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ORIGINAL PAPER

Synthesis of different nanometals using Citrus Sinensis peel (orange peel) waste extraction for valuable functionalization of cotton fabric

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Abstract

An eco-friendly process was used to impart multifunctional properties to cotton fabric using Citrus Sinensis peel (orange peel) extract. Two solvents have been used to prepare the extract, namely water and ethanol. Both extractions have been used as reducing and stabilizing agents in the synthesis of silver and zinc oxide nanoparticles. Prepared extracts and synthesized nanoparticles have been characterized using different techniques such as total phenol content, antioxidant activity, particle size analyzer, Fourier transform infrared, transmission electronic microscopy, and X-ray diffraction. The cotton fabric was treated with orange peel extraction, silver nanoparticles, and zinc oxide nanoparticles loaded with chitosan. The treated cotton samples were characterized by scanning electron microscopy, UPF value, antimicrobial activity, mosquito repellent effect, and self-cleaning properties.

Keywords Cotton fabric · Citrus Sinensis peel extract · Antibacterial · Antioxidant · Mosquito repellent · Self-cleaning · Ultraviolet protection

Introduction

Over the last few decades, natural fibers have attracted worldwide interest from researchers to produce soft, breathable, and multi-functional textile materials for use in a variety of fields (Kalia et al. 2011; Mohamed and Hassabo 2015a). On the other hand, natural fibers, especially cotton, are more susceptible to a wide variety of adverse effects, including transmission from disease, allergic reactions, and degradation of textiles, because of their frequent interaction with human skin, wide area, and potential for humidity absorption (Salam et al. 2019; Shahid ul et al. 2013). By undergoing photo-induced aging and yellowing, they can also lose performance properties. Therefore, it has become highly urgent and necessary for textile scientists to apply various innovative chemicals to produce a multi-functional cotton fabric (Abdel-Halim et al. 2011; El-Sayed et al. 2021; Saad et al. 2021a, b; Zayed et al. 2021, 2022).

Many chemicals that are used in textile finishing processes contain harmful substances. These chemicals pose a significant threat to all of us as they are introduced into the environment, which has accelerated research efforts to discover eco-friendly natural finishing agents (Anwar and Alghamdi 2020; Ragab and Hassabo 2021).

Orange, the tasty, juicy fruit belonging to the Rutaceae family, is known as Citrus Sinensis. Citrus Sinensis is one of the largest and most commonly cultivated fruit crops (Hussain et al. 2015). Orange peel is made up of cellulose, pectin, hemicellulose, coumarins, lignin, essential volatile oils, carotenoids, phenolic components, etc. (Hou et al. 2013). Because of bio-components in orange peel, orange peel extracts can be used to treat cotton fabric to enhance the functional properties of cotton fabric such as. antimicrobial activity (Wolela 2020), UV protection (Hou et al. 2013), and mosquito repellant properties (Gupta and Singh 2017).

In the modern century, nano-biotechnology is an increasingly growing research area with diverse applications in different scientific fields (Tanaka and Chujo 2014). Nowadays, chemical and biological processes are the most common approaches for the preparation of nanomaterials. Although

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the chemical procedures are very effective, the synthesis of nanomaterials is currently limited because of their adverse environmental effects (Yonezawa 2018). Otherwise, biological methods of synthesis of nanomaterials, such as the synthesis of metal nanoparticles requiring the use of species from living organisms, are considered environmentally sustainable and do not have any harmful impact on the environment (Bonnia et al. 2016). Besides, synthesized nanoparticles are deemed safe for use. Among the different biological species, plant extracts are environmentally friendly materials that have gained significant attention for the development of nanoparticles (Maqbool 2021; Mittal et al. 2013).

Orange peel extract can be used as a reducing agent for the synthesis of nanoparticles such as silver and zinc oxide nanoparticles because orange peel extract consists of many active phytochemicals that can be used as a reducing and stabilizing agent (Anwar and Alghamdi 2020). The application of metal and metal oxide nanoparticles on the fabric greatly affects the efficiency of the finished fabric. AgNPs and ZnONPs have received significant interest in providing multifunctional properties to cotton fabric such as antimicrobial activity and UV protection (Rehan et al. 2020).

This study aimed to treat the cotton fabric with Citrus Sinensis peel extract in the presence and absence of synthesized nanometals (AgNPs and ZnONPs) to give multi-functional properties to the fabric. The synthesis of nanometals was carried out through the biological reduction using the Citrus Sinensis peel extract, which offers an effective capping agent to the stability and viability of the synthesized nanoparticles.

Experimental

Materials

Cotton fabric (220 g/m^2) was purchased from Ghazel El-Mahala for Textile Industry Co., Egypt. Orange fruits (Citrus Sinensis) were purchased from the Egyptian local market. The orange peel has been obtained immediately after the fruit has been peeling.

Ethanol (95%), acetic acid, sodium carbonate, citric acid, sodium hypophosphite (SHP), silver nitrate, and sodium carbonate were provided from Fluka. Zinc acetate was purchased from El Nasr pharmaceutical chemicals Co.; chitosan low molecular weight (100,000–300,000) was purchased from ACROS Co.

Folin–Ciocalteu reagent was purchased from Sigma Chemicals Co.; tannic acid and methanol were purchased from Merck. All the chemicals and reagents were used as received without purification.

All the chemicals and reagents were used without any further purification.

Methods

Preparation of orange peels (Citrus Sinensis) extract

Oranges were thoroughly washed with water to remove the dust. Then, they were peeled. The peels were cut into small pieces. Two solvents were used to extract dyes and active ingredients from orange peels, namely water and ethanol 95%. The aqueous extract was prepared by placing 200 gm of orange peels into 1000 ml of water and heated to 100 °C for 4 h. Alcoholic extract was prepared by placing 200 gm of orange peels into 1000 ml of ethanol in the Soxhlet system and heated to 70 °C for 4 h. After that, the orange peel extracts were filtered using Whatman filter paper. Then, the extraction was stored at 4 °C. And then, the extract was filtered with stainless steel sieve (400 meshes) and cooled to room temperature, after that stored at 4 °C.

Phenolic colorants and pectin are the major molecules in orange peel extracts (Abd El-Rahman et al. 2019; Oreopoulou and Tzia 2007). Up to now, total phenolic phenols in orange peel have only been calculated and recorded (Moussaïd et al. 2011). However, certain phenolic dye components do remain unidentified (Moussaïd et al. 2011). Orange peel extracts without further purification were used in this analysis.

Synthesis of silver nanoparticles (AgNPs) using orange peel extract

AgNPs were synthesized using orange peel extractions as a reducing agent and silver nitrate salt solution as an Ag source. Ten milliliters from orange peel extract (aqueous or alcoholic) was added to aqueous silver nitrate solution (95 ml; 0.002 M) and kept for 10 min at 80 °C. To monitor the best condition of synthesizing AgNPs, the pH medium was changed from 4 to 10. An indicator of the formation of the Ag nanoparticles was the visual transition from the initially translucent yellow solution to a dark brown solution. The synthesized nanoparticle was further confirmed using a UV–Vis spectrophotometer (Moodley et al. 2018).

Synthesis of zinc oxide nanoparticles (ZnONPs) using orange peel extract

Zinc oxide nanoparticle has been synthesized as reported in our previous work (Zayed et al. 2021). In brief, 70 ml of orange peel extract (aqueous or alcoholic) was placed in a beaker, and the pH medium was adjusted to 8, 10, or 12 using sodium carbonate. Then, the temperature was raised to 70 °C, and at this temperature 30 ml of 1 N zinc acetate in distilled water was added to the orange peel extract drop by drop under

constant stirring for 30 min. Then, the solution was kept at this temperature for an additional 30 min under stirring. The produced powder was filtered and dried at 90 °C for 24 h. The produced powder was combinations of $Zn(OH)_2$ and $Zn(CO_3)_2$ or superposed from both of them as $Zn_5(OH)_6(CO_3)_2$. So, the calcination step is important to form ZnONPs; therefore, it was done at 400 °C for 4 h. The calcinated ZnONPs were used for further use.

