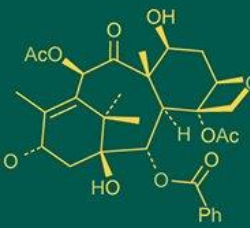
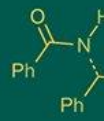


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UV protection properties of zinc oxide nano - coated cotton fabrics

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Abstract

An aqueous extract prepared from *Citrus reticulata* (orange) peel was used as an eco-friendly reducing and stabilizing medium for the green synthesis of zinc oxide nanoparticles (ZnO NPs), using zinc acetate and zinc nitrate as precursor materials. The synthesized nanoparticles were subsequently deposited onto 100% cotton fabric through the pad-dry-cure technique to impart enhanced ultraviolet (UV) protective properties. Among the different treatment conditions evaluated, the application of a 30% ZnO nanoparticle solution in combination with 2-6% citric acid or maleic acid resulted in superior UV-shielding performance. The presence and distribution of the nanoparticles on the fabric surface were further confirmed through SEM and EDX analyses. Compared with untreated cotton, the nanoparticle-finished fabrics demonstrated considerably improved ultraviolet protection factor (UPF) values, with the ZAC1-treated sample achieving the maximum UPF value of 48.20. The UV-protective functionality was retained after up to 10 washing cycles, indicating the potential of *Citrus reticulata* peel-derived ZnO nanoparticles as a sustainable and durable finishing agent for the development of UV-protective cotton textiles.

Keywords: Zinc oxide nanoparticles, green synthesis, *citrus reticulata* peel extract, cotton fabric, uv protection, ultraviolet protection factor (UPF), nano-coating, pad-dry-cure, sustainable textile finishing, washing durability

Introduction

Metal nanoparticle synthesis has emerged as an important area of research in nano-science due to the unique physical, chemical, and biological properties exhibited by nanoparticles. Over the past few decades, considerable attention has been focused on the synthesis and application of various metal nanoparticles, including iron oxide, silver, copper oxide, and zinc oxide nanoparticles. Among inorganic metal oxides, titanium dioxide (TiO₂), zinc oxide (ZnO), magnesium oxide (MgO), and calcium oxide (CaO) are particularly significant because of their excellent stability under harsh environmental conditions and their general recognition as safe for humans and animals. Among these, zinc oxide nanoparticles (ZnO NPs) have gained widespread interest owing to their versatile properties and broad range of applications in solar cells, sensors, piezoelectric devices, photodiodes, sunscreens, anti-reflective coatings, and photocatalytic systems (Sharma *et al.*, 2022) ^[10]. Furthermore, ZnO nanoparticles exhibit enhanced therapeutic efficacy when used in combination with other therapeutic agents. In the textile industry, ZnO serves as an effective functional modifier, contributing to the development of safe, durable, and multifunctional textiles for both apparel and technical applications (Mishra *et al.*, 2017) ^[8].

1.1 Properties of zinc oxide

Zinc oxide (ZnO), represented by the chemical formula ZnO, is an inorganic material widely known as a semiconductor with a broad bandgap of about 3.3 eV at room temperature. It is categorized as a II-VI semiconductor, as zinc and oxygen are elements from Groups II and VI of the periodic table, respectively. ZnO commonly occurs in two crystalline structures, wurtzite and zinc blende, among which the wurtzite phase is thermodynamically more stable under normal environmental conditions. In its natural form, ZnO is generally observed as a white powder with good transparency in the visible wavelength range and the ability to dissolve in both acidic and alkaline media. Its notable optical and electronic characteristics

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have contributed to its application in optoelectronic technologies, including visible-light-emitting devices and white LEDs. In addition, ZnO nanoparticles are considered relatively non-toxic and are known for properties such as self-cleaning ability and distinctive UV-visible surface plasmon resonance. These characteristics have increased their potential for diverse applications in technological, environmental, and biomedical fields. Zinc oxide nanoparticles (ZnO NPs) possess remarkable UV-absorbing and UV-scattering properties, which are among their most significant functional characteristics. Their nanoscale dimensions and high surface-area-to-volume ratio enable stronger interactions with ultraviolet radiation, thereby providing more effective UV shielding than conventional ZnO particles. In addition to their ability to protect against UV radiation, ZnO NPs demonstrate broad-spectrum antimicrobial activity against a variety of Gram-positive and Gram-negative bacteria and fungal species. Their antimicrobial effectiveness has also been reported against highly resistant bacterial spores (Aslam *et al.*, 2019) ^[1]. When incorporated into textile finishing processes, ZnO nanoparticles can provide fabrics with several desirable functional properties, such as UV protection, antibacterial performance, flame resistance, water repellency, and self-cleaning characteristics. The combination of these multifunctional properties makes ZnO NPs promising materials for the development of advanced protective textiles and high-performance composite materials.

1.2 Orange peel: a potential source for green synthesis of zinc oxide nanoparticles

Nagpur orange (*Citrus reticulata*) is a well-known mandarin variety predominantly cultivated in the Vidarbha region of Maharashtra, India. It is recognized for its distinctive dimpled peel and sweet, succulent pulp and is considered an important commercial citrus fruit. The crop is generally harvested during two major seasons, namely the Ambiya crop, which is relatively sour and available from September to December, and the Mrig crop, which is comparatively sweeter and harvested around January. Citrus fruits constitute the third-largest fruit crop in India, following banana and mango. In addition to the Vidarbha region, Nagpur mandarin is cultivated in several other parts of the country, including the Satpura Hills, Darjeeling, and Coorg. However, the processing and consumption of oranges generate considerable quantities of agro-industrial waste, with approximately 30-50% of the fruit being discarded as peels, seeds, and residual pulp. Improper disposal of this waste in landfills or water bodies can contribute to environmental pollution and result in the loss of potentially valuable bioactive resources. Therefore, the utilization of orange peel waste as a sustainable raw material for the green synthesis of zinc oxide nanoparticles offers an environmentally friendly approach to waste valorisation, while simultaneously reducing pollution and promoting sustainable resource management (en.wikipedia.org/wiki/Nagpur orange).

