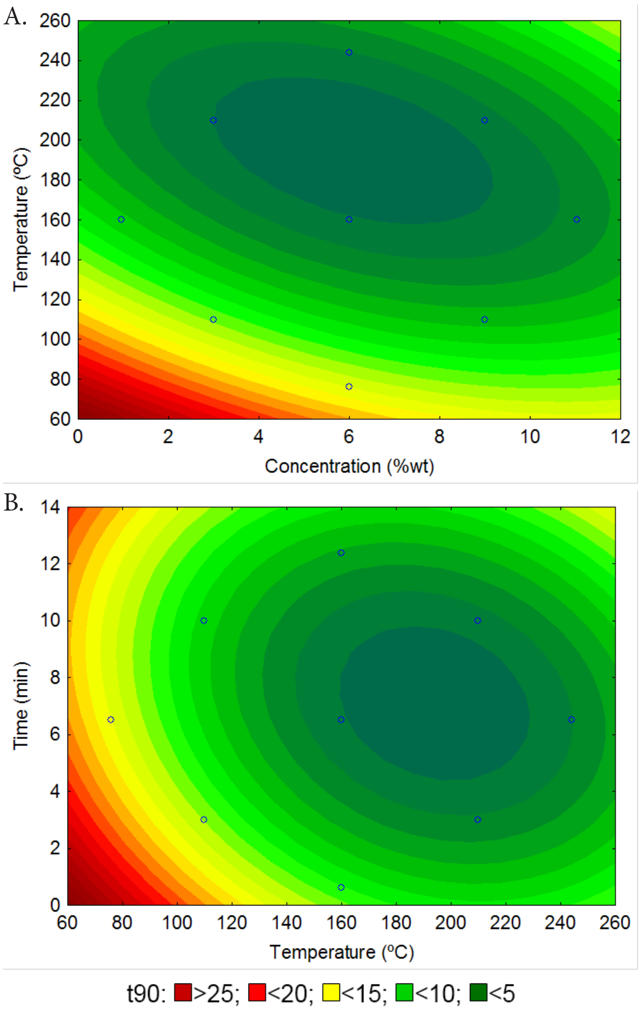

**Figure 5.** Surface response of t90 (min) for SA pretreatment (a) temperature versus concentration at the central time and (b) time versus temperature at the central concentration.

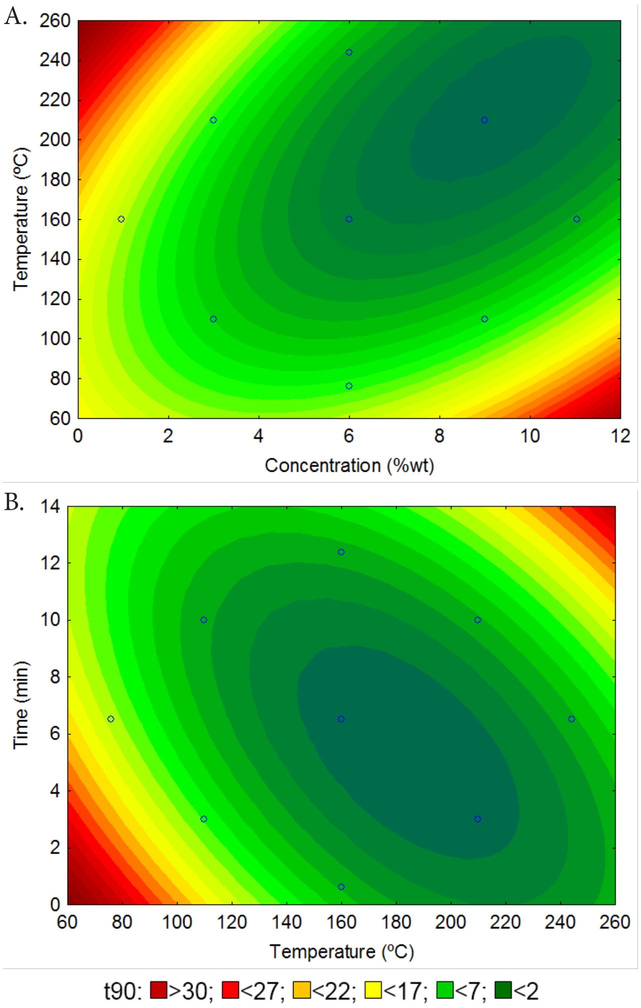

**Figure 6.** Surface response of t90 (min) for CA pretreatment (a) temperature versus concentration at the central time and (b) time versus temperature at the central concentration.

$$t_{90} = 3.39 + 2.38x_1 + 2.47x_1^2 - 1.44x_2 + 2.04x_2^2 - 2.79x_1x_2 - 1.71x_2x_3 \quad (4)$$

The equations (5) and (6) demonstrate the empirical model for mc of SA and CA treatment, respectively, provided by significant parameters ($p<0.05$).

$$mc = 5.33 + 1.95x_2 \quad (5)$$

$$mc = 13.01 - 1.30x_1^2 + 1.48x_2 \quad (6)$$

In the polynomial equations, $x_1$, $x_2$ and $x_3$ represent the coded values of binder concentration, curing temperature and curing time, respectively.

