Investigation of Bleaching of Cotton Fabrics with UV-TiO\(_2\)

Raziskava beljenja bombažnih tkanin z UV-TiO\(_2\)

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Abstract
Titanium dioxide exhibits photocatalytic properties under ultraviolet (UV) irradiation. In this study, an environmentally friendly, fast and efficient technique for bleaching cotton fabrics is presented, utilising the photocatalytic property of TiO\(_2\). Raw cotton fabric samples were treated with TiO\(_2\)-containing and TiO\(_2\)-free treatments (hydrogen peroxide and sodium hydroxide) under UV irradiation in order to bleach the samples. The results showed that cotton fabrics treated with TiO\(_2\) were bleached satisfactorily without severe strength loss.

Keywords: ultraviolet, photocatalytic, TiO\(_2\), cotton

1 Introduction
Cotton is the most widely used natural fibre, which is prized for its satisfactory comfort, soft touch, water absorbency, strength and easy maintenance properties [1]. Cotton fibres generally consist of 82–96% cellulose, 0.5–1% lignin, 2–6% hemicellulose and 5–7% pectin [2]. Raw cotton exhibits its hydrophobic character due to the waxy layer and pectin on it, which affects cotton finishing and dyeing processes [3]. The bleaching process is used to remove the impurities from cotton fibres. High temperatures (98 °C) and high concentrations of hydrogen peroxide (H\(_2\)O\(_2\)) are typically used in the bleaching process [4]. H\(_2\)O\(_2\) likely breaks down the double bonds in the colour forming components of cotton into colourless fragments [5, 6]. High temperatures required in H\(_2\)O\(_2\) bleaching increase the energy costs. In addition, peroxide bleaching effluent raises the pH value of the factory downstream and adds trace amounts of H\(_2\)O\(_2\) and stabilizers to it [7, 8]. Energy conservation, waste control and chemical recovery became emerging issues, resulting in an increase of research for more environmentally friendly technologies.
species [9]. Eren [10] reported that the H₂O₂ treatment under UV irradiation was successful for cotton bleaching as an Advanced Oxidation Process (AOP) [10]. The main oxidant in H₂O₂/UV AOP is the hydroxyl radical (•OH) formed under the UV irradiation of the H₂O₂ solution.

Titanium dioxide (TiO₂) is reported to exhibit self-cleaning and photocatalytic effects, and have the ability to modify surfaces when exposed to ultraviolet irradiation. TiO₂ is a non-toxic chemical and it has reasonable stability with a well-positioned valence, which makes this material important for catalytic reactions [11]. Furthermore, the redox potential of TiO₂ (2.9 eV), which is higher than that of the widely used oxidant H₂O₂ (1.77 eV), contributes to its use as a photocatalyst [12, 13]. When TiO₂ particles are subjected to UV irradiation (100–400 nm), electrons are transferred from the valence band to the conduction band to create electron-hole pairs that react with nearby oxygen or water molecules to form radicals that can oxidise various substances [14]. There are many studies in the literature reporting the photocatalytic property of TiO₂ under UV irradiation [11, 15–17]. The reactions associated with the photocatalytic effect of titanium dioxide are as follows [18, 19]:

\[
\begin{align*}
\text{TiO}_2 + h & \rightarrow \text{TiO}_2^+ (e^- + h^+) \quad (1) \\
\text{TiO}_2^+ (e^-) + \text{O}_2 & \rightarrow \text{TiO}_2^+ + \cdot \text{O}_2^- \quad (2) \\
\text{TiO}_2^+ (e^-) + \cdot \text{O}_2^- + 2H^+ & \rightarrow \text{TiO}_2 + \text{H}_2\text{O}_2 \quad (3) \\
\text{TiO}_2 (e^-) + \text{H}_2\text{O}_2 & \rightarrow \text{TiO}_2 + \cdot \text{OH} + \text{OH}^- \quad (4) \\
\text{TiO}_2 (h^+) + \text{H}_2\text{O}_{\text{ads}} & \rightarrow \text{TiO}_2 + \cdot \text{OH}_{\text{ads}} + H^+ \quad (5)
\end{align*}
\]

In this study, raw cotton fabric samples were bleached by applying H₂O₂ + NaOH, TiO₂ alone, TiO₂ + H₂O₂, and TiO₂ + H₂O₂ + NaOH under UV irradiation. The aim of the study was to bleach a cotton fabric at room temperature using UV light. Whiteness, air permeability, strength values, scanning electron microscope (SEM) analysis and Fourier transmission infrared spectroscopy (FTIR) analysis of the treated samples were compared to the untreated samples.

2 Materials and methods

2.1 Materials

A plain woven 100% cotton fabric weighing 104 g/m² was used in the experiments. The warp and weft densities of the fabric were 20 warp/cm and 20 weft/cm, respectively. Warp yarns contained the carboxymethyl cellulose (CMC) sizing agent. Hydrogen peroxide (H₂O₂) (Merck, Germany), sodium hydroxide (NaOH) (Merck, Germany) and titanium (IV) oxide extra pure (Tekkim Kimya, Turkey) were used during the experiments.