1.3 UV finishing of textiles

Recent advancements in nanotechnology have introduced innovative opportunities in textile finishing for the development of high-performance and multifunctional fabrics. The incorporation of nanostructured materials into conventional textile substrates can improve their physical,

mechanical, and functional characteristics. In particular, the use of green-synthesized nanoparticles as textile surface coatings has attracted significant research interest because of their ability to impart desirable functionalities, including ultraviolet (UV) protection, antimicrobial activity, self-cleaning performance, and other value-added properties. However, the retention of these functionalities after repeated laundering remains a major challenge in the application of nanoparticle-based textile finishes. The application of suitable cross-linking agents can provide an effective solution to this problem by enhancing the fixation and durability of nanoparticles on textile fibers. In addition to improving wash resistance, cross-linking treatments may contribute to the easy-care characteristics of cotton fabrics by strengthening the interaction between the cellulose substrate and the deposited nanoparticles. Therefore, ZnO nanoparticle-treated cotton fabrics can be subjected to a pad-dry-cure finishing process using environmentally friendly cross-linking agents. During the curing stage, the cross-linking treatment facilitates stronger chemical interactions between the cellulose chains and ZnO nanoparticles, thereby improving the adhesion and retention of nanoparticles on the fabric surface. As a result, the treated cotton fabric can exhibit enhanced durability and better retention of its functional properties following repeated washing. This approach offers considerable potential for the development of durable, multifunctional, and environmentally responsible textile materials (Sarwar *et al.*, 2019) ^[9].

2. Materials and methods

2.1 Selection and preparation process of *Citrus reticulata* peel powder

Nagpur orange (*Citrus reticulata*) is a commercially important mandarin variety predominantly cultivated in and around Nagpur, Maharashtra, India. The fruit is recognized by its characteristic dimpled peel and sweet, succulent pulp, contributing to Nagpur's reputation as the "Orange City." The trees generally undergo flowering during the monsoon period and produce two major fruiting seasons. The first harvest, referred to as the Ambiya crop, occurs from September to December and is generally characterized by a comparatively tangy flavour. The second harvest, known as the Mrig crop, begins in January and produces fruits with a relatively sweeter taste. For the present study, fresh Nagpur orange fruits were obtained from a local market in Dharwad, Karnataka. The fruits were initially rinsed thoroughly with distilled water to eliminate adhering dirt and other surface contaminants. The peels were then manually removed from the fruits and collected separately. The collected orange peels were dried in a hot-air oven at 35 °C for 48 hours to reduce their moisture content. The dried material was subsequently pulverized using a laboratory grinder and passed through an ASTM standard No. 30 sieve with a mesh size of 600 µm to achieve a relatively uniform particle size. The resulting orange peel powder was transferred to an airtight container and stored under suitable conditions until it was required for subsequent experimental procedures (Mahmoud *et al.*, 2016) ^[7].

2.2 Selection of precursors

Based on the research studies, zinc acetate dihydrate and zinc nitrate hexahydrate were selected as the zinc precursors for the present study. Powder obtained from *Citrus reticulata*

peels was utilized as a natural catalyst in the green synthesis of zinc oxide nanoparticles.

2.2.1. Zinc acetate dihydrate

Zinc acetate is a zinc-based inorganic compound represented by the chemical formula $\text{Zn}(\text{CH}_3\text{COO})_2$ and is frequently available in the hydrated form, zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$. It is typically characterized as a white crystalline solid with moderate solubility in water and can undergo thermal decomposition to form zinc oxide (ZnO). The compound can be synthesized through the reaction of zinc oxide with acetic acid and is commercially available in both anhydrous and dihydrate forms. Owing to its high degree of purity, good solubility, and ability to serve as an effective source of zinc during the formation of ZnO , zinc acetate is extensively utilized as a precursor for the preparation of ZnO nanoparticles. In addition to its role in nanomaterial synthesis, it has applications in pharmaceutical formulations, where it may function as an astringent. Zinc acetate and other acetate-based compounds are also valuable precursor materials for producing high-purity chemicals, catalysts, and advanced nanostructured materials. Consequently, zinc acetate has considerable significance in both scientific research and industrial applications (American Elements)

2.2.2 Zinc nitrate hexahydrate

Zinc nitrate is an inorganic zinc compound represented by the chemical formula $\text{Zn}(\text{NO}_3)_2$ and is commonly encountered in its hydrated form, zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$. It is generally present as a white crystalline solid with a highly deliquescent nature, allowing it to readily absorb moisture from the surrounding atmosphere. The compound exhibits high solubility in water and is also soluble in alcohol, which makes it suitable for use in a variety of chemical preparation and nanomaterial synthesis processes. Zinc nitrate finds applications in several industrial sectors, including the production of pharmaceuticals, dyes, catalysts, and other specialty chemicals. As a nitrate salt, it also possesses oxidizing characteristics. Its high purity and ability to undergo thermal decomposition to yield zinc oxide make it a useful precursor for the preparation of ZnO nanoparticles and other advanced nanostructured materials. Consequently, zinc nitrate is widely utilized in areas such as nanotechnology, catalysis, and materials science research (American Elements).

2.3 Standardization of protocol for green synthesis of zinc oxide nanoparticles

For the green synthesis of ZnO nanoparticles using zinc acetate dihydrate as the precursor, 0.04 M zinc acetate dihydrate was dissolved in 80 mL of Milli-Q water. The solution was continuously stirred for four hours in the presence of an aqueous extract prepared from *Citrus reticulata* peels. During the synthesis process, sodium hydroxide (NaOH) solution was added gradually in a dropwise manner to regulate and maintain the desired pH of the reaction mixture (Chitha *et al.*, 2015) ^[2].

