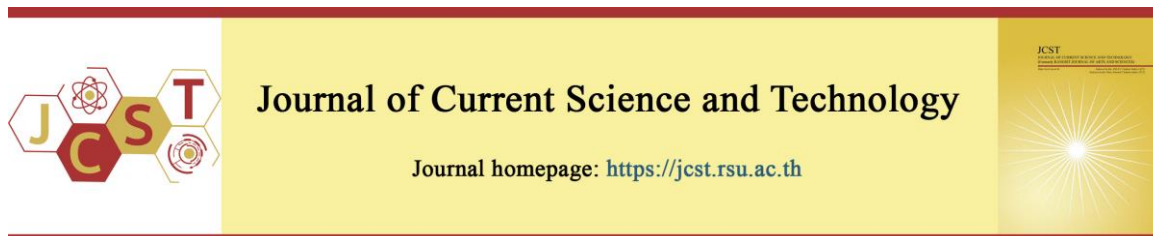


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Comparative Evaluation of Single and Hybrid Metal Oxide Nanoparticles for Multifunctional Hemp Textiles with Enhanced UV Protection and Self-Cleaning Performance

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Abstract

This study systematically investigated and compared the efficacy of single and hybrid metal oxide nanoparticles (NPs), including TiO₂, ZnO, and SiO₂, and their combinations, in imparting multifunctional properties to hemp fabrics. Despite increasing interest in multifunctional textile finishing, systematic comparative studies on single and hybrid metal oxide NP systems applied to hemp fabrics remain limited. For scalability and industrial applicability, commercial NPs were employed and applied to hemp textiles using a conventional pad-dry-cure method to evaluate wettability, UV protection, and photocatalytic self-cleaning performance. A commercial styrene–acrylic copolymer (SAC) emulsion was employed as a binder to facilitate the incorporation and adhesion of NPs onto the hemp fabric. XRD analysis confirmed the anatase phase of TiO₂, wurtzite structure of ZnO, and the amorphous nature of SiO₂, with crystallite sizes of 19.9, 36.2, and 22.4 nm, respectively. SEM–EDS examinations verified successful NP deposition and improved dispersion in hybrid and ternary systems. Contact angle measurements revealed a progressive increase in surface hydrophobicity from single to hybrid systems, with the ternary TiO₂–ZnO–SiO₂ nanocomposites exhibiting the highest water repellency due to hierarchical micro–nano surface structuring. UV protection was significantly enhanced after NP incorporation. The pristine hemp fabric exhibited moderate protection (UPF≈14), while the ternary nanocomposites achieved excellent protection (UPF 50++) with approximately 98–99% UV blocking, attributed to synergistic UV absorption and scattering effects. Assessment of photocatalytic self-cleaning based on methylene blue (MB) degradation showed superior performance for hemp finished with semiconductor NPs. The ternary nanocomposites exhibited the highest degradation efficiency (≈91%), followed by TiO₂–ZnO (≈89%), attributable to enhanced charge separation, reduced electron–hole recombination, and increased reactive oxygen species (ROS) generation. Overall, hybrid and ternary nanocomposite systems surpassed single oxides, highlighting the essential role of SiO₂ as a dispersion-supporting component. This work presents a practical and scalable approach for developing high-performance, multifunctional hemp textiles suitable for protective, healthcare, and sustainable apparel applications.

Keywords: hemp, titanium dioxide nanoparticles, zinc oxide nanoparticles, silicon dioxide nanoparticles, nanocomposite finishing, photocatalysis, wettability, UV protection, self-cleaning

1. Introduction

Natural cellulosic fibers have been utilized for centuries owing to their intrinsic advantages, including softness, high breathability, excellent moisture absorbency, moisture retention capacity, and ease of dyeing (Marinho, 2025). Among these fibers, hemp (*Cannabis sativa*) has recently attracted increasing attention due to its growing market demand and strong sustainability potential (Enarevba & Haapala, 2024). Although cotton remains dominant in the natural cellulose textile industry, its cultivation requires specific climatic conditions and substantial water resources, limiting its economic feasibility in many Southeast Asian regions (Schumacher et al., 2020). In contrast, hemp requires significantly lower amounts of water and pesticides, making it a more environmentally sustainable alternative. Hemp fibers exhibit several advantageous characteristics, including high absorbency, a distinctive texture, inherent ultraviolet (UV) protection, and favorable electrostatic and thermal properties. Hemp fibers consist of approximately 70–74% cellulose, 15–20% hemicellulose, 3.5–5.7% lignin, 0.8% pectin, and 1.2–6.2% wax (Manaia et al., 2019). These structural and compositional features make hemp a promising substrate for the development of advanced functional textiles (Rehan et al., 2020; Sasunthon et al., 2025). While textiles were traditionally used primarily for body covering, modern apparel increasingly emphasizes multifunctionality to enhance comfort, health, and overall quality of life. The growing demand for performance-driven textiles has stimulated extensive research into natural cellulosic materials with enhanced and multifunctional properties. In this context, nanotechnology has played a transformative role in the advancement of smart textile systems (Sarvalkar et al., 2022; Zhang et al., 2023). By enabling the manipulation and application of materials at the nanoscale (typically < 100 nm), nanotechnology offers unprecedented opportunities to tailor surface functionality and improve textile performance. One of the most effective strategies for developing multifunctional textiles involves the incorporation of nanomaterials into fiber substrates. Nanoparticles (NPs) have been widely employed for surface modification to impart functionalities such as antistatic behavior, UV protection, antimicrobial activity, far-infrared emission, flame retardancy, self-cleaning capability, and improved dyeability (Saleem & Zaidi, 2020). Among these nanomaterials, metal oxide NPs, including titanium dioxide (TiO_2), zinc oxide (ZnO), and silicon dioxide (SiO_2), have been extensively employed due to their high specific surface area, chemical stability, and multifunctional properties

(Mollick et al., 2023). TiO_2 NPs are widely recognized as efficient photocatalysts for environmental remediation because of their non-toxicity, chemical stability, cost-effectiveness, and favorable optical and electronic properties (Akram et al., 2024). TiO_2 exists in three crystalline phases: anatase, rutile, and brookite, with anatase (band gap ≈ 3.2 eV) exhibiting the highest photocatalytic activity under UV irradiation. Similarly, ZnO is an n-type semiconductor with a wide band gap (≈ 3.37 eV), high electron mobility, and large exciton binding energy (≈ 60 meV). These properties enable ZnO to provide multifunctional performance, including UV-blocking capability, antibacterial activity, and efficient photocatalytic oxidation (Klaykruayat et al., 2026). In contrast, SiO_2 is a wide-band-gap insulating oxide ($\approx 8\text{--}9$ eV) that does not exhibit intrinsic photocatalytic activity. Nevertheless, SiO_2 plays an essential role as a support material due to its high surface area, chemical stability, non-toxicity, and thermal resistance (El-Naggar et al., 2017). The incorporation of SiO_2 into TiO_2 - or ZnO -based systems enhances nanoparticle dispersion, increases surface hydroxyl group density, improves dye or pollutant adsorption, and facilitates interfacial charge transfer, thereby reducing electron-hole recombination. Consequently, TiO_2 - SiO_2 and ZnO - SiO_2 nanocomposites have demonstrated improved photocatalytic efficiency, durability, and reusability (Kara et al., 2024; Nautiyal et al., 2022; Sakti et al., 2024).