Fabric application

Fabric Pre-treatment The cotton fabric was cut into 20 × 20 cm and washed using a non-ionic detergent and air-dried. Afterthought, cotton fabrics were treated with 10 g/l citric acid and 5 g/l sodium hypophosphite through immersing in the treated bath for 5 min and squeezed with 100 percent wet pickup and then dried at 100 °C for 3 min.

Treatment of cotton fabric with orange peel extract Pre-treated cotton fabric was immersed in orange peel extractions (water or alcoholic) at the suitable conditions from previous work (Zayed et al. 2021, 2022).

Treatment of cotton fabric with synthesized AgNPs from orange peel extract Synthesized AgNPs in both orange peel extracts (at the optimum condition) were used for fabric treatments according to the following procedure (Zayed et al. 2022). Pre-treated cotton fabric was immersed in each orange peel extract for 10 min, then squeezed with 100% wet pickup, dried at 100 °C for 5 min, and cured at 140 °C for 3 min.

Treatment of cotton fabric with synthesized ZnONPs ZnONPs emulsion for fabric treatments was prepared in distilled water to obtain 10% in the presence of 10 g/l chitosan as polymeric materials according to the following procedure (Zayed et al. 2021): 1 g chitosan was dissolved in 100 ml distilled water under stirring. At 80 °C, 1 g calcinated ZnONPs was added under vigorous stirring; the stirring was continued for 30 min for good distribution of the nanoparticle inside the chitosan network. After that, the solution was homogenized using a homogenizer for 3 min at 20,000 rpm to ensure a completely homogenous distribution. Pre-treated cotton fabric was immersed in the final produced emulsion for 10 min, then squeezed with 100% wet pickup, dried at 100 °C for 5 min, and cured at 140 °C for 3 min.

Analysis and measurements

Characterization of orange peel extract and synthesized metal nanoparticles

The extract of orange peel is measured via the JASCO UV–visible absorption spectrophotometers from 300 to 800 nm to monitor the reduction of silver nitrate to silver nanoparticles. The FTIR of the orange peel was evaluated using the JASCO spectrometer tester. Transmission electron microscopy (TEM) images for orange peel extracts, synthesized metal nanoparticles, were investigated with a JEOL JEM-1200 EX transmission electron microscope operation.

The size of the synthesized metal nanoparticles was measured using laser particle size analyzer MasterSizer/2000 (MALVERN Instruments, UK) according to standard test methods ASTM E11:61 (ASTM Standard Test Method (E11-17) 2017), ISO 3310–1:2016 (ISO 3310-1:2016 2017), and ISO 565: 1990 (ISO 565:1990 2017).

With some changes as noted in the previous work, the total phenolic content in each orange peel extract was measured using the Folin–Ciocalteu method (Santhoshkumar et al. 2014; Singleton and Rossi 1965; Zayed et al. 2022).

The antioxidant properties of the bioactive orange peel extract and treated fabrics were monitoring through the radical scavenging capability on 2,2-diphenyl-2-picrylhydrazyl (DPPH) (Aryal et al. 2019; Fernandes et al. 2016; Rehan et al. 2018).

Characterization of treated fabric

SEM studied for treated fabrics was carried out using a scanning electron—JSM 5400 instrument (Joal, Japan).

The UV-protective factor was specified according to Australia/New Zealand standard test method (Australian/New Zealand Standard AS/NZS 4399:1996 1996) for untreated and treated cotton fabrics by absorption spectroscopy with the aid of a UV spectrophotometer (JASCO).

The self-cleaning activity was evaluated through the estimation of the degradation of methylene blue (MB) under UV irradiation (Zayed et al. 2021).

The color strength of treated cotton textile was measured by the Hunter Lab Ultra-Scan Pro at the National Research Centre in Egypt. The conventional form shall be represented as K/S. The K/S values were determined using the Kubelka–Munk equation (Hassabo 2005; 2011; Kubelka and Munk 1931; Mehta et al. 1984; Mohamed and Hassabo 2021; Waly et al. 2006, 2008):

$$K/S = \frac{(1-\boldsymbol{R})^2}{2\boldsymbol{R}} - \frac{\left(1-\boldsymbol{R_o}\right)^2}{2\boldsymbol{R_o}}$$

where K is the coefficient of absorption; S is the coefficient of dispersion; R_{kmax} is the reflectance of the cloth at its maximum wavelength.

Several standard test methods have been used to evaluate the mechanical and physical properties. Tensile strength and elongation at break are conducted on a tensile strength apparatus type FMCW 500 (Veb Thuringer Industrie Werk Rauenstein 11/2612 Germany) (ASTM Standard Test

Method (D5035-2011 (Reapproved 2019)) 2019). The dry crease recovery angle (CRA) was measured and evaluated for treated fabrics (AATCC Test Method (66–2014) 2017). Fabric roughness was measured using surface roughness measuring instrument SE 1700 (ASTM Standard Test Method (D7127-13) 2016). Stiffness was performed using the cantilever apparatus (ASTM Standard Test Method (D1388–14e1) 2016).

Assessment of mosquito repellent performance The insect repellent effect, knockdown, and death resulting from tarsal contact with the treated material were measured by standard World Health Organization test (World Health Organization 2009).

Anthropophilic Aedes (*Aedes aegypti*) was used to monitor mosquito repellents, and it was host-seeking at age uniform (5–7 days) after emergence. One hundred mosquitoes were enclosed during the test using a metal frame cage (35 × 40 cm per side). The cage bottom and topsides were solid, screen or netting on the backside, a transparent sheet of acrylic (for viewing and monitoring) on the right and left sides, and a fabric sleeve on the front for hand entry.

The fabric for investigation (10 × 10 cm) has been placed in the cage and counted for the period examined; the sum of mosquitoes that land on and/or knockdown or death to the fabric was recorded.

A freshly treated fabric with a pad-dry technique without curing was used for this investigation. A single evaluation requires the use of the same mosquitoes constantly and is done within a day. Three replication experiments have been conducted over multiple days of various mosquito lots.

The number of repellent and knockdown mosquitoes was recorded at fixed periods (10, 30, and 60 min depending on repellent and knockdown rates). Death of mosquitoes after 1, 6, and 12 h has been observed and recorded (conducted in parallel with a control sample).

Insect protection (insect repellency) (*P*), insect knockdown (*K*), or insect death (*D*) is expressed as a proportion of the number of mosquitoes landing on or knockdown or death of the treated fabric (*T*) concerning the number of mosquitoes landing on or knockdown or death of the control fabric (*C*) of the same individual:

$$\text{Insect protection } (P) = 1 - \frac{T}{C} = \frac{C - T}{C} \quad \text{(landing on)}$$

$$\text{Insect knock down}(K) = 1 - \frac{T}{C} = \frac{C - T}{C} \quad \text{(knock down)}$$

$$\text{Insect death } (D) = 1 - \frac{T}{C} = \frac{C - T}{C} \quad \text{(death)}$$

Corrected repellency, knockdown, and death rates were determined using Abbot's formula (Abdel-Mohdy et al. 2008):

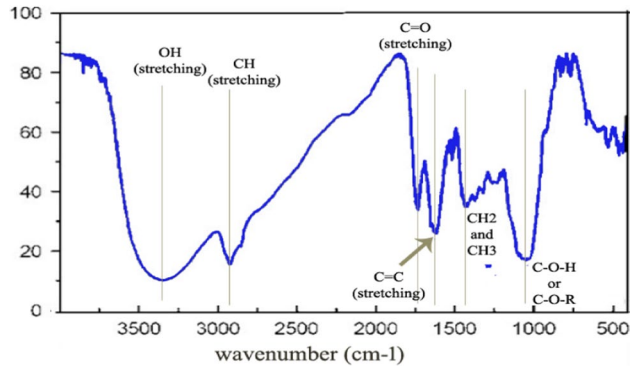

Fig. 1 FTIR spectrum of orange peel extract

Table 1 Yield extract, total phenolic contents, and antioxidant activity of orange peel extract