The experiments were conducted in a specially designed UV cabinet (Figure 1). The size of the cabinet was 100 cm × 70 cm × 138 cm. The UV cabinet was equipped with 18 UV lamps on both sides and the top of the cabinet with a total power of 470 W. The wavelength of the UV lamps was 254 nm.

![Figure 1: UV cabinet setup](image)

2.2 Methods

A suspension solution (T) was prepared by adding 30 g of TiO₂ to 1000 mL of distilled water. The photocatalytic treatment solutions were prepared by adding 50 g/L of H₂O₂ (T+H) or 50 g/L of H₂O₂ and 30 g/L of NaOH (T+H+N) to the suspension solution (Table 1) [17]. In addition, a control treatment solution (H+N) was also prepared with a mixture of 50 g/L of H₂O₂ and 30 g/L of NaOH without TiO₂. All solutions were prepared at room temperature (20 °C).

Hence, five types of cotton fabric samples were obtained: raw (R), H₂O₂ + NaOH treated (H+N), TiO₂ treated (T), TiO₂ + H₂O₂ treated (T+H), and TiO₂ + H₂O₂ + NaOH treated (T+H+N) samples.

<table>
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<th>Table 1: Types and contents of treatment solutions</th>
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<td>Treatment solution</td>
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The samples were immersed in the treatment solution and passed through the foulard to adjust a wet pick-up of 100%. After impregnations, the samples were placed in the UV cabinet, hanging in the centre of the cabinet. The impregnated samples were processed in the UV cabinet for different treatment times (15 min, 30 min, 45 min and 60 min). A subsequent rinsing was applied to the samples with distilled water to remove any residual chemicals. All experiments were repeated 3 times.

2.3 Analysis of samples

Determination of whiteness
The whiteness values (Stensby) of samples were measured according to ASTM D1925, using a Konica Minolta CM 3600d spectrophotometer (Tokyo, Japan).

Air permeability
The air permeability tests of fabric samples were performed under standard laboratory conditions (20 °C ± 2 °C temperature; 65% ± 2% relative humidity). The tests were performed in an SDL Atlas Digital Air Permeability Tester (Model M 021A) according to the ISO 9237 standard (ISO 9237). The selected test pressure was 100 Pa and the test area was 5 cm².

Tensile strength measurements of fabrics
Tensile testing was performed according to ISO 13934:1999 on a Shimadzu Model AG-X-Plus Tensile Tester (Kyoto, Japan) under standard laboratory conditions (20 °C ± 2 °C temperature; 65% ± 2% relative humidity).

SEM analysis
Scanning electron microscope (SEM) images were taken to observe the surface morphology of the TiO₂ treated and raw fabric samples. The images were taken using the in-house method at 1000× magnification.

Fourier transmission infrared spectroscopy (FTIR) analysis
The FTIR-ATR spectra of the raw fabric and the fabric coated with TiO₂ alone were measured with a Shimadzu instrument in the range of 500–4000 cm⁻¹.

3. Results and discussion

3.1 Determination of whiteness
The whiteness values of samples were measured in order to see the effects of respective treatments and evaluate the photocatalytic effect of TiO₂ under UV irradiation. The results are presented in Figure 2. The whiteness values of all samples treated with TiO₂ containing solutions under UV irradiation were higher than the whiteness values of samples treated with the same solutions without UV irradiation. These results show the successful photocatalytic effect of TiO₂. Supporting this, it was observed that the whiteness of the H+N samples under UV irradiation and the whiteness of the H+N samples without UV irradiation did not significantly differ. Figure 2 shows that the raw fabric has a whiteness degree of 47.22 Stensby, while the T+H and UV treated samples (60 min treatment time) have the best whiteness degree of 69.18 Stensby. The highest whiteness degrees were achieved with the T+H treatment under UV irradiation. Considering the processing times, the T+H samples yielded Stensby whiteness degrees of 62.29, 65.65, 68.60 and 69.18 for 15, 30, 45 and 60 min treatment times, respectively. These results show that the degree of whiteness increases as the process time increases. It was observed that the whiteness degrees of samples coated only with TiO₂ under UV irradiation also increased but could not reach the whiteness achieved by the T+H treatment. It was seen that after 60 minutes of processing, the whiteness degree of the samples coated only with TiO₂ reached 61.00 Stensby. In addition, the whiteness degree of the samples treated with the T+H+N recipe was close to the whiteness degree of the samples treated only with samples coated only with TiO₂.

As a result of reactions occurring during the exposure to UV irradiation, TiO₂ is known to react with superoxide and hydroxyl radicals. Oxidative radicals can attack and depolymerise the polysaccharide pectin and hemicellulose [20]. It was noted that the whiteness degree of all TiO₂ coated samples was higher than that of the raw sample. It was observed that the N+H treatment did not have a positive effect on the whiteness of samples under UV light. The addition of H₂O₂ to the TiO₂ solution supported the bleaching and the whiteness levels were slightly higher than the samples treated with TiO₂ alone. However, when NaOH was added to the TiO₂ and H₂O₂ recipe, the degree of whiteness was reduced.
This result agreed with the literature that reports that the addition of NaOH reduces photooxidation [21]. According to the findings, adding TiO₂ to H₂O₂ significantly improves the photocatalytic activity to bleach cotton fabric samples, while the addition of NaOH to the solution has the opposite effect and reduces the photooxidation due to the alkaline medium.