In a similar procedure, 0.03 M zinc nitrate hexahydrate was dissolved in 80 mL of Milli-Q water and mixed with the aqueous extract of *Citrus reticulata* peels. The reaction mixture was stirred continuously for five hours to facilitate the formation of ZnO nanoparticles. The pH of the solution

was controlled by the gradual addition of sodium hydroxide solution in a dropwise manner throughout the synthesis process (Koao *et al.*, 2015) ^[5].

2.4 Optimization of treatment conditions for finishing of cotton fabrics

2.4.1 Selection of fabric

Cotton is a natural textile fiber obtained from the seed hairs of the cotton plant and is widely recognized for its versatility and extensive use in the global textile industry. It can be manufactured into fabrics with a variety of structures and weave patterns. India is one of the world's leading cotton-producing countries, contributing approximately 22% of global cotton production. Owing to its inherent breathability and moisture-absorbing capacity, cotton fabric can effectively absorb perspiration and facilitate the transfer of body heat and moisture to the surrounding environment, thereby providing comfort to the wearer. Considering these desirable properties, a medium-weight, 100% cotton fabric with a plain weave structure was selected as the substrate for the application of green-synthesized zinc oxide nanoparticles prepared using *Citrus reticulata* (orange) peel extract.

2.4.2 Desizing and scouring

The cotton fabrics were subjected to a combined one-bath desizing and scouring treatment using the specified formulation. The treatment was carried out at elevated temperatures, where the alkaline medium containing hydroxide compounds and caustic soda facilitated the simultaneous removal of sizing agents and impurities from the fabric. Desizing is an essential preparatory process in which sizing materials applied to cotton yarns during weaving are eliminated, thereby improving the fabric's absorbency and making it suitable for subsequent wet processing and finishing treatments.

Recipe

Sodium hydroxide - 2% owf

Sodium carbonate - 2% owf

Turkey red oil - 2% owf

Material to Liquor Ratio (MLR) - 1: 20

Time - 85 min

Temperature - 80 to 90 °C

The cotton fabric was first weighed, and the required quantities of sodium hydroxide, sodium carbonate, and Turkey Red Oil (TRO) were determined based on the fabric weight and the specified material-to-liquor ratio (MLR). The calculated amounts of sodium hydroxide and sodium carbonate were dissolved in water, and the resulting solution was heated to approximately 80 °C. The fabric was subsequently immersed in the prepared alkaline bath and treated for 85 minutes while maintaining the temperature within the range of 80-90 °C. Following the treatment, the fabric was thoroughly rinsed with running water to eliminate residual alkali and other processing chemicals. Finally, the washed fabric was shade-dried under ambient conditions for further processing.

2.5 Selection of cross-linking agents

Cross-linking agents are used as durable press finishing agents to produce wrinkle resistant cotton fabrics and garments in the textile industry.

2.5.1 Citric acid

Citric acid ($C_6H_8O_7$) is a naturally occurring organic acid that is abundant in citrus fruits, particularly lemons and oranges. It is a tricarboxylic acid and plays an essential biochemical role as an intermediate in the citric acid cycle, a metabolic pathway involved in energy production in aerobic organisms. Citric acid is commercially produced on a large scale, with global annual production exceeding two million tonnes. Owing to its versatile properties, it is extensively utilized as an acidifier, flavour enhancer, preservative, and chelating agent in various industrial applications. In the textile field, citric acid is also recognized for its ability to facilitate crosslinking between hydroxyl groups present in cellulose fibres, particularly under elevated temperature conditions (Ramachandran, 2019) ^[11].

2.5.2 Maleic acid

Maleic acid (MA), also known as cis-butenedioic acid, is an organic dicarboxylic acid containing two carboxyl functional groups and has the molecular formula $C_4H_4O_4$. It exists as the cis-isomer of butenedioic acid, while fumaric acid represents its corresponding trans-isomer. Maleic acid is primarily utilized as an intermediate in the production of fumaric acid and has relatively limited applications compared with maleic anhydride, from which it is derived. In textile applications, maleic acid acts as a bifunctional carboxylic acid that can form an ester bond with cellulose but, by itself, has limited ability to establish crosslinks between cellulose chains. Therefore, sodium hypophosphite (NaH_2PO_2) is employed as a catalyst to promote the crosslinking reaction. The catalyst facilitates reactions involving the carbon-carbon double bond ($C=C$) of maleic acid that has already been esterified with cellulose. Subsequent curing at elevated temperatures promotes the formation of crosslinks within the cotton cellulose structure, resulting in the incorporation of phosphorus-containing linkages into the cellulose network (Hameed *et al.*, 2016) ^[3].

2.6 Pad-dry-cure method

The pad-dry-cure technique is a commonly employed textile finishing process used for applying various functional coatings and chemical finishes to fabric. In this method, the textile material is immersed in the prepared nano-coating formulation and subsequently passed through the rollers of a padding mangle to remove excess solution and achieve uniform application. The treated fabric is then subjected to drying, followed by curing under controlled conditions to enhance the fixation and durability of the applied finish. The detailed procedure adopted in the present study is described below:

Recipe

Material to Liquor Ratio (MLR) - 1:20

Ultraviolet protection factor classification

Table 2: Classification of Ultraviolet Protection Factor (UPF) Ratings and Corresponding UV Radiation Protection Levels

UPF range	Effective UVR transmission (%)	% UV radiation blocked	Protection category	UPF rating
15 to 24	6.7-4.2	93.3-95.9	Good protection	15, 20
25 to 39	4.1-2.5	96.0-97.4	Very good protection	25, 30, 35
40 to 50, 50+	<2.5	97.5 to 98+	Excellent protection	40,45,50, >50

Synthesized Zinc oxide NPs - 4% stock solution

Citric acid/Maleic acid - 2, 4, 6% each owf

The cotton fabric samples were separately treated with ZnO nanoparticle solutions containing each of the two crosslinking agents. The fabric specimens were immersed in the respective treatment solutions for 10 minutes and subsequently passed through a pneumatic padding mangle (R. B. Electronic and Engineering, Mumbai) operating at a speed of 3 m/min and a pressure of 1 kg/cm². The padding process was carried out to eliminate excess solution and maintain a wet pick-up of approximately 70%. Following padding, the treated fabrics were shade-dried and subsequently cured for 10 minutes at three different temperatures, namely 40 °C, 50 °C, and 60 °C.