Solvent types	Yield extract (%)	Total phenol content (mg GA equivalent/g wet extract)	Antioxidant activity (DPPH) scavenging (%)
Water extract	2.55	58.2 ± 2.1	82 ± 2.5
Ethanol extract	2.73	60.3 ± 1.4	89 ± 1.4

Results and discussion

Characterization of orange peel extract and synthesized AgNPs

$$\text{Corrected repellency } \% = \frac{\text{Percent observed repellency} - \text{Percent untreated repellency}}{100 - \text{Percent untreated repellency}} \times 100$$

$$\text{Corrected knockdown } \% = \frac{\text{Percent observed knockdown} - \text{Percent untreated knockdown}}{100 - \text{Percent untreated knockdown}} \times 100$$

$$\text{Corrected mortality } \% = \frac{\text{Percent observed mortality} - \text{Percent untreated mortality}}{100 - \text{Percent untreated mortality}} \times 100$$

Antibacterial activity The antibacterial activity was quantitatively tested against *Staphylococcus aureus* (ATCC 29,213) as a gram-positive bacteria and *Escherichia coli* (ATCC 25,922) and *Candida Albicans* (ATCC 10,231) as fungi according to the AATCC 100–2004 (bacterial reduction method) (AATCC Test Method (100–2019) 2019; Khattab et al. 2020; Zayed et al. 2021). The method of disc diffusion to analyze the antimicrobial activity of treated fabrics has been used through the AATCC Test Method (147–2016) (AATCC Test Method (147–2016) 2017; Hassabo and Mohamed 2019; Hassabo et al. 2019; Mohamed and Hassabo 2018) by testing the area of the inhibition zone (*r*) (Ibrahim et al. 2017).

Area of the zone inhibition (mm^2) = total area−fabric area

Durability The durability of the treated fabric was evaluated after washing the treated cotton fabric with 2 g/l non-ionic detergents (Hostapal) for 10 min at 40 °C and then drying at 100 °C for 3 min.

Various types of research ensure that solvents are responsible for the dissolution of plant endogenous compounds (Abarca-Vargas et al. 2016; Aryal et al. 2019). The hydroxyl group in its molecular form makes phenolic known as a polar compound, which provides more solubility in polar solvents. The highly effective solvents in extraction were polar solvents like ethanol and water more than nonpolar solvents. A polar solvent, hydrogen bonding, can easily interact with the hydroxylic group in phenolic compounds.

Figure 1 shows the spectrum of an orange peel extract being analyzed by FTIR. The FTIR spectrum of orange peel extract displays a peak in the region of 3395–3450 cm^{-1}, with the broadband being caused by O–H stretching and N–H of the fatty acids, carbohydrates, and lignin units found in orange peels (Marcus and Nwineewii 2015). Furthermore, for asymmetric and symmetric stretching, the C–H bond in the CH_2 group yields a peak at 2935 and 2864 cm^{-1}, respectively.

Because of C=O extending between 1742 and 1623 cm^{-1}, there is considerable overlapping of alternate bands. The carbonyl group may be a component of fatty acids (1740 and 1720 cm^{-1}) or amides (1655 cm^{-1}). There is also a stretching peak at 1585 cm^{-1} due to C–N bonding.

Furthermore, there is a notable tiny shoulder band between 2750 and 2500 cm^{-1} owing to carbonyl C=O in

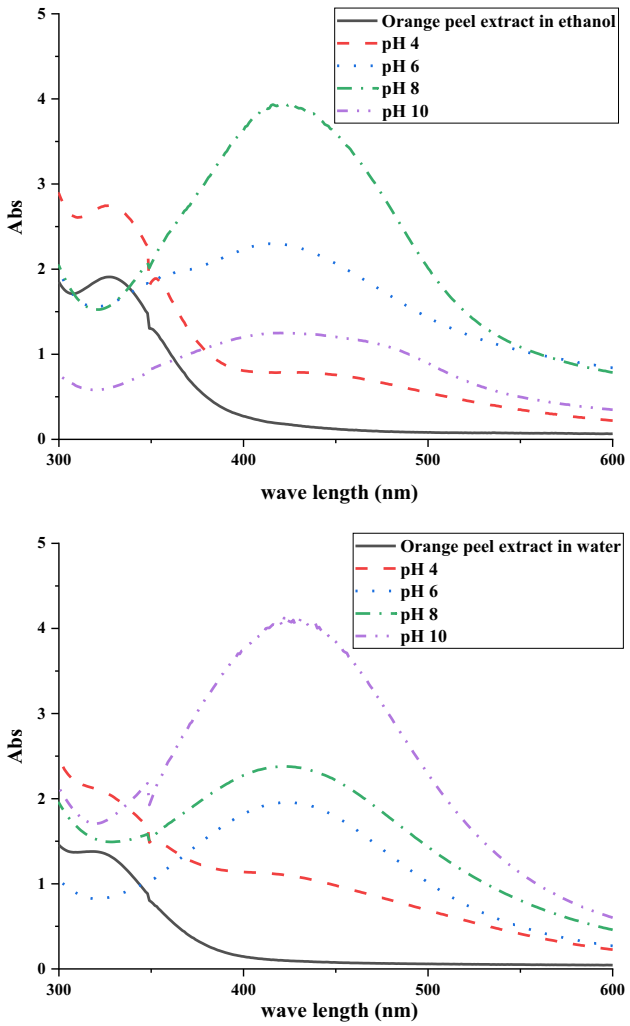

Fig. 2 UV spectra for synthesized AgNPs using both orange peel extracts (water and ethanol) at different pHs

the form of H–C=O and another band between 1750 and 1625 cm^{-1} due to aliphatic C=O bonds in the form of aliphatic ketones or esters. In addition, the orange peel exhibits an asymmetric band at 1500–1375 cm^{-1}, indicating N–O stretching from aliphatic nitrogen (Kwaambwa and Maikokera 2007). In addition, an absorption peak at 1235 cm^{-1} is caused by a C–O stretch from alcohol or phenol. A chemical connection between the aromatic ring and oxygen results in another significant peak at 1168 cm^{-1} (Zayed et al. 2022).

One of the big compounds in orange peel is phenolic compounds. An ecological process is known to be a more effective, healthy, and eco-friendly process for environmental extraction for orange peel using ethanol and water as solvent. In both orange extracts, the determination of total phenolic compounds was calculated by the colorimetric process Folin–Ciocalteu. As seen in Table 1, the total yield of orange peel extract is 2.73 and 2.55%, respectively, in both solvents (ethanol and water), and the total phenolic compounds of orange peel extract are 60.3 ± 1.4 and 58.2 ± 2.1, respectively, in various solvents (ethanol and water). This difference in total phenol content is because the water is regarded as a high polar solvent and ethanol as a low polar solvent. It is accepted that the elevated activity of antioxidants owing to the scavenging activity was responsible for high phenolic extracts.

In addition, both orange peel extracts (water and ethanol) demonstrated higher antioxidant activity, with high concentrations of phenol overall, 82 ± 2.5 and 89 ± 1.4, respectively, for ethanol and water extract. The phenolic compounds in both orange peel extracts suggest that they are effective antioxidants and can play a key role in the bio-reduction of metal ions (M^{+}) to metal nanoparticles (M°) (Iravani et al. 2014).

Figure 2 shows and illustrates the UV–Vis spectrum of synthesized silver nanoparticles, using the extract from the orange peel. A peak absorption at 420 nm is the UV–Vis spectrum of the colloidal solution for silver nanoparticles (AgNPs). In addition, the pH medium also influences the synthesis of AgNPs.

During the synthesis process of AgNPs, the color change in 10 min from the first yellow to dark brown suggests the formation of silver nanoparticles (AgNPs) (Ajayi and Afolayan 2017). In addition, increasing the pH media makes the solution become darker brown within 10 min. There is no affinity for AgNPs in both extracts in the acidic medium at the low pH level (pH 4), whereas the pH medium is increased to 6 causing the initial development of AgNPs. In both extracts, the synthesized AgNPs were improved by increasing the pH medium. In addition, AgNPs formation is higher in ethanol extract more than in water extract. Furthermore, increasing pH up to 10 led to particles coagulation.