The development of multifunctional textiles incorporating photocatalytic metal oxide NPs presents significant opportunities for practical applications. Through a single finishing process, semiconductor oxides can impart simultaneous photocatalytic, self-cleaning, and UV-protective properties to textile substrates (Mushtaq et al., 2024). Self-cleaning functionality is particularly advantageous for daily wear, as well as for medical, hygienic, and military textiles (Dalawai, 2020). It reduces the need for frequent laundering, lowers water and detergent consumption, saves energy, extends fabric lifespan, and decreases operational costs. Furthermore, such systems contribute to sustainable textile technologies by minimizing chemical discharge and resource consumption. Self-cleaning cellulosic textiles have received substantial research attention due to their inherent susceptibility to staining, resulting from abundant surface hydroxyl groups that readily absorb moisture and contaminants (Diaa & Hassabo, 2022; Pakdel et al., 2023). Self-cleaning functionality can be achieved through two main mechanisms: (I) photocatalytic breakdown of organic contaminants and (II) superhydrophobic surface

modification to repel liquids. Numerous studies show that TiO₂ and ZnO-treated cotton fabrics can successfully dissolve stains, organic contaminants, and microbes by photocatalytic reactions under UV irradiation. In addition to self-cleaning capability, UV protection is a critical functional requirement for textile materials. Prolonged exposure to UV radiation can lead to severe health effects, including erythema, photoaging, and skin cancer, many of which can be mitigated by effective UV-blocking textiles (Mondal, 2022). Previous studies have examined both single and hybrid metal oxide systems, such as TiO₂, ZnO, SiO₂, TiO₂-ZnO, TiO₂-SiO₂, and MnO₂-ZnO to achieve enhanced multifunctional textile performance (Kara et al., 2024; Klaykruayat et al., 2026; Lam et al., 2021; Nitayaphat et al., 2018; Wang et al., 2024). Nonetheless, systematic comparative studies assessing single versus hybrid metal oxide NP systems on hemp fabrics are scarce. Consequently, we investigated the application of TiO₂, ZnO, SiO₂, and their hybrid and ternary combinations to hemp fabrics to systematically assess their wettability, photocatalytic self-cleaning efficiency, and UV protection properties. Commercially available NPs were utilized to examine their feasibility for practical and large-scale textile finishing processes. Overall, this study provides valuable practical insights into the development of scalable, multifunctional hemp-based textiles for advanced apparel, healthcare, and protective applications, while enhancing the value of hemp fibers through improved UV protection, self-cleaning functionality, and potential healthcare-related applications. However, several limitations of the present study should be acknowledged. In particular, the potential toxicological effects, as well as the wash fastness and long-term durability of the NP-finished textiles, were not investigated.

2. Objectives

This study aims to systematically investigate and compare the effectiveness of single and hybrid metal

oxide nanoparticles (NPs), including TiO₂, ZnO, SiO₂, and their combinations, in imparting multifunctional properties to hemp fabrics. The research focuses on evaluating the photocatalytic self-cleaning performance and UV protection of hemp textiles treated with commercially available NPs using a practical and industry-relevant pad-dry-cure finishing process. Particular emphasis is placed on elucidating the role of SiO₂ as a supporting component in hybrid nanoparticle systems, especially in improving nanoparticle dispersion, interfacial interactions, and overall functional performance. In addition, the study aims to achieve enhanced UV protection with an excellent UPF rating (UPF > 40) and improved photocatalytic degradation efficiency of methylene blue under UV irradiation, compared with untreated and single-NP-treated fabrics. The study also seeks to clarify the synergistic effects of binary and ternary metal oxide combinations and to demonstrate the potential of hemp, a commodity fiber in northern Thailand, as a sustainable textile substrate for multifunctional and high-value-added applications.

3. Materials and Methods

3.1 Materials

The primary textile material in this study was a plain-woven hemp fabric from Chiang Mai province, Thailand, with a density of 198 g/m² (36 warp and 28 weft yarns per inch). The hemp fabric was scoured using a Triton X100 non-ionic detergent at a concentration of 2.5 g/L for 30 min at 50°C to eliminate dust and dirt. Then, the hemp fabric was rinsed and dried at 80°C for 30 min. Metal oxide nanoparticles (NPs), including ZnO, TiO₂ in the anatase phase, and SiO₂, as well as methylene blue (MB), were purchased from Sigma-Aldrich (Germany). A commercial SAC (styrene-acrylic copolymer) emulsion (Appretan N96131, Vickers Laboratories Limited, England) was used as a binder for incorporating NPs into the hemp fibers.

Table 1 Experimental design

No.	Sample code	TiO ₂ (w/v)	ZnO (w/v)	SiO ₂ (w/v)	SAC (w/v)	Dry fabric weight (g)	Fabric weight after padding (g)
1	UT	-	-	-	-	1.98 ± 0.02	3.56 ± 0.04
2	BB	-	-	-	3	1.98 ± 0.02	3.56 ± 0.04
3	TT	1.50	-	-	3	1.98 ± 0.02	3.56 ± 0.04
4	ZZ	-	1.50	-	3	1.98 ± 0.02	3.56 ± 0.04
5	SS	-	-	1.50	3	1.98 ± 0.02	3.56 ± 0.04
6	TZ	0.75	0.75	-	3	1.98 ± 0.02	3.56 ± 0.04
7	TS	0.75	-	0.75	3	1.98 ± 0.02	3.56 ± 0.04
8	ZS	-	0.75	0.75	3	1.98 ± 0.02	3.56 ± 0.04
9	TZS	0.50	0.50	0.50	3	1.98 ± 0.02	3.56 ± 0.04

3.2 Methods

3.2.1 Functionalization of Hemp with Metal Oxide NPs

The individual and hybrid applications of metal oxide nanoparticles (TiO_2 , SiO_2 , and ZnO) were implemented on hemp fabrics using the pad-dry-cure technique. The pad-dry-cure technique was selected because it requires a lower binder content than other polymeric coating methods and is widely used in the textile industry. Based on the preliminary experiments, the coating formulations were prepared and subsequently applied to hemp fabric samples, as detailed in Table 1. Each coating formulation was subjected to sonication using an ultrasonic processor equipped with a 1/4" probe (VCX130, Sonics & Materials, Inc., USA) at an amplitude of 80% and a frequency of 30 kHz for 20 min under pulse conditions of 5 seconds on and 5 seconds off at room temperature to obtain a homogeneous solution free from particle agglomeration. A $10 \times 10 \text{ cm}^2$ scoured hemp fabric sample was immersed in the formulation solution for 30 min at room temperature. Thereafter, the wetted fabric sample was compressed using a padding machine (Labtec, Newave Lab Equipments Co. Ltd., Taiwan) at a pressure of 0.5 kg/cm^2 to achieve a wet pick-up of 80%. The padded fabric sample was then dried in a mini-stenter (LABTEC, Pingzhen City, Taiwan) at 100°C for 5 min, followed by a curing process at 150°C for 5 min. In this study, the total NP concentration was intentionally fixed at 1.5% (w/v) for all formulations to enable a systematic and fair comparison between single, binary, and ternary metal oxide systems under consistent overall loading conditions. For the hybrid systems, the NP components were equally partitioned by mass in order to simplify the comparative experimental design and evaluate the synergistic effects among different metal oxides. Nevertheless, differences in particle density, particle size, and specific surface area among TiO_2 , ZnO , and SiO_2 may result in variations in the actual particle number and effective surface coverage, even at identical mass concentrations. Therefore, the authors acknowledge that the comparisons may be influenced by particle-count-level differences, which represent a limitation of the present study.