2.7 Application of nanoparticles on the cotton fabric

The selected cotton fabric was wet-sized and subsequently scoured to remove impurities and prepare the material for further treatment. Fabric specimens measuring 25 × 25 cm were prepared and treated using the pad-dry-cure method. A 4% stock solution of the nano-formulation was prepared for each of the two precursors, and the fabric samples were treated separately according to the parameters specified below.

Parameters and variables for coating of cotton fabrics with green ZnO NPs

Table 1: Experimental Parameters and Treatment Variables Used for ZnO Nanoparticle Coating of Cotton Fabrics

Parameters	Variables
Nano concentrations (4%)	5,10,15,20,25,30
Method of application	Pad-Dry-Cure
Eco-friendly Cross linking agents	Citric acid and Maleic acid
Cross linking agents (%)	2,4,6
Curing temperature	40 °C, 50 °C, 60°C

2.8 UV properties of green ZnO nano-coated cotton fabrics

2.8.1 Ultraviolet protection factor (UPF)

The Ultraviolet Protection Factor (UPF) is a measure used to evaluate the effectiveness of a textile material in protecting the skin from harmful ultraviolet (UV) radiation. In the present study, the UPF values of the ZnO-treated cotton fabrics were determined to assess their UV radiation-blocking efficiency. The measurements were carried out using a LabSphere UV-100F Ultraviolet Transmission Analyzer in accordance with the AATCC 183 standard. The instrument measures the spectral transmission of fabric samples over the wavelength range of 280-400 nm and provides the UPF rating along with the average transmittance values for UVA and UVB radiation.

2.9 Statistical analysis used for the study

Cotton fabric samples were coated with green-synthesized zinc oxide (ZnO) nanoparticles and subsequently evaluated for their physical and multifunctional properties. The experimental data obtained from the various tests were statistically analyzed using Windostat 9.2 software. Standard deviation was calculated to assess the variation and consistency of the experimental results.

Furthermore, Analysis of Variance (ANOVA) for a two-factor factorial experiment was employed to determine the influence of green-synthesized ZnO nanoparticle coating on the physical, mechanical, and functional properties of the treated fabrics and to establish the statistical significance of the differences among the experimental variables. The wash durability of the treated fabric samples was evaluated by conducting a paired *t*-test. In the experimental design, green-synthesized zinc oxide nanoparticles were considered as the main treatment (T_1), while the cross-linking agents (T_2) and application method (T_3) were considered as sub-treatments.

The individual and combined effects of these treatments on the physical, mechanical, and functional properties of the fabric samples were statistically assessed.

3. Results and Discussion

3.1 Functional properties of green ZnO nano-coated cotton fabrics

Green-synthesized ZnO nanoparticles were prepared using two different precursor materials and applied to cotton fabrics in combination with two separate crosslinking agents. The resulting ZnO nanoparticle-coated fabrics were evaluated under laboratory conditions to determine their multifunctional properties. The experimental data obtained from the various tests were subsequently subjected to statistical analysis. For ease of identification and analysis, the treated fabric samples were assigned specific codes, and the details of the sample numbering system are presented below:

Table 3: Sample Codes and Treatment Conditions of ZnO Nanoparticle-Coated Cotton Fabrics

Samples	Treatments
ZnO-1 precursor	Green ZnO NPs with zinc acetate dihydrate precursor
ZnO-2 precursor	Green ZnO NPs with zinc nitrate hexahydrate precursor
Control	Untreated
ZAC1/ ZAC2	ZnO NPs with zinc acetate dihydrate treated with citric acid
ZAM3/ZAM4	ZnO NPs with zinc acetate dihydrate treated with Maleic acid
ZNC5/ZNC6	ZnO NPs with zinc nitrate hexahydrate treated with citric acid
ZNM7/ZNM8	ZnO NPs with zinc nitrate hexahydrate treated with maleic acid

3.2 Standardization of protocol for green synthesis of Zinc oxide nanoparticles

The aqueous extract obtained from *Citrus reticulata* (orange) peel is rich in bioactive compounds, particularly phenolics and flavonoids, which possess the ability to participate in the reduction and stabilization of metal ions. Owing to the presence of these phytochemicals, the aqueous orange peel extract was employed as a biological catalyst for the green synthesis of zinc oxide (ZnO) nanoparticles. Zinc acetate dihydrate and zinc nitrate hexahydrate were selected as the two zinc precursor materials for the present study.

According to the study reported by Nava *et al.* (2017) [6], the phytochemical constituents present in *C. reticulata* peel extract interact with the zinc precursor compounds during the synthesis of ZnO nanoparticles. Upon heating the reaction mixture at temperatures ranging from 80 to 90 °C, the hydroxyl groups of the aromatic compounds present in the extract interact with zinc ions and facilitate the formation of intermediate zinc-organic complexes. These complexes subsequently undergo thermal decomposition, resulting in the formation and release of ZnO nanoparticles. Thus, the naturally occurring phytochemicals present in the orange peel extract play an important role in facilitating the green synthesis of zinc oxide nanoparticles.