Figure 3 indicates the particles size for synthesized AgNPs in water and ethanol in various pH media (6, 8, and 10) using orange peel extract as a reducing and stabilizing agent. By increasing the pH medium, the synthesized AgNPs particles size is reduced.

The particle size of orange peel in water and alcohol is also found to be around 1000 nm. Thus, in aqueous media, the size of the particulate of synthesized AgNPs in pH 4, 6, 8 and 10 was 220, 186, 9, and 7 nm, while in alcoholic medium, the particulate size of AgNPs in pH 4, 6, 8, and 10, respectively, was 24, 5, 1, and 0.95 nm.

Figure 4 displays TEM photographs for synthesized AgNPs using orange peel extract in water or ethanol at various pH media (6, 8, and 10). TEM images are shown as a good distribution spherical shape. The TEM survey indicates that the particles have narrow distribution ranges of 35 and 45, respectively, for orange peel extract in water and ethanol at pH 8. TEM images show that thin, spherical nanoparticles closer to 1 nm in diameter were observed for synthesized AgNPs by increasing the pH medium to pH 10.

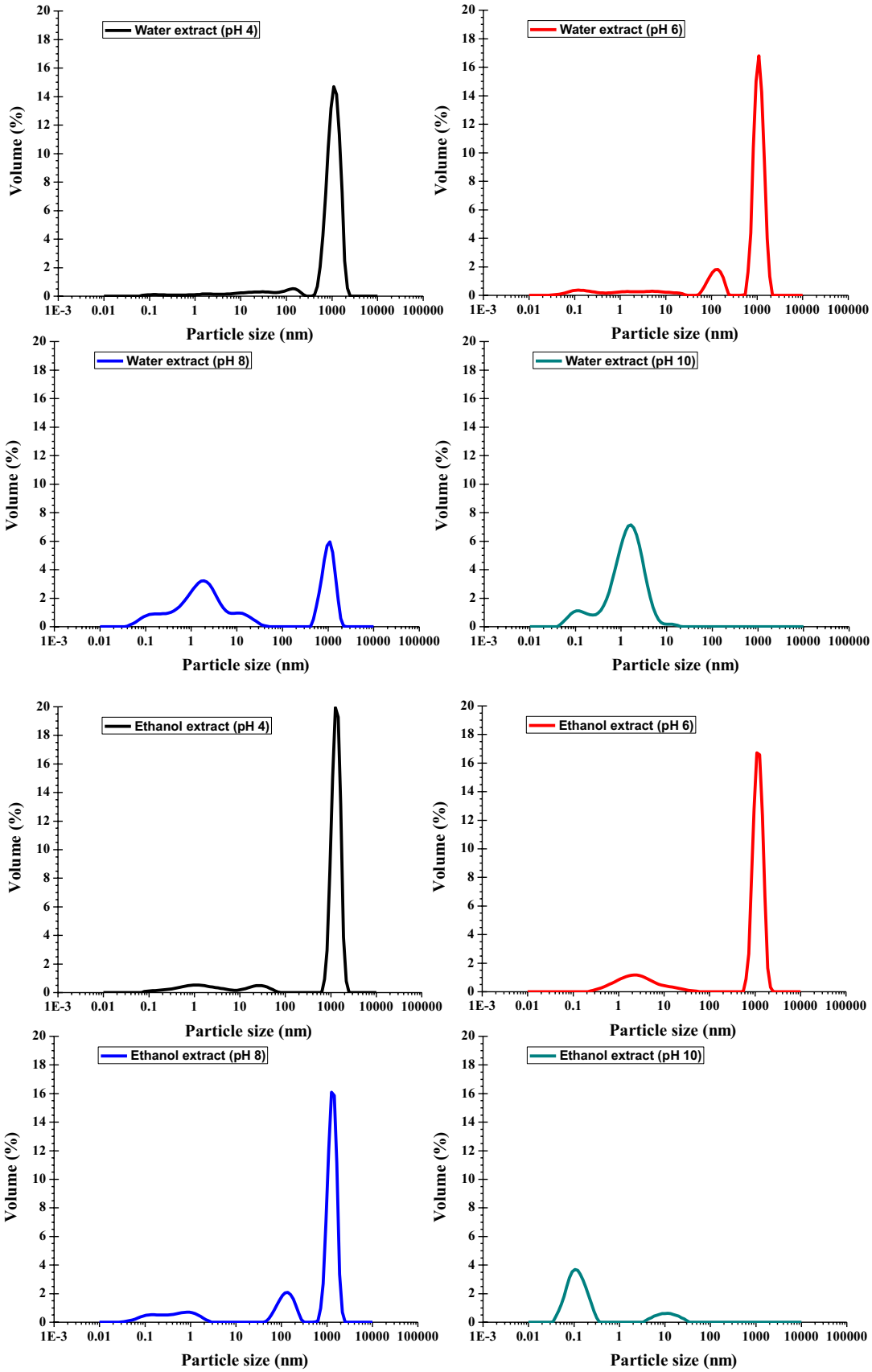

Fig. 3 Particle size for synthesized AgNPs using both orange peel extracts (water and ethanol) at different pHs

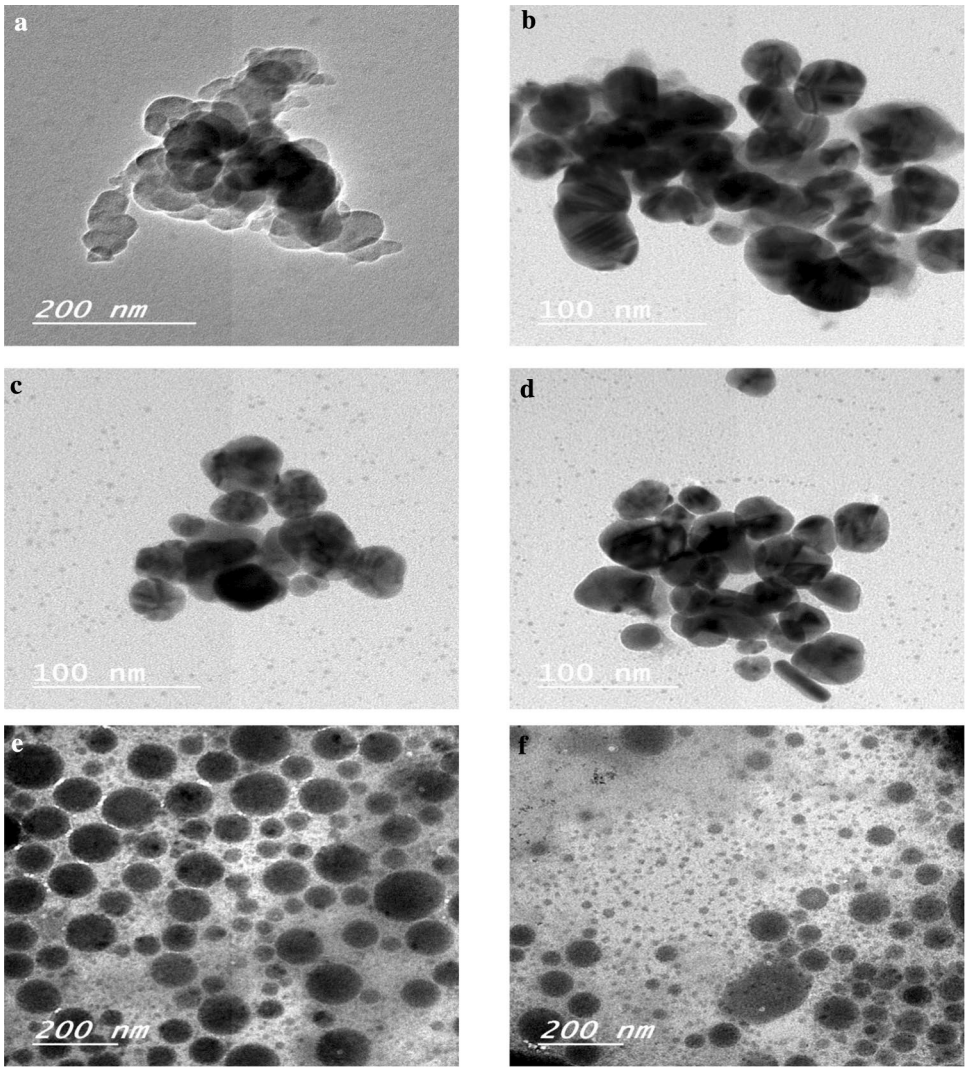

Fig. 4 TEM image for synthesized AgNPs using both orange peel extracts (water and ethanol) at different pHs: **a** water extract pH 6, **b** ethanol extract pH 6, **c** water extract pH 8, **d** ethanol extract pH 8, **e** water extract pH 10, **f** ethanol extract pH 10