3.2 Air permeability
Air permeability is an important aspect that describes the ability of air to pass through the fabric. It was found that the air permeability of the samples was lower in UV-treated fabrics compared to the raw fabric. The reason for this can be explained by a slight increase in fabric density compared to the raw fabric as a result of the treatment of the fabric. However, as it can be seen in Figure 3, it was observed that the air permeability values of samples were lower than of other samples in the UV treatment with the solutions containing TiO₂. From the SEM images in Figure 5, it was observed that TiO₂ particles penetrate the voids of the fabric, which is believed to reduce the air permeability by showing a coating effect on the fabric surface.

![Figure 2: Degrees of whiteness of cotton fabrics](image)

![Figure 3: Air permeability of samples](image)
3.3 Tensile strength measurements of fabrics
The results of tensile strength tests are presented in Figure 4. The results show that the strength values of treated fabrics did not significantly differ from those of the raw fabric. Although the UV treatment time did not seem to affect the strength values in general, it was observed that the strength values of the samples impregnated with the T+H solution decreased with increasing time. This is due to the reduction in strength values as a result of the attack of cellulose by oxidative radicals from H₂O₂ under UV light [22]. Since NaOH slows down the oxidation process, no significant loss of strength was observed in the processes containing NaOH [21]. The strength values of TiO₂ treated fabrics are generally higher than those of fabrics not treated with TiO₂. Tensile strength depends not only on the mechanical strength of fibres, but also on the frictional properties of fibres. The accumulation of TiO₂ particles in the fabric affects frictional properties [9]. According to this situation, the highest strength values were observed in the samples impregnated with the T+H+N solution. Except for the samples treated with the T+H solution, the UV process had no negative effect on strength.

3.4 Surface morphology of cotton fabrics
The surface morphology of the cotton fabric was observed using the scanning electron microscope (SEM) images. The impurities on the untreated cotton fabric are seen in Figure 5a. The surface of the untreated fibre appears to be a clean surface without particles (Figure 5a). The presence of TiO₂ particles was evident in the SEM images of the TiO₂ treated samples.

![Figure 4: Tensile strength values of samples](image1)

![Figure 5: SEM images of cotton fibre](image2)
3.5 FTIR analysis results of cotton fabrics

The FTIR analysis results of samples are presented in Figure 6. No significant peak differences were observed between the FTIR results of the raw cotton fabric and the TiO$_2$ coated fabric alone. The peaks of TiO$_2$ and cotton are similar [23, 24]. In Figure 6a, the OH functional groups in cellulose are shown by bands at around 3300 cm$^{-1}$. The FTIR spectroscopy, a surface sensitive technique, can detect the presence of wax and pectin. The peaks at 2916 cm$^{-1}$ represent wax in cellulose and hemicellulose, and the C-H stretching vibration in lignin, indicating the presence of wax in the fibre. The peaks at 1750 cm$^{-1}$ and 1200 cm$^{-1}$ represent the free form of carboxylate in hemicellulose in the structure of cotton [25]. The bending vibrations of C–H and C–O groups in cellulose polysaccharide rings are observed in absorption bands at around 1300 cm$^{-1}$. The (C–O) and (O–H) stretching vibrations of polysaccharide in cellulose are responsible for the intense peaks observed at 1029 cm$^{-1}$. The peak at 897 cm$^{-1}$ indicates that beta-glycosidic linkages exist between monosaccharides [26]. The peak at 690 cm$^{-1}$ is specific to the Rutile TiO$_2$ vibration (Figure 6b) [27, 28].

4 Conclusion

In this study, the photooxidation effect of TiO$_2$ on the bleaching of a cotton fabric was investigated.

Cotton fabrics were impregnated with different types of H$_2$O$_2$, TiO$_2$ and NaOH, and exposed to UV irradiation for different durations. The presence of TiO$_2$ on the surface of treated cotton samples was confirmed by the SEM images of samples. While TiO$_2$ alone yielded increases in whiteness values, its use in combination with H$_2$O$_2$ yielded higher whiteness values under UV irradiation. It was observed that the whiteness levels of all TiO$_2$-added samples were higher than of the raw fabric, which is consistent with the literature [11]. As a result, the whiteness of cotton fabric can be increased by using TiO$_2$ alone under UV irradiation, resulting in lower chemical consumption. The air permeability of treated samples decreased after the TiO$_2$ treatments, which was associated with the accumulation of TiO$_2$ into the pores on the fabric.

Since photooxidation take place at room temperature compared to conventional process performed at the boil, it has the advantage of energy savings. Furthermore, using less water and chemicals makes this method attractive. The bleaching process was conducted under UV light only at room temperature, and a more environmentally friendly, faster and more efficient method of bleaching cotton fabric was presented. It is believed that this method may provide benefits in reducing the carbon footprint of cotton bleaching in the textile industry and may contribute to sustainability.
References


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