3.2.2 Morphology Analysis

Analyzing the morphology of the metal oxide NP-treated fabrics is crucial for assessing the distribution of NPs on the hemp textiles. The crystallinity of the fabric treated with metal oxide NPs was analyzed via X-ray diffraction (XRD, Bruker AXS Model D8 Advance, Germany) utilizing Cu radiation ($1.5406 \text{ \AA}$) at 40 kV, scanning from 10° to 80° (2θ). The crystalline size of the samples was determined using Eq. (1) (Jariyaboon et al., 2023)

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D denotes the crystallite size (nm), K is the Scherrer constant (0.9), λ represents the wavelength of X-ray radiation (0.15406 nm), β is the value of the full width at half maximum (FWHM) peak (radians), and θ is the diffraction angle (radians). Furthermore, the surface morphology of the treated fabrics was analyzed using a field emission scanning electron microscope (FE-SEM, JEOL JSM7800F, Japan) at an accelerating voltage of 2.0 kV and a magnification of 5,000x. Prior to observation, a thin gold film was deposited on all samples via sputter coating. Elemental mapping was performed using SEM-EDS (Scanning Electron Microscope and Energy-Dispersive X-Ray Spectroscopy) with a JEOL JSM-IT700HR microscope from Japan. The accelerating voltage was set at 5.0 kV, with a magnification of 800x.

3.2.3 Wettability Analysis via Contact Angle Measurement

Surface wettability can be evaluated through contact angle measurement, reflecting the interaction between a liquid droplet and a solid surface (Mushtaq et al., 2024). The water contact angles of the hemp samples were measured using the sessile drop method with a Theta Lite tensiometer (Theta Lite TL100, Biolin Scientific, Gothenburg, Sweden). A $10 \mu\text{L}$ droplet of DI (deionized) water was ejected from a microsyringe located approximately 2 mm above the fabric sample surface, and its profile was recorded at 6 frames per second. The contact angle was automatically measured using OneAttension software (Biolin Scientific AB, Gothenburg, Sweden; software provided with the equipment). The given values denote the mean of five measurements obtained within the initial 3 seconds following the droplet's contact with the sample. The contact angle of a liquid droplet on a solid surface is determined by the balance of forces at the three-phase boundary (Diaa & Hassabo, 2022). This equilibrium arises from the interplay among the interfacial tensions at the solid-vapor, solid-liquid, and liquid-vapor interfaces. Generally, surfaces with contact angles lower than 90° are considered hydrophilic, as the liquid spreads easily due to strong solid-liquid interactions and higher surface energy. In contrast, contact angles greater than 90° indicate hydrophobic surfaces, where the droplet remains more spherical because of weaker solid-liquid interactions and lower surface energy. Therefore, increasing contact angle values correspond to enhanced hydrophobicity, while decreasing values indicate increased hydrophilicity.

Table 2 Classification of UVR protection efficacy (AATCC TM183-2010)

UPF	UVR transmittance (%)	UVR blocking (%)	UVR protection efficiency
40-50+	Less than 2.5	More than 97.5	Excellent
25-39	4.1-2.6	96.0-97.4	Very good
15-24	6.7-4.2	93.3-95.9	Good

3.2.4 UV Protection Measurement

The UVR protection efficacy of hemp fabric samples was assessed utilizing AATCC Test Method 183-2010, which quantifies transmittance in the 280-400 nm wavelength range using a double-beam scanning spectrophotometer (Camspec M550SPF, Spectronic Camspec Ltd., Leeds, UK). Each hemp sample (5 x 5 cm²) was placed in the sphere flush with the sample transmission port opening. Next, the sample was oriented in one direction for the first UV transmission measurement, then rotated 45° for the second measurement and a further 45° for the third. Therefore, each sample was measured in triplicate. Ultraviolet protection factor (UPF) values and UVR transmittances of fabric samples were documented. For each sample, three measurements were performed and the average of all scans was taken as the final value. Thus, higher UPF values indicate better UVR blocking in fabrics (Table 2). UPF values are calculated using Equation (2). Equations (3) and (4) show the average UVA (315-400 nm) and UVB (290-315 nm) transmittance values.

$$UPF = \frac{\sum_{290\text{ nm}}^{400\text{ nm}} R_{\lambda} S_{\lambda} \Delta\lambda}{\sum_{290\text{ nm}}^{400\text{ nm}} R_{\lambda} S_{\lambda} T_{\lambda} \Delta\lambda} \quad (2)$$

$$T(UVA) = \frac{\sum_{315\text{ nm}}^{400\text{ nm}} T_{\lambda} \Delta\lambda}{\sum_{315\text{ nm}}^{400\text{ nm}} \Delta\lambda} \quad (3)$$

$$T(UVB) = \frac{\sum_{290\text{ nm}}^{315\text{ nm}} T_{\lambda} \Delta\lambda}{\sum_{290\text{ nm}}^{315\text{ nm}} \Delta\lambda} \quad (4)$$

Where R_{λ} , S_{λ} , $\Delta\lambda$, and T_{λ} represent the relative erythema spectrum effectiveness, solar spectrum irradiance, wavelength interval (nm), and mean spectrum transmittance, respectively.

3.2.5 Self-cleaning Measurement

The photocatalytic self-cleaning performance of pristine hemp fabric and metal oxide NP-finished hemp fabrics under different treatment conditions was evaluated through the degradation of methylene blue (MB) dye. MB is frequently employed as a model dye in photocatalytic studies due to its distinct color and its suitability for quantitative evaluation of self-cleaning performance (Sakti et al., 2024). The

assessment was conducted by applying 0.01% (w/v) MB solution onto 5 × 5 cm hemp fabric specimens, followed by drying at room temperature. Thereafter, the stained samples were irradiated using a 125 W UV light source (Philips HPL-N lamp) at a distance of 23 cm for designated exposure periods of 0, 1, 3, and 5 h. The self-cleaning efficiency was determined by monitoring the change in color strength (K/S value) of the stained fabrics. The reflectance (%) of the hemp samples was measured using a spectrophotometer (GretagMacbeth Color i5, USA) and the K/S values were calculated according to the Kubelka–Munk equation (Eq. 5):

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (5)$$

where R represents the reflectance at the maximum absorption wavelength of MB, K is the absorption coefficient, and S is the scattering coefficient.

4. Results and Discussion

4.1 XRD Analysis

The XRD patterns of TiO₂, ZnO, and SiO₂ NPs are presented in Figures 1–3. The diffraction peaks of TiO₂ and ZnO were in good agreement with the standard JCPDS card numbers 21-1272 (TiO₂) and 36-1451 (ZnO), confirming the characteristic crystalline phases of the NPs. XRD data are usually used to determine the atomic structure and crystal structure of materials. The diffractogram of TiO₂ exhibited Bragg reflections at 25.3°, 37.9°, 48.2°, 53.9°, 55.2°, 62.7°, 70.2° and 75.1°, corresponding to the (101), (004), (200), (105), (211), (204), (220), and (215) tetragonal crystal planes of the anatase phase of TiO₂ (Kara et al., 2024). The polycrystalline ZnO demonstrated a hexagonal wurtzite structure, as evidenced by the presence of nine main peaks occurring at approximate positions 31.7°, 34.5°, 36.2°, 47.4°, 56.6°, 62.8°, 66.5°, 68.2°, and 69.2°, corresponding to the crystallographic planes (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively (Kara et al., 2024). Figure 3 presents the diffraction pattern of SiO₂ NPs, where a broad peak centered at 2θ ≈ 21.7° is assigned to the

(100) plane and no other diffraction peaks are detected, indicating the amorphous nature of SiO_2 in good agreement with the reference JCPDS file No. 89–0510 for SiO_2 (Ali et al., 2024). The absence of any other distinct diffraction peaks further confirms the lack of long-range crystallinity. The successful deposition of metal oxide nanoparticles onto hemp fabrics was further confirmed by XRD analysis. Figure 4(a) presents the XRD pattern of TiO_2 -coated hemp fabric, showing distinct diffraction peaks at approximately 25.7° , 38.1° , 48.9° , 54.2° , 55.8° , 63.2° , and 75.6° , corresponding to the (101), (004), (200), (105), (211), (204), and (215) planes, respectively.