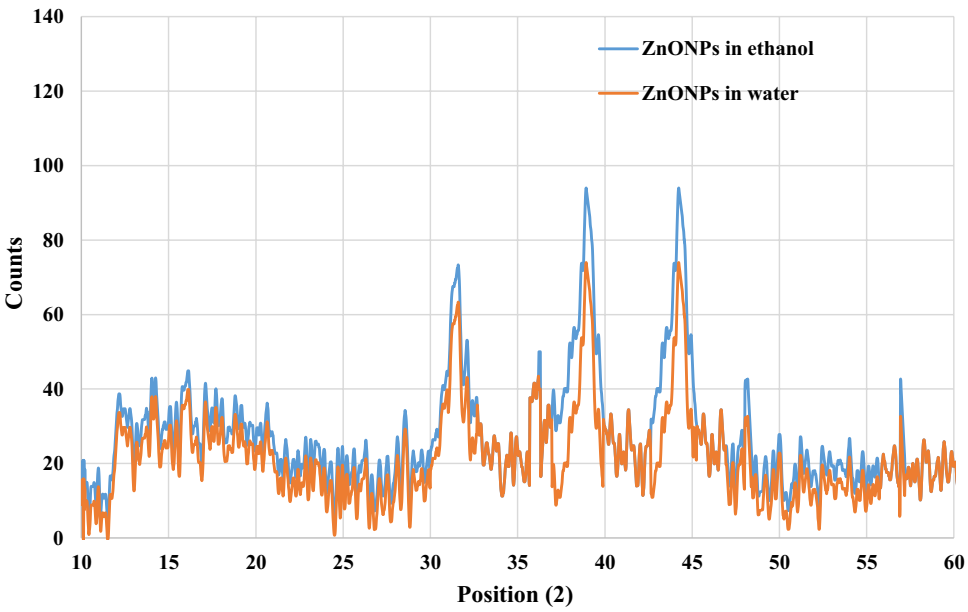

Fig. 5 XRD spectra for synthesized AgNPs using both orange peel extracts (water and ethanol) at pH 10

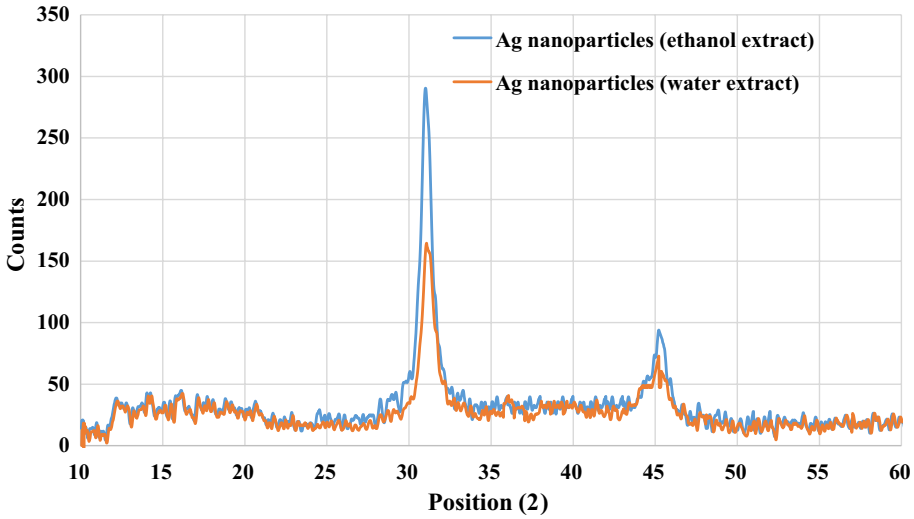

Fig. 6 XRD spectra for synthesized ZnONPs using both orange peel extracts (water and ethanol) at pH 12

For synthesized AgNPs at pH 10, the X-ray diagrams in Fig. 5 show the same closer intensity and width series for synthesized AgNPs using both extracts. The XRD pattern shows two intense peaks in the whole spectrum of 2θ values ranging from 10 to 60. The intense peaks were observed at 2θ values of 32.1 and 45.4 corresponding to (111) and (200) planes for silver, respectively (Miao et al. 2016, 2018).

Characterization of synthesized ZnONPs using orange peel extract

In two solvents, namely water and ethanol, the orange peel was finally extracted. The synthesis of ZnONPs at different pHs (6, 8, 10, and 12) was based on water and ethanol extracts.

Several types of the study show that solvents are responsible for the dissolution of the endogenous chemicals of plants (Abarca-Vargas et al. 2016; Aryal et al. 2019). The presence of a hydroxyl group in their molecular structures means that phenolic known as a polar chemical is more soluble in polar liquids. The more efficient solvent in extractors than nonpolar solvents was polar solvents such as ethanol and water. The polar solvent's hydrogen connection can interact with the phenolic groups of hydroxyls.

For synthesized ZnONPs at pH 12, the X-ray diagrams in Fig. 6 show the same closer intensity and width series for synthesized ZnONPs using both extracts. The findings presented in the literature by several studies, in terms of values 2.7, 2.5, 2.5, 1.8, and 1.6, were compared with obtained *d*-spacing values at 2 theta positions (2θ; 31.56, 36.21, 38.81, 48.21, and 56.94) for synthesized ZnONP products using both orange peel extract (water and ethanol) (El-Naggar et al. 2017; Ibrahim et al. 2017, 2018; Mohamed and Hassabo 2015b).

Figure 7 shows and demonstrates the particle sizes of orange peel extract at around 500 and 1000 nm for extract in ethanol and water, respectively. Figure 7 shows and demonstrates the particle sizes of ZnO nanoparticles, which were synthesized using extract of orange peel at different pH media (6, 8, 10, and 12). The particles size of synthesized ZnONPs can be seen to decrease with the increase of the pH medium. This reduction in particles size may be due to the deposited impact of orange peel components on the ZnONPs surface.

It is also noted that ZnONPs synthesized by orange peel ethanol extract are better than water extract in the various examined pH media (6, 8, 10, and 12). It is noticed that, at pH 6, there are no ZnO nanoparticles formed, which provide the lower affinity for producing ZnONPs in an acidic medium (El-Naggar et al. 2017; Ibrahim et al. 2017, 2018). Increasing the pH medium to 8 causes the beginning formation of ZnONPs but not in the same size which provides three particle size ranges (1–7, 9–10, and 80 nm) in both extracts. Further increasing the pH medium till 10 and 12 led to uniform particle size in the producing ZnONPs in both extracts. Comparing the produced nanoparticles in both mediums (pH 10 and pH 12) using both extracts, providing that, at pH 12, ZnONPs is smaller, more compacting in one particle size. Therefore, this investigation provided that the best pH medium for synthesis smaller ZnONPs in one particle size is 12.

No doubt that in pH 8 ZnONPs in both extracts are very similar to synthesis, when the pH medium is up to 10 and the ZnONPs are beginning to form. As the pH medium in the two extracts increased, the synthesized ZnONPs were increased. In addition, pH 12 was an ideal tool for the shaping of ZnONPs in both extracts.