3.3 Optimization of treatment conditions for finishing of cotton fabric

Zinc oxide (ZnO) is a wide-band-gap semiconductor characterized by a band-gap energy of approximately 3.37 eV, a high excitation energy of about 60 meV, and good chemical and thermal stability. These distinctive properties have made ZnO a promising nanomaterial for diverse applications, including optoelectronic and optical devices,

piezoelectric systems, surface acoustic wave filters, photonic crystals, photodetectors, gas sensors, solar cells, antibacterial applications, and UV-protective textile finishes.

In the present study, ZnO nanoparticles were green-synthesized using *Citrus reticulata* peel extract with zinc acetate and zinc nitrate precursors at a concentration of 4%. To optimize the concentration of the nanoparticle treatment, 100% cotton fabric was selected and treated with varying concentrations of the prepared ZnO nano-solutions using the pad-dry-cure method. The curing temperature and concentration of the cross-linking agents were subsequently optimized to obtain enhanced functional performance of the treated fabrics.

Among the different treatment conditions investigated, cotton fabrics treated with a 30% concentration of ZnO nano-solution in combination with 2%, 4%, and 6% concentrations of citric acid and maleic acid as cross-linking agents demonstrated superior UV-protection properties. The fabrics cured at 40 °C, 50 °C, and 60 °C also exhibited improved UV-protective performance. The formation and deposition of ZnO nanoparticles on the treated cotton fabrics were further confirmed through scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis.

SEM and EDX analysis

The surface morphology of both untreated and ZnO nanoparticle-treated cotton fabrics was examined using scanning electron microscopy (SEM) to evaluate the changes resulting from the treatment. As illustrated in Fig. 1, the control fabric exhibited a relatively smooth and clean surface, whereas the treated fabrics showed the presence of a thin and fairly uniform layer of nanoparticles deposited on

the fibre surface. Noticeable deposition of ZnO nanoparticles was observed in the fabrics treated using both ZnO-1 and ZnO-2 precursors. The EDX spectra of the fabrics treated with citric acid and maleic acid confirmed the presence of zinc, oxygen, and carbon elements, whereas these elements were not detected in the untreated control fabric. The elemental composition obtained for the different fabric samples is presented in Table 1.

The EDX analysis showed distinct signals corresponding to zinc and oxygen, along with carbon, confirming the formation and deposition of zinc oxide on the treated fabric surfaces. The elemental composition of the samples was determined from the EDX spectra. Among the tested samples, the highest zinc content was recorded for ZAC2 (9.55%), followed by ZAM3 (9.08%) and ZAC1 (8.45%), while the lowest zinc content was observed in ZAM4

(7.78%). The control fabric also exhibited the presence of other elemental constituents; however, no zinc was detected in the untreated sample.

For the fabrics treated using the ZnO-2 precursor, the EDX spectra exhibited prominent zinc signals ranging from 8.82% to 8.21%, while the oxygen content varied between 42.63% and 40.21%. The detection of zinc and oxygen in the treated samples provides evidence for the presence of ZnO nanoparticles on the fabric surface. The EDX micrographs further supported the elemental composition of the synthesized ZnO nanoparticles. The presence of zinc and oxygen, with zinc concentrations ranging from 7.58% to 9.55%, indicates successful deposition of ZnO with no significant evidence of impurities. The corresponding EDX results are presented in Fig. 2.