The critical value of each variable in the experimental design was calculated by Statistica software and is presented in Table 3. In the case of SA, the critical values provide the conditions under which the resulting sample will have the best possible photoactivity within the limits proposed in this model. Therefore, these conditions were chosen for further deactivation evaluation. For CA, however, there are restrictions that prevent the use of critical values as the optimum point: i) resazurin test limitation due to high CA concentration and ii) sample degradation at high temperatures, experimentally observed by the yellowing of the sample.

Therefore, a simple evaluation of the best result was performed on experimental design points. Even though experiment 9 presented the best activity value, using it is not recommended as it presents the highest error between the observed and predicted values. This error is most likely explained by the resazurin test limitations observed experimentally for this sample, resulting from low experimental pH . Consequently, the point at which the best photoactivity result was obtained, for an evaluated activity range in the test with resazurin, was experiment 4, where concentration was 9%wt, curing temperature was 210 °C and curing time was 3 min.

## Deactivation Evaluation

The deactivation evaluation was performed on substrates treated at optimal conditions, which in turn were obtained for each binder in the previously discussed experimental design. The result of the activity after prolonged exposure to UV radiation and effluent flow can be seen in Fig. 7. There is an increase in the ‘t90’ variable when UV exposure time rises, i.e. there is a photocatalytic activity reduction for both binders tested. For CA treated samples, deactivation took place after 6 h of exposure, while SA treated samples presented slower deactivation, becoming significant only after 10 h of exposure. However, after 16 to 24 h of exposure, the final photocatalytic activity for both samples was statistically equal.

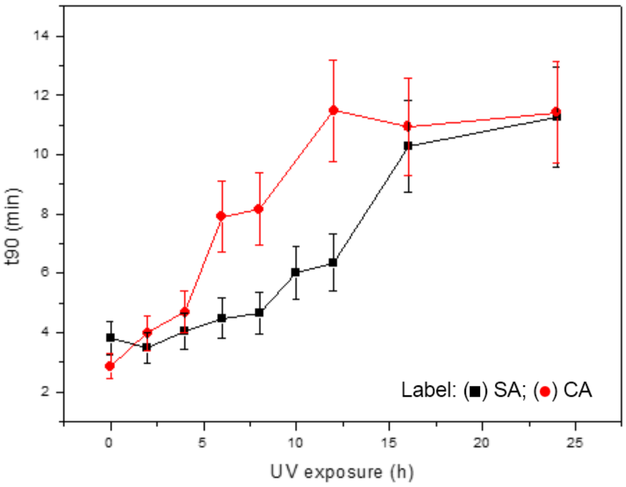

**Figure 7.** Photocatalytic activity as a function of UV exposure time.

These results could be related to weight loss generated by the water flow and air bubbling to which substrates were submitted. However, as can be seen in Table 4, there was no reduction of the deposited catalyst mass, that is, there was no significant displacement of the photocatalyst from the textile matrix.

The durability of the mass deposited on the samples after UV exposure is very important since it determines whether the use of this method of immobilizing the photocatalyst is feasible. However, investigating the causes of the samples' deactivation becomes necessary, mainly because at the 4 to 12 h interval, the substrates presented different activities when compared to each other.

In order to find an explanation for this behavior, an additional experiment was performed in which the $TiO_2$ was subjected to the same UV exposure conditions (water and 24 hours of exposure), but using a batch reactor in a slurry system, without any binder. Thereafter, a standard rhodamine B test was performed and the results were compared with those usually obtained from the fresh photocatalyst under the same conditions. There was no significant reduction in activity when these tests were compared and, therefore, the result of the deactivation of the substrates could not be explained by the decomposition or deactivation of the photocatalyst itself, but rather by the interaction with the materials and methods used in the deposition of the photocatalyst. In this matter, the authors understand that a better explanation of the deactivation patterns should be properly addressed in a future work.

**Table 4.** Photocatalyst mass after UV exposure.

| UV exposure (h) | Photocatalyst mass (mg) SA | CA |
|---|---|---|
| 0 | 18.3 | 18.2 |
| 2 | 16.6 | 19.0 |
| 4 | 19.7 | 23.6 |
| 6 | 18.6 | 20.7 |
| 8 | 17.7 | 21.7 |
| 10 | 20.6 | 23.7 |
| 12 | 18.4 | 22.9 |
| 16 | 21.6 | 18.3 |
| 24 | 20.6 | 18.7 |

## SEM Analysis

The SEM images for cotton textile without any treatment (Fig. 8a.) and after treatment with SA at 110 °C (Fig. 8b) and 210 °C (Fig. 8c), both at 2 min intervals, are presented. In both treatments, formation of photocatalyst agglomerates can be observed, which causes an adverse effect on the photocatalytic activity. However, the treatment at 210 °C presented a better photocatalyst distribution on the textile surface. The improved activity presented by the samples treated at higher temperatures can also be justified by this distribution improvement.