Figure 8 shows the TEM representation ZnONPs synthesized at different pH media (6, 8, 10, and 12). using the water and ethanol extracts from orange peel, and the TEM pictures

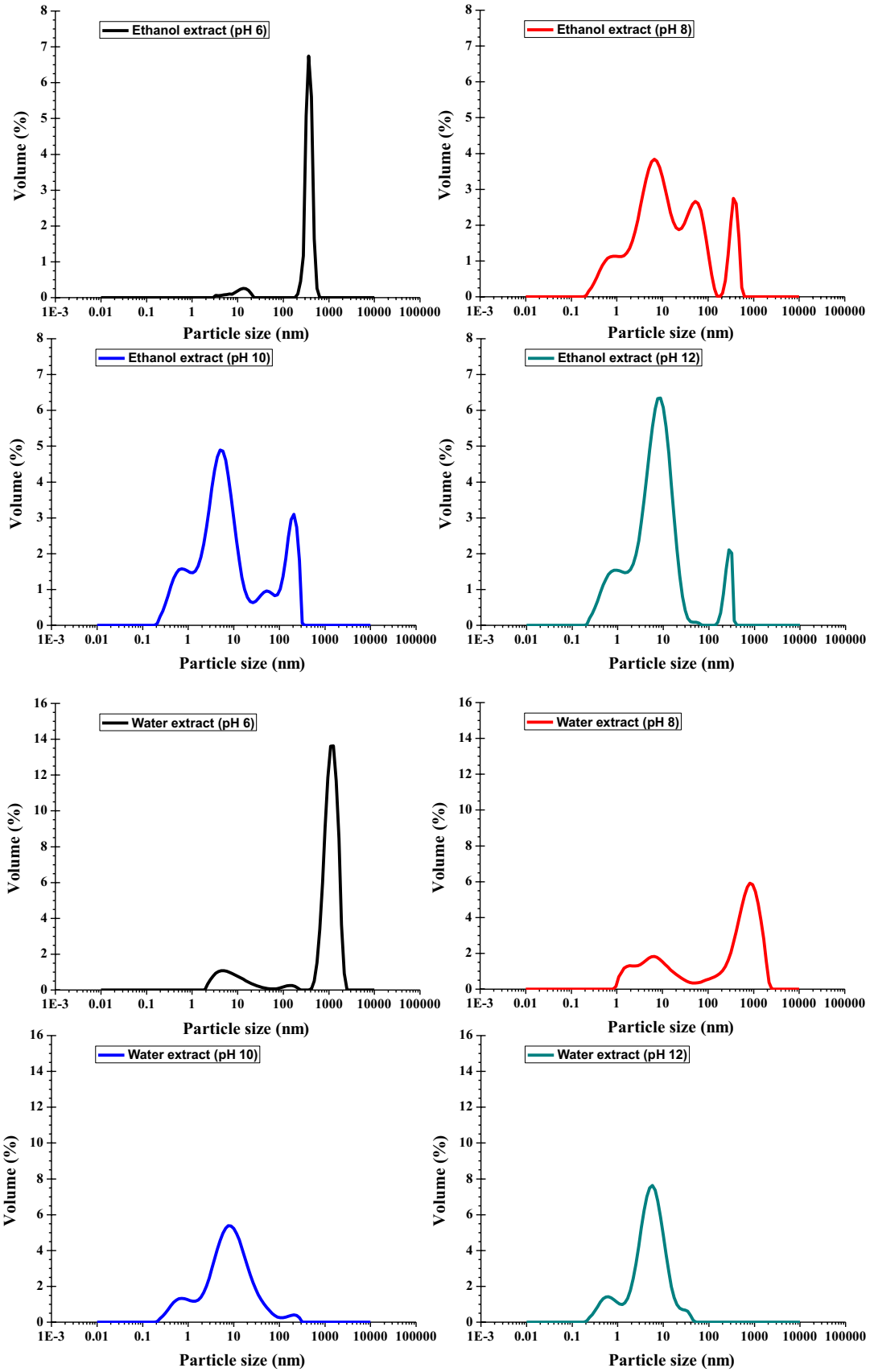

Fig. 7 Particle size for synthesized ZnONPs in both orange peel extracts (water and ethanol) at different pHs

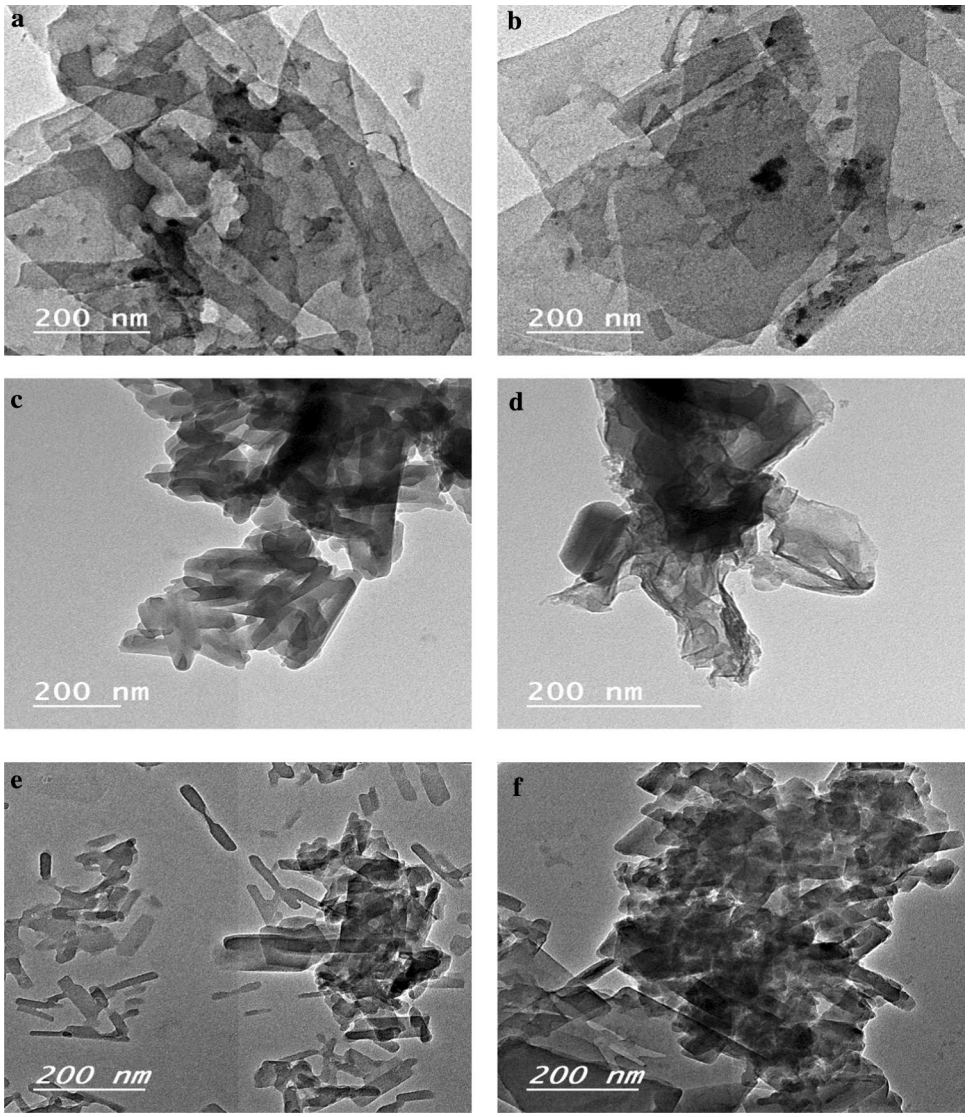

Fig. 8 TEM image for synthesized ZnONPs using both orange peel extracts (water and ethanol) at different pHs: **a** water extract pH 8, **b** ethanol extract pH 8 **c** water extract pH 10, **d** ethanol extract pH 10, **e** water extract pH 12, **f** ethanol extract pH 12

are seen as rod forms with good distribution. The TEM study shows that the particles in the water and ethanol extract at pH 8 have small-scale scatters of 80 and 60 nm, respectively.