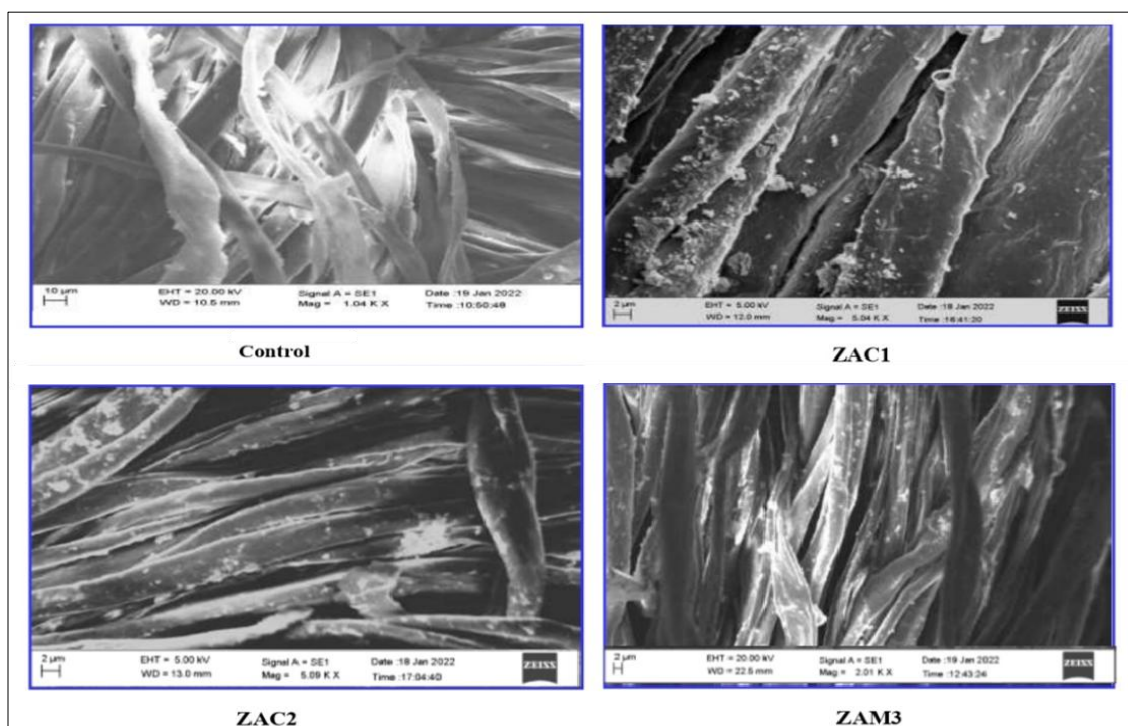


Fig 1: Scanning electron microscopy analysis of green zinc oxide nanoparticles

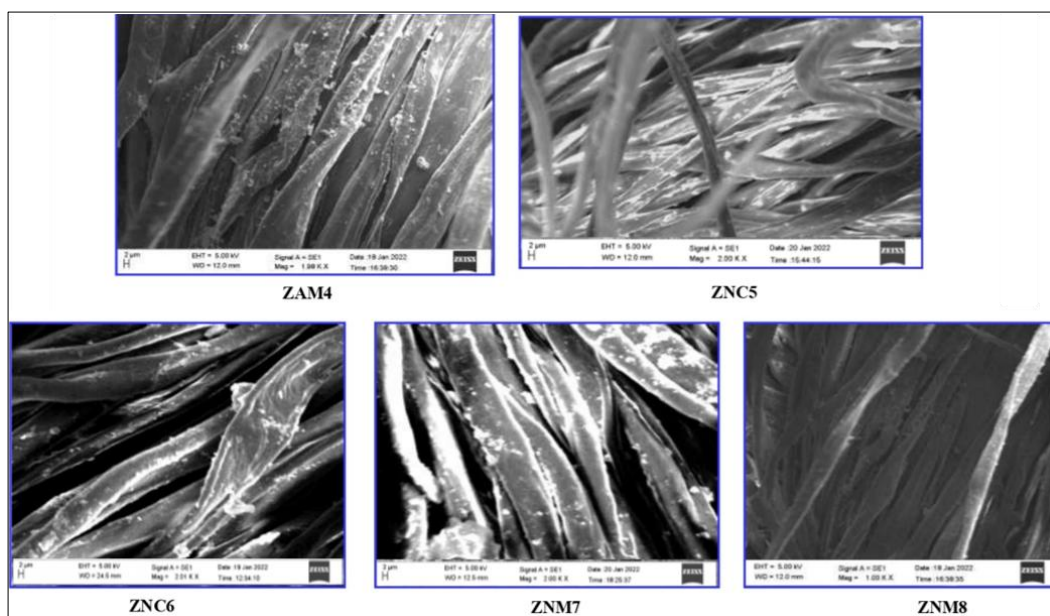


Fig 2: (Contd.....) Scanning electron microscopy analysis of green zinc oxide nanoparticles