These peaks verify the presence of crystalline anatase TiO_2 on the hemp substrate. Similarly, Figure 4(b) displays the XRD pattern of ZnO -coated hemp fabric, where characteristic peaks appearing at approximately 31.8° , 34.6° , 36.4° , 47.5° , 56.7° , 62.9° , 68.3° , and 69.4° correspond to the (100), (002), (101), (102), (110), (103), (112), and (201) planes, respectively, confirming the formation of crystalline ZnO nanoparticles on the hemp fabric surface. Furthermore, the average crystallite sizes calculated using the Debye–Scherrer equation (Table 3) were approximately 19.9 nm for TiO_2 , 36.2 nm for ZnO , and 22.4 nm for SiO_2 .

Table 3 Data used for crystalline size calculations of TiO_2 , ZnO , and SiO_2 NPs using the Scherrer equation

Nanoparticles	Wavelength (λ) (nm)	β (radians)	Peak position (2θ)	Size (nm)
TiO_2	0.15406	0.00714	25.3	19.9
ZnO	0.15406	0.00403	36.2	36.2
SiO_2	0.15406	0.00630	21.7	22.4

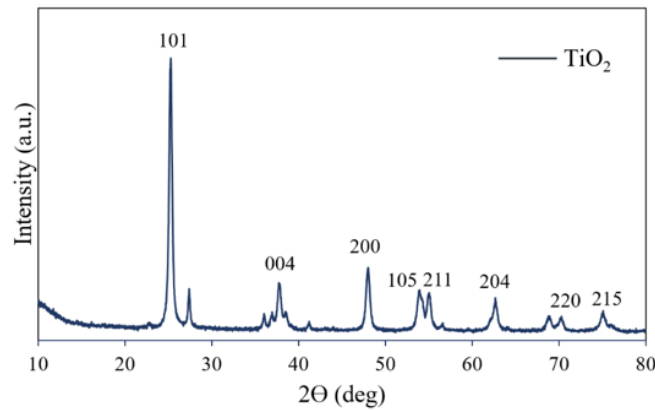


Figure 1 XRD pattern of TiO_2 powder

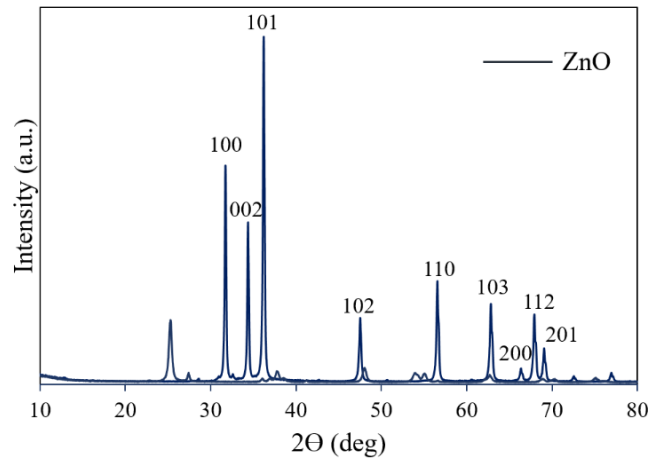


Figure 2 XRD pattern of ZnO powder

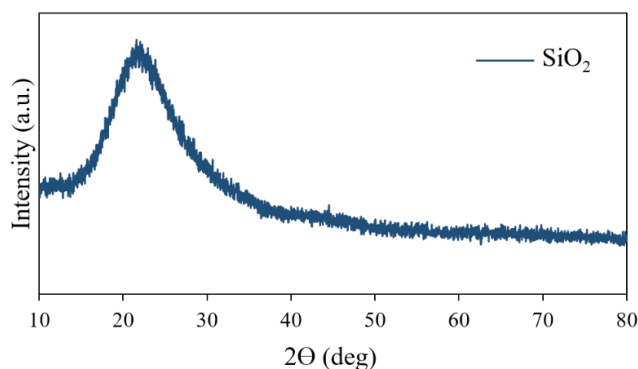


Figure 3 XRD pattern of SiO₂ powder

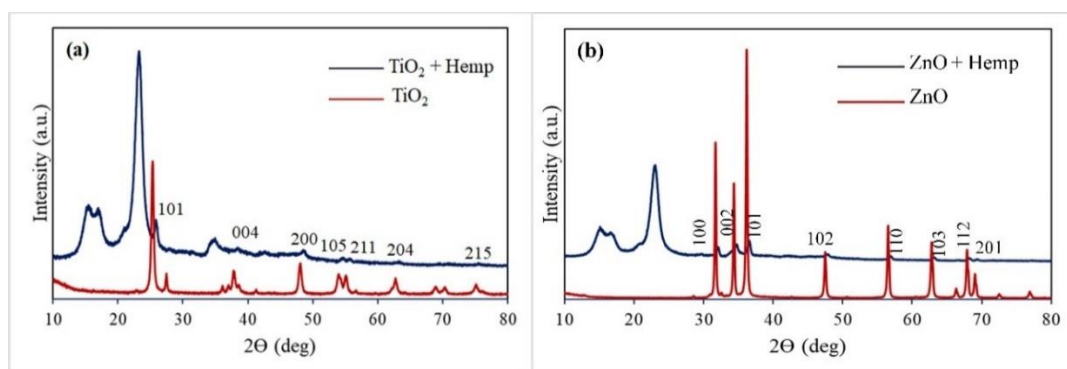


Figure 4 XRD patterns of hemp fabrics treated with (a) TiO₂ NPs and (b) ZnO NPs

4.2 SEM-EDS Analysis

Figure 5 presents the SEM micrographs of the treated hemp fabric samples under various finishing conditions at a magnification of x5000, illustrating the overall distribution of NPs on the fiber surface. The SAC-treated hemp sample (BB) displayed a noticeably smoother surface morphology, which can be attributed to the formation of a continuous polymeric layer that partially covered the native fibrillar grooves and minimized the appearance of micro-cracks. Upon incorporation of single metal oxide NPs (TT, ZZ, SS), the surface texture changed significantly. Small nano-sized protrusions and some particle aggregates could be seen on the SAC-coated surface, confirming that the nanoparticles were successfully deposited. TT and ZZ showed a fairly even distribution of small particles with little agglomeration. In contrast, SS showed a more uniform and fine texture without obvious large particles, which is consistent with the small and amorphous nature of SiO₂ (Nitayaphat et al., 2018). EDS analysis (Figure 6) further confirmed the presence of the respective elements (Ti, Zn, and Si) on the fiber surface, validating effective NP anchoring within the SAC matrix. The relatively low but detectable weight percentages indicate surface-level

deposition rather than bulk incorporation, which is desirable for surface-functional textile applications (Attia et al., 2017). More noticeable structural changes were observed in the hybrid nanocomposite systems (TZ, TS, and ZS). These samples showed denser and more uneven surface structures compared to the single-oxide systems. In particular, TS exhibited better particle dispersion, suggesting that SiO₂ may function as a structural spacer that helps reduce the aggregation of TiO₂ particles. Similarly, the ZS system presented a more compact and uniform textured surface than ZnO alone, indicating improved stabilization due to the synergistic interaction between the two oxides within the polymer matrix. The ternary TZS system exhibited pronounced morphological modification. The surface appeared more uniformly covered, and pore regions were partially filled by nanoparticle–polymer complexes. EDS spectra confirmed the simultaneous presence of Ti, Zn, and Si, demonstrating successful ternary integration. Overall, the SEM results confirm that adding NPs increases surface roughness and makes the surface structure more complex and uneven. This effect is especially clear in the binary and ternary systems, where a more hierarchical surface structure is formed.