In contrast, ZnONPs are made in nano-form, in the presence of extracts from orange peel in both water and ethanol. TEM images demonstrate that, during the phases of synthesis, thin, rod nanoparticles are formed in a small cluster by increasing pH, as seen in Fig. 8 until pH 12.

Characterization of treated fabric

Pre-treated cotton fabric with citric acid and sodium hypophosphite was treated with orange peel extract in water and ethanol (pH 8, temp. 70 °C, time 15 min) and also with synthesized AgNPs (at pH 10) and synthesized ZnONPs (at pH 12). The treated fabric was investigated for its physical, mechanical, and functional properties.

Morphological behavior of treated fabric

The SEMs and the EDX spectrum of cotton fabrics treated with orange peel of synthesized AgNPs and synthesized ZnONPs are seen in Fig. 9.

The SEM picture for treated fabric with orange peel extracts showed that the surface is very rugged relative to the untreated fabric, and pores on the cotton surface were filled with composites when treatment, creating the roughness behavior.

SEM images revealed the ZnONPs surface deposition that provides only or inside the deposited thin film of the chitosan biopolymer network with the presence of nanoparticles. The

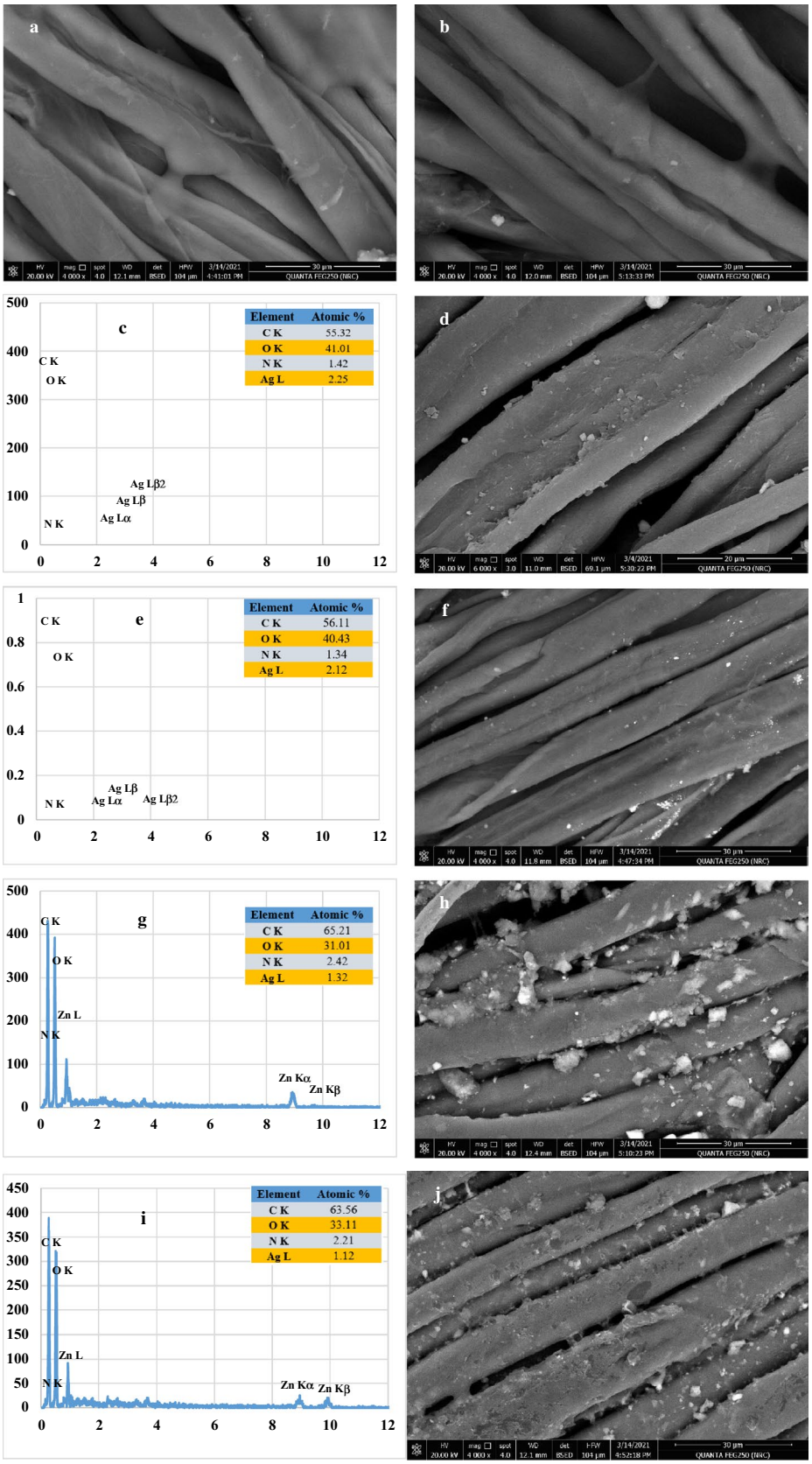

Fig. 9 SEM and EDX image for treated fabrics with *orange peel* extracts in the presence and absence of synthesized metal nanoparticles: **a** treated fabric with orange peel extract in water, **b** treated fabric with orange peel extract in ethanol, **c** and **d** treated fabric with synthesized AgNPs using orange peel extract in water, **e** and **f** treated fabric with synthesized AgNPs using orange peel extract in ethanol, **g** and **h** treated fabric with synthesized ZnONPs using orange peel extract in water, **i** and **j** treated fabric with synthesized ZnONPs using orange peel extract in ethanol

images from SEM show that the ZnONPs used were well deposited.

It is observed that fabrics treated using the synthesized ZnONPs acquire more roughness surfaces than those treated with AgNPs. This reflects the importance of biopolymer in producing homogeneous distribution and penetration for the nanoparticles on treated fabrics' surfaces.

Particularly noteworthy was the fact that the EDX picture suggests the presence of the different metals on surface cotton, when treated with AgNPs using orange peel extracts. As used with ZnONPs, the presence of various metals is associated with orange peel extract.

Furthermore, Ag and Zn elements were tested by the EDX spectrum on the processed materials. The X-ray spectroscopy (EDX) energy-dispersion technique was employed to determine the presence of the Ag and Zn element on the cotton surface. Due to the inclusion of AgNPs and ZnONPs, the EDX patterns found that carbon and oxygen elements on all the samples and Ag or Zn elements. The spectra provide that the surface of treated cotton fabrics has AgNPs or ZnONPs fixed on the surface.

Physical and mechanical properties

For cotton textiles before and after treatment, orange peel extracts in the presence and absence of metal nanoparticles at optimum conditions, tensile strength, elongation at a break, air permeability, roughness, and crease recovery angle have been observed, and the data are listed in Table 2.

The physicomechanical properties of the cotton fabrics treated were quite concerned. It was evident, after treatment with orange peel extracts in either water or alcohol; the crease recovery angle (CRA) improves significantly as surface ruggedness, air permeability, tensile strength, and elongation at a break were decreased. This suggests that the under-examination orange peel extracts were deeply embedded into the microstructure of the cotton fiber, thus forming a thin layer on the surface of the cotton and resolving to be responsible for those modifications (El-Naggar et al. 2017; Hebeish et al. 2016; Mohamed et al. 2017a; Salama et al. 2017).

Besides, the pre-cross-linking treatment of cotton fabric with citric acid-catalyzed with SHP was also a factor for these observed decreases. The development of covalent cross-linkages between adjacent cellulosic chains would provide the cotton structure with rigidity during this pretreatment phase. In the meanwhile, the cotton fabrics will chemically decay by citric acid.

Further notice from the physical and mechanical properties of the treated fabrics is that treated fabric with ZnONPs/chitosan composite provides good values compared with the untreated ones or treated fabrics with AgNPs or orange peel extracts even in water or alcohol extracts. These results confirm that biopolymer materials play an important role in enhancing mechanical or physical properties. The key enhancement of the crease recovery angle was possible due to creating an extreme cotton structure network closely cross-linked by covalent chemical linkages between the cellulose chain and biopolymers (El-Naggar et al. 2017; Hebeish et al. 2016; Mohamed et al. 2017a; Salama et al. 2017).