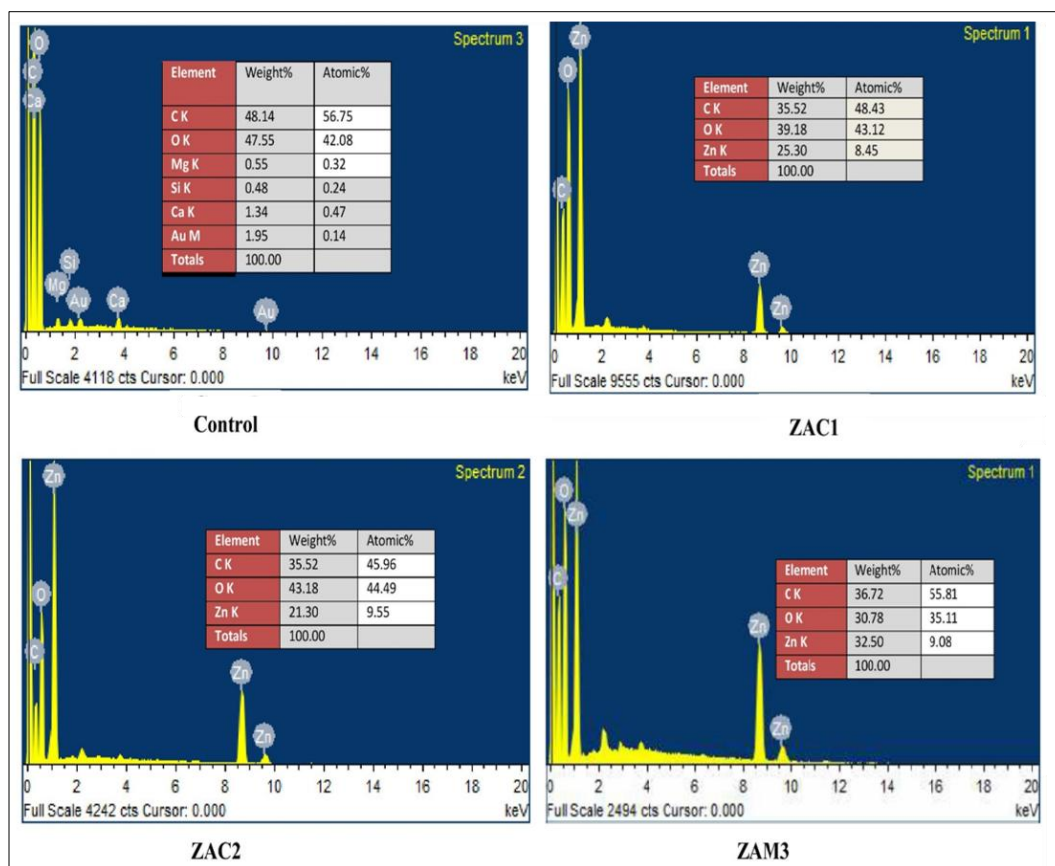


Fig 3: Energy dispersive X-ray analysis of green zinc oxide nanoparticles

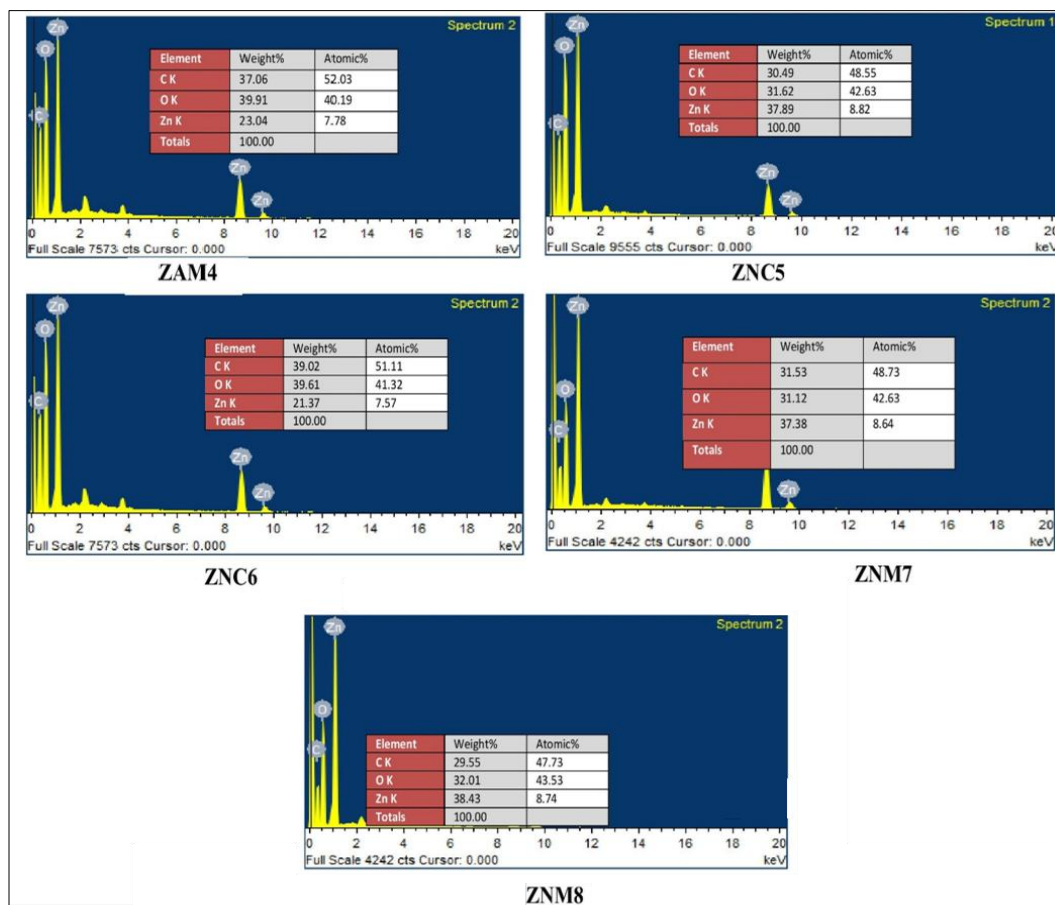


Fig 4: Cont: Energy dispersive X-ray analysis of green zinc oxide nanoparticles

Table 4: EDX Analysis of green ZnO nano- coated cotton fabrics

Samples	Crosslinking agents	Atomic weight%					
		Zn	O	C	MgK	Ca K	Au M
Control	-	-	42.08	56.75	0.32	0.47	0.14
ZnO-1 precursor							
ZAC1	Citric acid	8.45	43.12	48.43	--	--	--
ZAC2		9.55	44.49	45.96	--	--	--
ZAM3	Maleic acid	9.08	35.11	55.81	--	--	--
ZAM4		7.78	40.19	52.03	--	--	--
ZnO-2 precursor							
ZNC5	Citric acid	8.82	42.63	48.55	--	--	--
ZNC6		8.35	40.21	51.44	--	--	--
ZNM7	Maleic acid	8.21	42.06	49.73	--	--	--
ZNM8		8.74	43.53	47.73	--	--	--

3.4 Ultraviolet protection factor (UPF)

Cotton is widely preferred among natural fibres because of its desirable characteristics, including softness, skin comfort, biodegradability, moisture absorbency, and overall wearability. In the present study, zinc oxide (ZnO) nanoparticles synthesized using two different precursors, designated as ZnO-1 and ZnO-2, were prepared and applied to cotton fabrics as a functional coating.

From Table 2, it is evident that the UV profile of the treated samples was higher with an excellent protection factor compared to the control. It can also be observed that from all the samples, ZAC1 has registered the highest UPF value

with 48.20 per cent followed by ZAC2 with 47.87%. From ZnO-2 precursor coated fabrics, ZAC5 (41.04%), ZAC6 (40.39%) have shown lower values of UV protection against UVA and UVB percentage blocking. It is also observed that higher values of UV absorbance were obtained with the ZnO-1 precursor compared to the ZnO-2 treated fabrics. The statistical analysis of the data indicated that there is a highly significant difference between nanoparticles and crosslinking agents at 1 percent level of significance.

Kathirvelu *et al.* (2009) ^[4] found similar results when they explored the UV protection of zinc oxide nanoparticles and their application to cotton and polyester/cotton woven and knitted fabrics. In all cases, the woven fabrics performed better than the knitted materials in terms of UV blocking. This was apparent for both 100 percent cotton and 100 percent polyester/cotton mixes. The authors came to the conclusion that ZnO nanoparticles can absorb UV light, making it easier for UV light to reach fabrics.