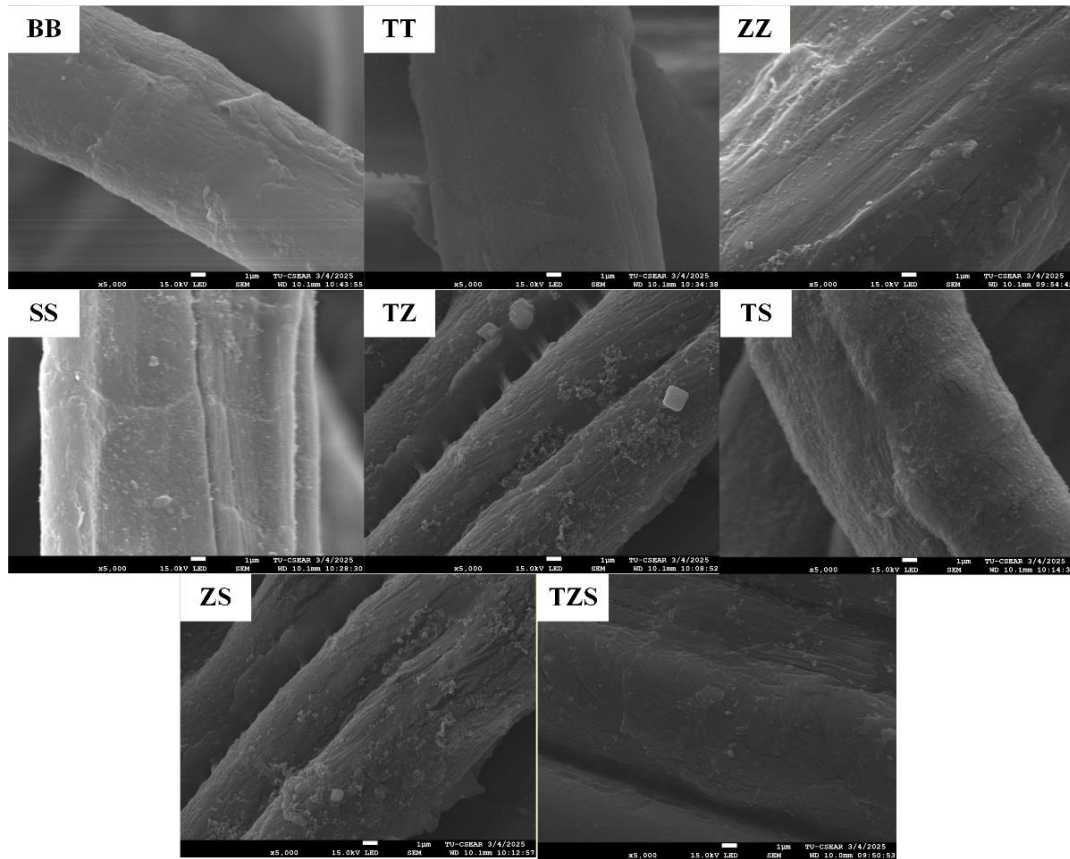


Figure 5 SEM micrographs of hemp fabric samples under different finishing conditions at a magnification of 5000x

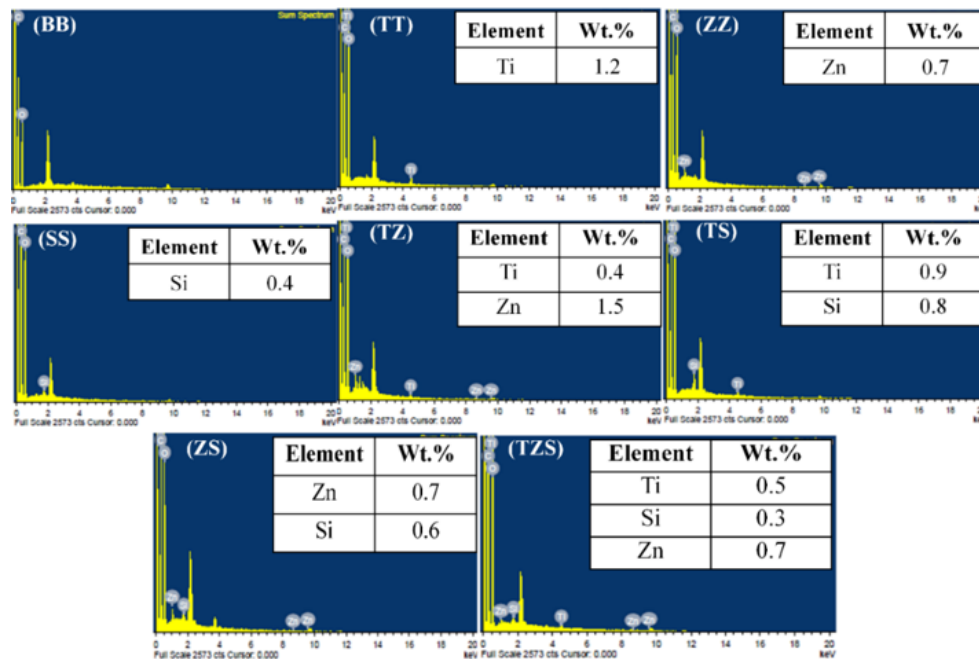


Figure 6 EDS patterns and elemental compositions of hemp samples under different finishing conditions

4.3 Wettability Analysis

The surface wettability of untreated and finished hemp fabrics was evaluated using static water contact angle measurements (Figure 7). The results clearly demonstrate that NP incorporation significantly altered the surface hydrophilicity of the hemp fabric samples. The untreated hemp fabric (UT) exhibited a low contact angle ($\approx 6.5^\circ$), confirming its inherently hydrophilic nature. This behavior is attributed to the abundance of hydroxyl groups present in cellulose and hemicellulose, which readily interact with water molecules through hydrogen bonding (Schellbach et al., 2016). Furthermore, the porous structure of the plain weave hemp fabric encourages rapid capillary wicking, resulting in immediate droplet spreading. Upon treatment with SAC (BB), a slight increase in contact angle was observed, suggesting that the binder reduced the surface energy of the hemp fibers and partially blocked the surface porosity of the textile substrate. Incorporation of single metal oxide nanoparticles further increased the contact angle, as shown in Figure 8. Among the three samples, SS showed only a slight increase in contact angle ($\approx 38^\circ$); however, it still demonstrated hydrophilic character, likely due to the high density of surface $-\text{Si}-\text{OH}$ groups (Gao et al., 2020). This outcome parallels previous research (Sakti et al., 2024), which demonstrated that augmenting the silica content imparted hydrophilic characteristics to the coated fabric, leading to the total dispersion of water

droplets. The ZZ exhibited a higher contact angle ($\approx 51.3^\circ$), while TT reached approximately 54° . The higher contact angle in TT compared to ZZ can be attributed to more uniform NP distribution and the formation of nanoscale asperities that enhance surface roughness. The increased roughness amplifies the apparent contact angle according to the Wenzel model, where surface structuring intensifies intrinsic wettability characteristics (Rananavare et al., 2025). Hybrid nanocomposite systems demonstrated a more pronounced enhancement in hydrophobicity. The ZS and TS showed moderate enhancement, while TZ reached nearly 86° . The highest contact angle was obtained for the ternary nanocomposite (TZS). This progressive increase indicates a synergistic effect among multiple NPs, likely associated with improved particle dispersion and the formation of hierarchical micro–nano surface roughness (Kara et al., 2024). The nano-scale roughness generated by the deposition of NPs decreases the actual contact area between the water droplet and the textile surface. This is because a reduction in the solid–liquid contact area results in an increase in the apparent contact angle (Mushtaq et al., 2024). Overall, the results indicate that single metal oxides moderately enhance surface hydrophobicity, whereas hybrid and particularly ternary nanocomposite systems yield a synergistic impact, resulting in moderately improved water repellency performance.