Treatment at optimum conditions for SA (Fig. 8d) presented good photocatalyst distribution with even smaller clusters than the treatments discussed above. Greater agglomerate formation for CA treated samples is observed in Fig. 8e, as well as a higher deposit of photocatalyst mass when compared to the samples treated with SA.

It is worth mentioning that all treatments resulted in a cotton fiber completely covered by $TiO_2$ in comparison to the untreated fabric. When considering the irregularity of the cotton fibers or even textile surface, a uniform and homogeneous distribution of $TiO_2$ particles on the cotton surface is unlikely. However, through this analysis, we can clearly see improvements in the particles distribution. Furthermore, it is important to note that the SEM images are obtained in a very small substrate area and, as a result, may not represent the sample as a whole.

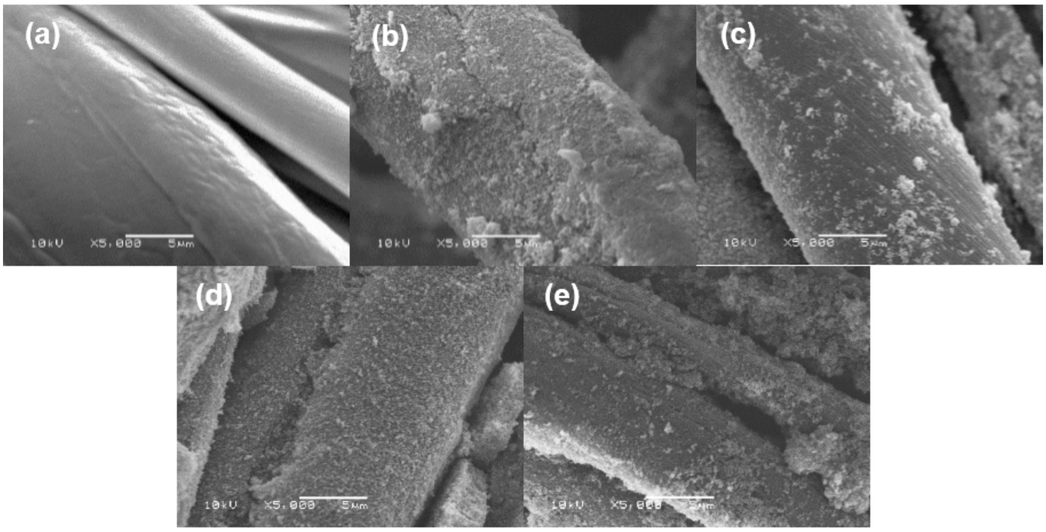

**Figure 8.** SEM images for (a) blank sample and samples treated with (b) SA 6%wt at 110ºC for 2 min, (c) SA 6%wt at 210ºC for 2 min, (d) SA optimum conditions and (e) CA optimum conditions.

## CONCLUSION

In this study, the use of two different binders from the polycarboxylic acid group (succinic and citric acid) in the immobilization of a titanium dioxide photocatalyst on 100% cotton textile by dip-pad-cure method was evaluated. For this, a photoactivity test for photocatalysts immobilized on glass, as proposed in the literature, was adapted for use on textile substrates. The treatments were also compared by the deposited photocatalyst mass on the samples. In addition, the morphology of the resulting material was also investigated by SEM analysis. The results indicate a successful $TiO_2$ immobilization on textile substrates with the use of polycarboxylic acids as binders, forming stable and active materials at prolonged UV irradiation periods.

The parameters evaluated by the experimental design in the pretreatment of the textile promote significant change in the deposited amount and distribution of the photocatalyst mass, which most likely resulted in the photoactivity changes reported. Since the increase of the photocatalyst mass is not always accompanied by higher photocatalytic activity, the distribution may play an important role in this matter. Moreover, for both tested binders, the curing temperature proved to be a very important factor, as it relates to the degree of advancement of the cellulose esterification and crosslinking reactions. These reactions are essential for binder adhesion on the textile surface.

Both binders, when used under optimum conditions of concentration, curing temperature and time, which were determined through experimental design, provided stability to the catalyst mass deposited on the substrate even after long periods of exposure to UV and friction.

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## ABBREVIATIONS

| | |
|---|---|
| BTCA | 1,2,3,4-Butanetetracarboxylic acid |
| CA | Citric acid |
| IR | Infrared |
| mc | Deposited photocatalyst mass |
| PA | 1,2,3-propanetricarboxylic acid |
| SA | Succinic acid |
| SEM | Scanning electron micrograph |
| t90 | Time it took to reach 90% of the total conversion |
| UV | Ultraviolet. |

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