Tran Thi and Lee (2017) ^[12] used the microwave approach to manufacture a new UV-blocking and self-cleaning cotton fabric coated with zinc oxide (ZnO). The results reveal that the identified UV protection factors indicate excellent UV-blocking properties of the ZnO-coated textile fabric synthesized at pH 6-7, 8-9 and 10-11 with UPFs of 222.52, 162.68 and 202.57, respectively. The findings also suggest that cotton fabric treated with ZnO has a high capacity for water absorption, making it perfect for self-cleaning textiles that resist coffee stains. rewrite for plagiarism checking

Table 5: Ultraviolet protection factor of green ZnO nano-coated cotton fabrics

S. No	Precursor	Cross linking agent	Sample	Percentage Blocking		Mean UPF	UPF Rating	Protection category
				UVA	UVB			
1			Control	9.66	11.68	8.92	<15	poor
2	ZnO-1	Citric acid	ZAC1	2.42	2.09	48.20	40 -50	Excellent
3			ZAC2	2.58	2.17	47.87	40 -50	Excellent
4		Maleic acid	ZAM3	2.71	2.29	44.27	40 -50	Excellent
5			ZAM4	2.53	2.34	43.59	40 -50	Excellent
6	ZnO-2	Citric acid	ZNC5	2.65	2.48	41.04	40 -50	Excellent
7			ZNC6	2.71	2.54	40.39	40 -50	Excellent
8		Maleic acid	ZNM7	2.70	2.42	42.02	40 -50	Excellent
9			ZNM8	2.66	2.39	42.25	40 -50	Excellent

ANOVA Table

Table 6: Analysis of Variance for the Effects of Nanoparticles and Cross-Linking Agents on the Ultraviolet Protection Factor (UPF) of Cotton Fabric

Particulars		UPF
C.D. (0.01)	Nano particles (NPs)	44.85**
	Cross Linking agents (CLA)	3663**
	NPs x CLA	11.27
	C.V.%	11.47

**Highly significant @ 1 per cent level

3.5 Wash durability of the green ZnO nano-coated cotton fabrics for UPF

protective finish are presented in Table 3. The ZnO

The results of the wash durability assessment of the UV-nanoparticle-coated fabrics exhibited significantly higher UPF values and provided excellent UV protection compared with the untreated control fabric. However, the effectiveness of the finish gradually decreased with an increase in the number of washing cycles. The *t*-test results indicated a significant difference in UV protection among the different wash cycles. The application of ZnO nanoparticles resulted in a substantial improvement in the UV-protective performance of the fabrics, which was maintained up to 10 washing cycles. However, after 15 or more washing cycles, a noticeable reduction in UV protection was observed, as shown in Fig. 3.

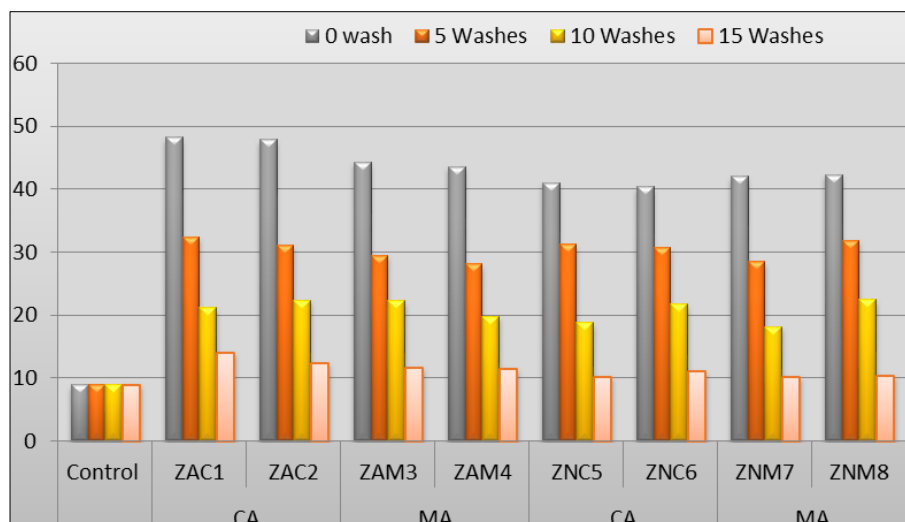


Fig 3: Wash durability of the green ZnO nano-coated cotton fabrics for UPF

Table 7: Wash durability of the green ZnO nano-coated cotton fabrics for UPF

S.No	Precursor	Crosslinking agent	Samples	0 wash	After wash			
					5 Washes	10 Washes	15 Washes	
1	ZnO-1	Citric acid	Control	8.92	8.92	8.92	8.92	
2			ZAC1	48.20	32.45	21.22	13.95	
3		Maleic acid	ZAC2	47.87	31.17	22.33	12.44	
4			ZAM3	44.27	29.46	22.27	11.65	
5	ZnO-2	Citric acid	ZAM4	43.59	28.12	19.84	11.53	
6			ZNC5	41.04	31.21	18.85	10.19	
7		Maleic acid	ZNC6	40.39	30.76	21.73	11.17	
8			ZNM7	42.02	28.47	18.13	10.20	
9			ZNM8	42.25	31.92	22.42	10.43	
		Mean		39.83	27.94	19.39	11.00	
		Standard Deviation		11.91	7.65	4.64	1.78	
		T-test			11.93**	10.61**	14.27**	

**Highly significant @ 1 per cent level

4. Conclusion

The results demonstrate that green synthesized ZnO nanoparticles effectively enhance the ultraviolet (UV) protective properties of cotton fabric. Among the different concentrations tested, a 30% ZnO nanoparticle coating produced the best performance, providing an excellent UPF rating of 40-50. Cotton fabrics coated with ZnO nanoparticles synthesized from the ZnO-1 precursor exhibited higher UV protection than those coated with the ZnO-2 precursor. The coated fabrics also showed good wash durability, retaining effective UV protection up to 10 laundering cycles, although a gradual decline in protection was observed after 15 washes. The superior UV-blocking performance is attributed to the nanoscale size of the ZnO particles, which provides a larger surface area for absorbing and scattering harmful UV radiation. According to Rayleigh's scattering theory, nanoparticles in the size range of 20-40 nm are particularly effective in scattering UV light, thereby improving the UV protection of the fabric. These findings confirm that green synthesized ZnO nanoparticles are a promising, eco-friendly, and durable functional finish for developing UV-protective cotton textiles.

5. References

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