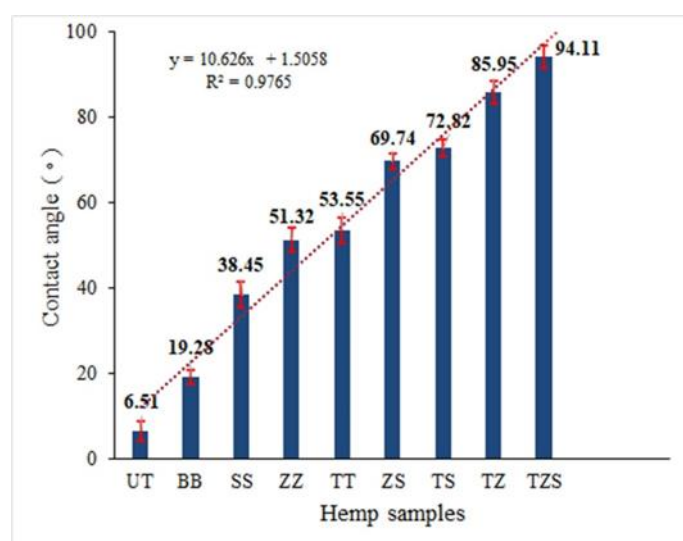


Figure 7 Contact angles of hemp fabric samples under different finishing conditions

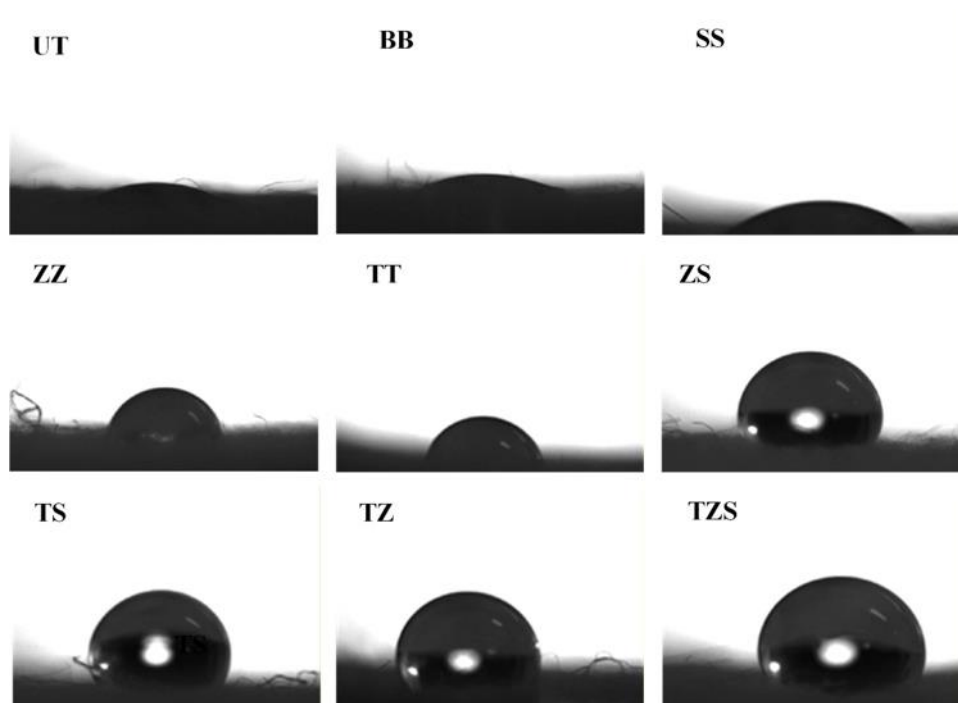


Figure 8 Hydrophobicity of finished hemp fabrics

4.4 UV Protection Measurement

Solar radiation comprises UV, visible, and infrared components (Khan et al., 2018). UVR is further classified into UVA (315–400 nm), UVB (290–315 nm), and UVC (100–290 nm). Due to the filtering effect of the upper atmosphere, UVC and most UVB are absorbed by the ozone layer. However, the residual UV radiation reaching the Earth's surface still possesses sufficiently high energy to cause biological damage and is associated with various skin disorders, including cancer (Saha et al., 2024). Therefore, evaluating the UV protection performance of apparel materials is of critical importance. The ultraviolet protection factor (UPF) rating system is widely employed in the textile and apparel industry to quantify the effectiveness of fabrics in blocking UVA and UVB radiation. According to AATCC Test Method 183–2010, textiles are classified based on their UPF values: fabrics with UPF 15–24 provide good protection, 25–39 indicate very good protection, and 40–50+ represent excellent protection against UV radiation. Higher UPF values correspond to superior UV-shielding performance. The UT exhibited a UPF value of 13.5, corresponding to moderate UV protection. This relatively low performance is attributed to the absence of effective UV-absorbing chromophores and the limited presence of conjugated carbon-carbon double bonds within the cellulose

structure of hemp fibers (Kibria et al., 2022). In contrast, incorporation of metal oxide NPs together with SAC significantly enhanced the UV-protective performance, as demonstrated by increased UPF values and reduced UVA and UVB transmission (Table 4). Treatment with SiO₂ nanoparticles (SS) resulted in only a slight improvement (UPF $\approx$ 24). This modest enhancement is expected because amorphous SiO₂ does not intrinsically absorb UV radiation; instead, it primarily enhances light scattering and forms a thin surface coating on the fibers (Dhineshababu et al., 2016; Gao et al., 2020). Thus, its contribution is mainly physical rather than photochemical. In comparison, fabrics coated with semiconductor metal oxides exhibited markedly improved UV shielding. The ZZ achieved substantial UVA and UVB blocking, with a UPF of approximately 33. This performance is attributed to the wide band gap energy of ZnO (3.37 eV), which enables strong absorption across both UVA and UVB regions (Klaykruayat et al., 2026). The TT demonstrated slightly higher protection (UPF $\approx$ 45), owing to the high refractive index and strong photon scattering capacity of TiO₂, particularly in its anatase phase (band gap 3.2 eV), which efficiently reflects and absorbs UV radiation (Rabiei et al., 2022). In addition, the slightly higher UPF performance of TT compared with ZZ may also be associated with

Table 4 UPF and UV protection class of finished hemp fabrics (AATCC TM183-2010)

Sample	UVA Blocking (%)	UVB Blocking (%)	UPF rating	UPF class	Thickness (mm)	Unit mass (g/m ²)
UT	83.25 ± 2.45	89.65 ± 1.72	13.48 ± 1.75	No class	0.67 ± 0.01	198 ± 0.52
BB	86.39 ± 2.82	92.48 ± 2.01	19.14 ± 2.41	Good	0.70 ± 0.01	205 ± 0.65
TT	91.09 ± 2.82	97.88 ± 1.98	45.29 ± 1.99	Excellent	0.73 ± 0.02	215 ± 0.99
ZZ	89.39 ± 1.89	96.25 ± 2.56	32.64 ± 2.02	Very good	0.74 ± 0.02	218 ± 1.20
SS	87.62 ± 2.12	95.41 ± 2.71	24.08 ± 2.91	Good	0.72 ± 0.01	212 ± 1.17
TZ	96.19 ± 1.84	98.71 ± 2.01	65.03 ± 1.93	Excellent	0.77 ± 0.02	232 ± 0.01
TS	94.35 ± 2.33	98.22 ± 1.99	52.44 ± 2.32	Excellent	0.76 ± 0.01	228 ± 0.01
ZS	93.48 ± 1.86	97.52 ± 2.44	44.39 ± 2.06	Excellent	0.75 ± 0.01	226 ± 0.01
TZS	97.92 ± 1.83	99.09 ± 2.01	82.25 ± 2.66	Excellent	0.78 ± 0.02	239 ± 0.01

variations in fabric structural parameters after nanoparticle deposition. As shown in Table 4, the incorporation of nanoparticles increased the fabric thickness and unit mass, which may further reduce UV transmission through the textile structure. Therefore, the enhanced UV-blocking performance observed in the treated fabrics is likely governed not only by the intrinsic UV-absorbing and scattering properties of the metal oxide nanoparticles, but also by the increased compactness of the fabric structure resulting from nanoparticle loading. Hybrid nanocomposite systems further enhanced UV protection through synergistic effects. Incorporating SiO₂ into TiO₂ or ZnO matrices improved NP dispersion, suppressed aggregation, and increased surface roughness and interfacial light scattering (Edan et al., 2025; Rangelova et al., 2022). Consequently, TS and ZS coatings achieved UPF values of approximately 52.4 and 44.4, respectively. Similar enhancements in UV shielding, attributed to improved particle distribution and coating uniformity, have been reported for silica-supported metal oxide systems (Liu et al., 2024). The TZ exhibited superior broadband absorption, achieving a UPF of approximately 65. The combination of these two semiconductors broadens the UV absorption spectrum and promotes multiple internal reflections within the coating layer, thereby increasing attenuation of incident radiation (Hirano et al., 2022). Among all samples, the ternary nanocomposite (TZS) demonstrated the highest performance, with UVA and UVB blocking efficiencies of 97.92% and 99.09%, respectively, and a UPF of about 82.3. This outstanding performance exceeds the minimum requirement for “excellent UV protection” (UPF > 40) according to AATCC TM183-2010. The exceptional UV shielding capability of the TZS coating is

attributed to the synergistic integration of (I) strong UV absorption by TiO₂ and ZnO and (II) enhanced light scattering, improved dispersion, and more homogeneous surface coverage provided by SiO₂. The multi-component nanocomposite system forms a dense and continuous protective barrier on the fiber surface, thereby effectively minimizing UV transmission through the fabric. Similar synergistic enhancements in multifunctional textile coatings have also been reported for hybrid metal oxide nanostructures (Araújo et al., 2021; Kara et al., 2024). In addition, previous studies by Kara et al. (2024) and Nautiyal et al. (2022) on TiO₂ - and ZnO-based nanocomposite coatings applied to cotton textiles demonstrated comparable enhancement trends; however, the UPF values achieved in the present study were comparatively higher. Collectively, these findings confirm that hybrid nanocomposite coatings outperform single metal oxide systems and highlight the critical supporting role of SiO₂ in maximizing UV protection efficiency through improved nanoparticle dispersion and interfacial interactions. Therefore, the TZS formulation represents a highly promising candidate for the development of advanced UV-protective hemp textiles suitable for outdoor, healthcare, and protective clothing applications.

4.5 Self-cleaning Property

The self-cleaning functionality of textiles plays a crucial role in maintaining daily health and hygiene. To evaluate the photocatalytic self-cleaning performance of hemp fabrics finished with single and hybrid metal oxide NPs, the degradation of MB was monitored by measuring the color strength (K/S) as a function of irradiation time (Figure 9). A decrease in the K/S value indicates progressive photocatalytic decomposition of the stain. The time-dependent visual

appearance of MB-stained hemp samples is presented in Figure 10. At 0 h, differences in color intensity among the samples were observed, likely due to variations in surface wettability induced by NP treatment, as supported by the contact angle measurements. Upon UV irradiation, the MB stains gradually faded over 1, 3, and 5 h. The UT and BB samples, which did not contain metal oxide NPs, exhibited only slight discoloration after 5 h of UV exposure, with a reduction of less than 10% in K/S values (Figure 9). This limited fading is primarily associated with direct photolysis of MB rather than true photocatalytic activity (Sakti et al., 2024).

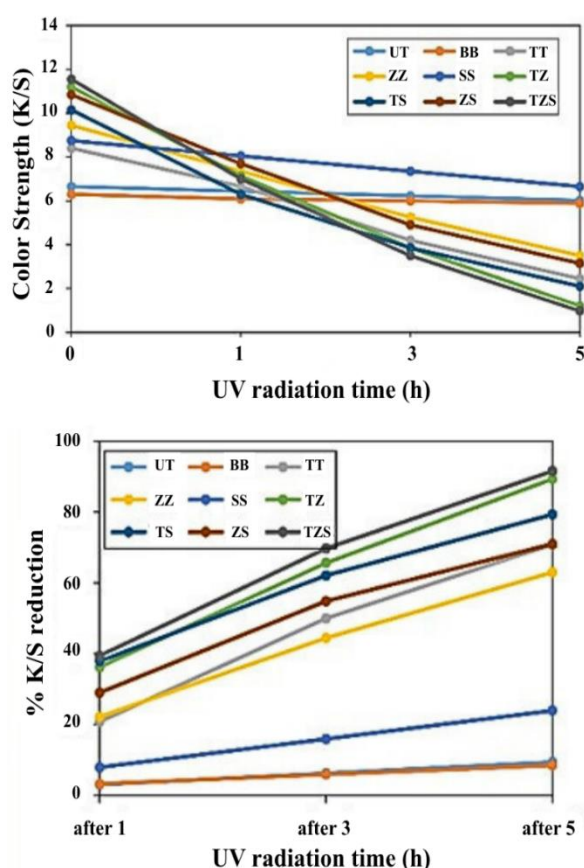


Figure 9 Time-dependent K/S and % K/S reduction of MB-stained hemp fabrics under UV irradiation.

Moreover, the SAC-only coating may hinder dye accessibility due to the formation of a thin polymeric layer on the fiber surface, resulting in low apparent self-cleaning efficiency. In contrast, hemp fabrics treated with metal oxide NPs showed pronounced MB degradation. Among the single metal oxides, TT demonstrated the highest degradation efficiency ($\approx 71\%$ K/S reduction), followed by ZZ

($\approx 63\%$), whereas SS exhibited comparatively low activity ($\approx 24\%$), consistent with the non-semiconducting nature of SiO_2 . The superior performance of TiO_2 and ZnO is attributed to their semiconductor properties, which enable the generation of reactive oxygen species (ROS), including hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\text{O}_2\bullet$), through photoinduced electron-hole pair formation under UV irradiation (Mushtaq et al., 2024).

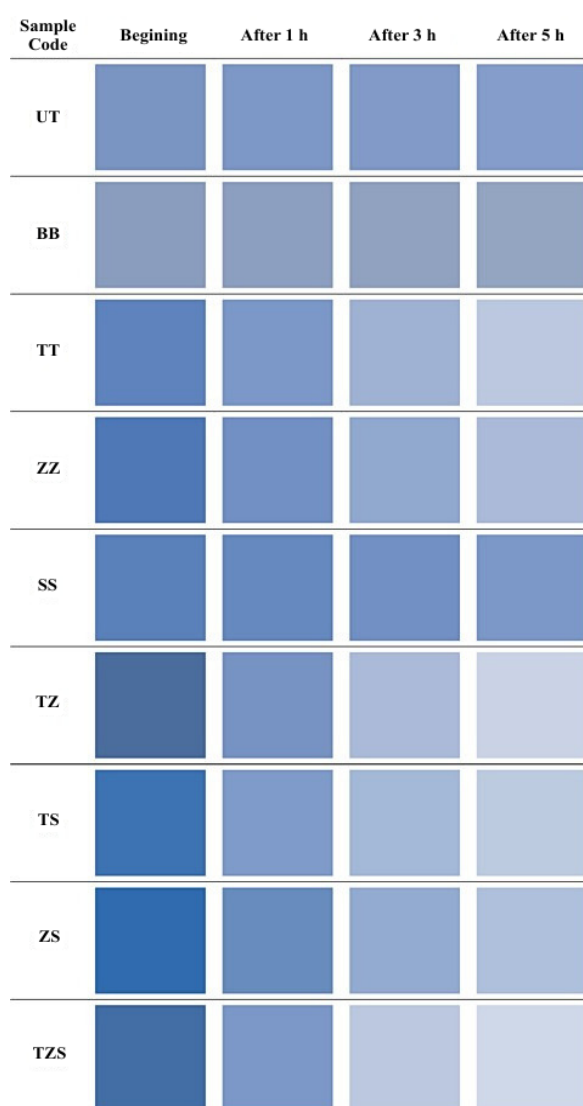


Figure 10 Time-dependent visual appearance of MB-stained hemp fabrics after UV irradiation

Upon UV excitation, electrons are promoted from the valence band to the conduction band, leaving behind positively charged holes. These charge carriers

participate in redox reactions with adsorbed oxygen and water molecules, producing ROS that oxidatively degrade organic dye molecules on the fabric surface. Therefore, the enhanced self-cleaning efficacy of TiO₂- and ZnO-treated fabrics is predominantly influenced by persistent ROS generation, effective charge separation, and ongoing photocatalytic oxidation, rather than merely by heightened surface hydrophobicity (Diaa & Hassabo, 2022). Notably, hybrid nanocomposite systems exhibited significantly enhanced degradation efficiency. The TZ system achieved approximately 89% K/S reduction, demonstrating a clear synergistic effect. The formation of a heterojunction interface between TiO₂ and ZnO facilitates charge separation, suppresses electron-hole recombination, and enhances ROS production. The incorporation of SiO₂ further improved performance in TS ($\approx 79\%$) and ZS ($\approx 71\%$) systems by promoting better NP dispersion, increasing effective surface area, and providing additional adsorption sites for MB molecules. The ternary nanocomposite system (TZS) exhibited the highest degradation efficiency ($\approx 91\%$), which can be attributed to synergistic photocatalytic interactions between TiO₂ and ZnO that enhance interfacial charge transfer and prolong electron-hole lifetimes, thereby maximizing ROS generation ($\bullet\text{OH}$, $\text{O}_2\bullet^-$, and h^+). Meanwhile, SiO₂ contributes by improving NP dispersion and facilitating dye adsorption at the catalyst-substrate interface, thereby accelerating oxidative degradation. Overall, the photocatalytic self-cleaning performance followed the order: TZS > TZ > TS > ZS > TT > ZZ > SS > BB $\approx$ UT. These results confirm the synergistic advantage of hybrid metal oxide nanocomposites in enhancing the self-cleaning functionality of hemp fabrics. In contrast, single-oxide systems exhibited moderate activity due to comparatively lower ROS production and faster electron-hole recombination rates. Our findings are consistent with previous studies (Kara et al., 2024; Nautiyal et al., 2022; Sakti et al., 2024). From a practical perspective, the photodegradation of the MB stain under UV irradiation enhances the susceptibility of the stained fabrics to removal by common household detergents. Consequently, hemp textiles may require less frequent washing, leading to potential reductions in energy consumption and detergent usage. In this regard, the present study was designed primarily to compare the photocatalytic performance of the treated hemp fabrics under controlled and reproducible UV irradiation conditions. Such conditions enabled systematic

comparison of the effects of different metal oxide NP systems. Nevertheless, further investigations under simulated solar irradiation or natural sunlight conditions are warranted in future work to assess their practical outdoor applicability and real-world photocatalytic performance.

5. Conclusion

This study demonstrated that the incorporation of metal oxide NPs significantly enhanced the multifunctional performance of hemp fabrics. For scalability and industrial applicability, commercial NPs were employed and applied to hemp textiles using a conventional pad-dry-cure method to evaluate wettability, UV protection, and photocatalytic self-cleaning performance. As a result, single and hybrid metal oxide NPs were successfully transferred to hemp fabrics with unit-mass increases of up to approximately 20%. XRD analysis confirmed the anatase phase of TiO₂, the wurtzite structure of ZnO, and the amorphous nature of SiO₂, with crystallite sizes of 19.9, 36.2, and 22.4 nm, respectively. SEM-EDS examinations confirmed successful nanoparticle deposition and improved dispersion in hybrid and ternary systems. Contact angle measurements revealed a progressive increase in surface hydrophobicity from single to hybrid systems, with the ternary TiO₂-ZnO-SiO₂ nanocomposite exhibiting the highest water repellency due to hierarchical micro-nano surface structuring. Single semiconductor oxides (TiO₂ and ZnO) improved UV protection and photocatalytic self-cleaning properties due to their intrinsic band gap characteristics and ability to generate reactive oxygen species under UV irradiation, whereas SiO₂ primarily contributed as a structural support material. The introduction of hybrid and ternary nanocomposite systems resulted in clear synergistic effects. The TiO₂-ZnO heterojunction facilitated efficient charge separation and suppressed electron-hole recombination, thereby enhancing ROS generation and photocatalytic efficiency. Meanwhile, SiO₂ improved nanoparticle dispersion, increased surface roughness, and enhanced dye adsorption, contributing to improved wettability control and UV shielding performance. Among all formulations, the ternary TiO₂-ZnO-SiO₂ nanocomposite exhibited the highest hydrophobicity, superior UV protection (UPF > 80), and the greatest MB degradation efficiency ($\approx 91\%$), confirming the advantage of multi-component systems over single oxides. The superior performance is due to improved charge separation and increased ROS formation, which promote more effective

photocatalytic degradation. Overall, this research provides a systematic comparative evaluation of single, binary, and ternary metal oxide NP systems on hemp textiles. The findings highlight the synergistic interactions between semiconductor oxides and silica support in enhancing multifunctional textile performance. The proposed finishing strategy is practical, scalable, and industry-relevant, offering a sustainable pathway for adding value to hemp fibers for advanced protective, healthcare, and high-performance textile applications. However, the durability and wash fastness of the nanoparticle coatings were not evaluated in this study. Future work should therefore investigate the long-term stability of the NP-coated fabrics, including the retention of UV protection and photocatalytic self-cleaning performance after repeated laundering cycles, to further assess their practical applicability.

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7. Abbreviations

Abbreviation	Full Term
BB	hemp treated with styrene-acrylic copolymer
K/S	color strength
MB	methylene blue
NP	nanoparticle
SAC	styrene-acrylic copolymer
SEM-EDS	scanning electron microscopy coupled with energy dispersive spectroscopy
SS	hemp treated with silicon dioxide
TS	hemp treated with titanium dioxide and silicon dioxide
TT	hemp treated with titanium dioxide
TZ	hemp treated with titanium dioxide and zinc oxide
TZS	hemp treated with titanium dioxide, zinc oxide, and silicon dioxide
UPF	ultraviolet protection factor
UT	untreated hemp
UVA	ultraviolet A

Abbreviation	Full Term
UVB	ultraviolet B
UVC	ultraviolet C
UVR	ultraviolet radiation
XRD	x-ray diffraction
ZS	hemp treated with zinc oxide and silicon dioxide
ZZ	hemp treated with zinc oxide

8. CRediT Statement

Pisutsaran Chitichotpanya: Conceptualization, Methodology, Writing – Original Draft, Writing – Review & Editing, Supervision, Funding Acquisition
Nattaya Vuthiganond: Investigation, Methodology, Data Curation, Formal Analysis, Resources, Visualization.

Chayanisa Chitichotpanya: Conceptualization, Methodology, Writing – Review & Editing, Investigation, Formal Analysis.

Saichalee Thaploka: Conceptualization, Essential Intellectual Contributor, Methodology, Validation, Formal Analysis.

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