Metal content (%), antioxidant performance, and the ultraviolet protection factor (UPF)

A flame atomic absorption system has measured quantitatively the overall content of silver and zinc metal percentage per 1 g processed with treated fabric with synthesized AgNPs and ZnONPs.

Table 2 Physical and mechanical properties for treated fabrics with *orange peel* extracts (water and alcoholic) in the presence and absence of synthesized AgNPs and ZnONPs

Extraction process	Metal nanoparticle	*R* (μm)	Tensile strength	Elongation at a break (%)	CRA (W + F°)	Air permeability ($cm^3/cm^2/s$)
Blank fabric		21.45	152.12	39.21	198.65	221.87
Water extract	Absent	21.28	134.71	36.19	222.12	219.58
	AgNPs	21.13	116.85	32.99	235.25	217.91
	ZnONPs	21.2	125.78	34.59	248.38	216.25
Alcohol extract	Absent	21.38	124.65	31.18	231.91	220.57
	AgNPs	21.33	97.71	24.41	244.78	219.16
	ZnONPs	21.36	111.18	27.79	257.65	217.75

Cotton fabric was treated with orange peel extract in water and alcohol in the presence and absence of metal nanoparticles at 70 °C for 15 min

The natural effect of human antioxidants on medical fabrics is due to its free radical scaling action of the oxygen species from their hydroxyl groups, which prevent the cell decay and growth of new skin cells. Phenols and flavonoids, which are a key component of orange peel, known as a bioactive compound, are antioxidants.

The antioxidant function of treated cotton textiles in the presence and absence of nanoparticles is assessed using 2,2-diphenyl-2-picrylhydrazyl (DPPH) in the presence of both extracts in water and alcohol for their antioxidant production, and the findings are shown in Table 3. Cotton is classified as cellulose fiber, and its structure has an aliphatic hydroxyl feature. Table 3 does not produce any antioxidant performance that is attributable to the low sensitivity of DPPH to track very low antioxidant performance, as this aliphatic hydroxyl group resulted in weak antioxidative performance (Rehan et al. 2019).

So, the cotton fabric treated in the presence and absence of AgNPs with both orange peel in water and alcoholic extracts has an antioxidant performance primarily due to the redox nature of flavonoid and phenol compounds. These compounds have hydroxyl aromatic groups that play an important role in the development of a free radical.

Flavonoids can spray the free radicals and chelate onto metals like AgNPs. Phenolic acids containing aromatic hydroxyls and carboxyl groups normally act as antioxidants by trapping free radicals. Thus, in the presence of AgNPs and without AgNPs, the treated cotton fabric may increase the antioxidative property that requires it to be taken into account in medical applications with orange peel extracts in water or alcoholic (Rehan et al. 2018).

In addition, Table 3 registers the UPF for untreated and treated cotton fabrics for both water and alcoholic extracts with orange peel in the presence and absence of AgNPs and ZnONPs, and provided that all treated fabrics have UPF values higher than untreated, confirming that UV blocking content is present in orange peel extracts. This can be attributable to the polyphenol and flavonoid compounds that can absorb UV radiation, making the processed material easier to block UV radiation and shield the human skin from toxic ultraviolet radiation. Further investigation, treated fabric with ZnONPs provides higher UPF values than treated fabric with/without AgNPs.

Self-cleaning activity

Methylene blue (MB) is a common coloration for the evaluation of the photocatalytic activity. Two pathways will contribute to the photocatalytic transformation of MB by irradiated ZnONPs: (1) oxidation: complete mineralization of the base to carbon and mineral ions; (2) reduction: the leuco methylene blue form (LMB) is readily oxidized by dissolved oxygen (see below equations) (Minella and Minero 2019):

$$\mathrm{MB} + n\,\mathrm{h_{vb}} + (^{\cdot}\mathrm{OH}) \rightarrow \mathrm{CO_2} + \mathrm{NO_3^-} + \mathrm{SO_4^{-2}} + \mathrm{NH_4^+} \quad (1)$$

$$\mathrm{MB} + 2\,\mathrm{e_{cb}^-} + \mathrm{H^+} \rightarrow \mathrm{LMB} \rightarrow 2\,\mathrm{LMB} + \mathrm{O_2} \rightarrow \mathrm{MB} + \mathrm{H_2O} \quad (2)$$

The presence of oxygen also decreases the formation of leuco MB for two reasons: (1) the ambient O_2 scavenged the conductive strips almost entirely and (2) the potential MB leuco type automatically responded to O_2 for a color MB.

The self-cleaning properties of the cotton textiles treated with *orange peel* extracts and synthesized AgNPs and ZnONPs have been tested to eliminate MB stains. By testing the color strength of a treated fabric as opposed to an untreated one, the photocatalytic behavior of treated cotton fabrics was examined through the photodegradation of MB dye. Untreated and treated cotton textiles have also tested their self-cleaning potential by changing the color strength of methylene blue (MB) before or after exposure to sunlight (UV).

The ZnONPs are famous for their potential to generate free radicals because of the exposure to light photons known as self-cleaning property. The function of freely formed

Table 3 Metal content (%), antioxidant performance, and ultraviolet protection factor (UPF) for treated fabrics with orange peel extracts in water and alcoholic solution in the presence and absence of metal nanoparticles

Extract	Ag content (%)/1 g fabric	Zn content (%)/1 g fabric	Antioxidant performance (%)		UPF	
			Before washing	After washing	Before washing	After washing
Blank	0	0	0	0	0.1	0.1
Water extract						
Absent	0.01	0.02	77 ± 1.2	62 ± 0.8	17.2	15.1
AgNPs	0.41	–	71 ± 0.4	68 ± 1.1	5.4	4.1
ZnONPs	–	0.62	41 ± 0.1	38 ± 1.4	56.3	46.3
Ethanol extract						
Absent	0.01	0.02	76 ± 1.4	56 ± 1.1	26.9	11.0
AgNPs	0.41	–	60 ± 0.7	47 ± 0.2	8.3	3.2
ZnONPs	–	0.65	41 ± 0.6	38 ± 0.9	59.7	56.2

radials is to change the unsaturated chromophore into a saturated undyed molecule in the decomposition of color and its shape. This activity is known as the decomposition of color.

Figure 10 indicates the *K*/*S* and *K*/*S* reduction percent of the untreated and treated cotton fabrics with *orange peel* extracts in the presence and absence of synthesized AgNPs and ZnONPs after UV exposure for 12, 24, and 48 h. Data show that the discoloration of treated materials is greater than that of untreated materials. Just ZnONPs with chitosan biopolymer applied to textiles had been discolored rather than *orange peel* extracts in the presence and absence of synthesized AgNPs. This may be triggered by ZnONP's impregnation into the chitosan biopolymer network, which is the primary incentive for enhanced color adsorption and decreases the impact of nanoparticles on the surface of the textile fabric.

Besides, treated fabrics using extracts such as *orange peel* only improve their absorption (dying uptake) and have not been able to provide self-cleaning as predicted, so that their discoloration values almost are equal to untreated fabrics, whereas ZnONPs/chitosan on their cotton surface increases their self-cleaning operation over time. In comparison, ZnONPs impregnation in chitosan gives the largest dying intake relative to the treated fabric with both orange peel extracts in the presence of AgNPs since two functional groups are present in the main chitosan structure (hydroxyl and amine), which provide the suitability of the treating composite containing ZnONPs on the surface of the cellulosic fabric.

On the other hand, the involvement of chitosan in dye discoloration provides a high value because of the position of chitosan in the treatment solution's diffusion of the nanoparticles. The homogenous distribution of this part on the textile's surface allows good distribution, which contributes to a more effective decomposition of colors.

The color intensities of MB stains on the fabric coating fabrics decreased significantly as a result of a photocatalytic degradation operation of ZnONPs accumulated on the fabric

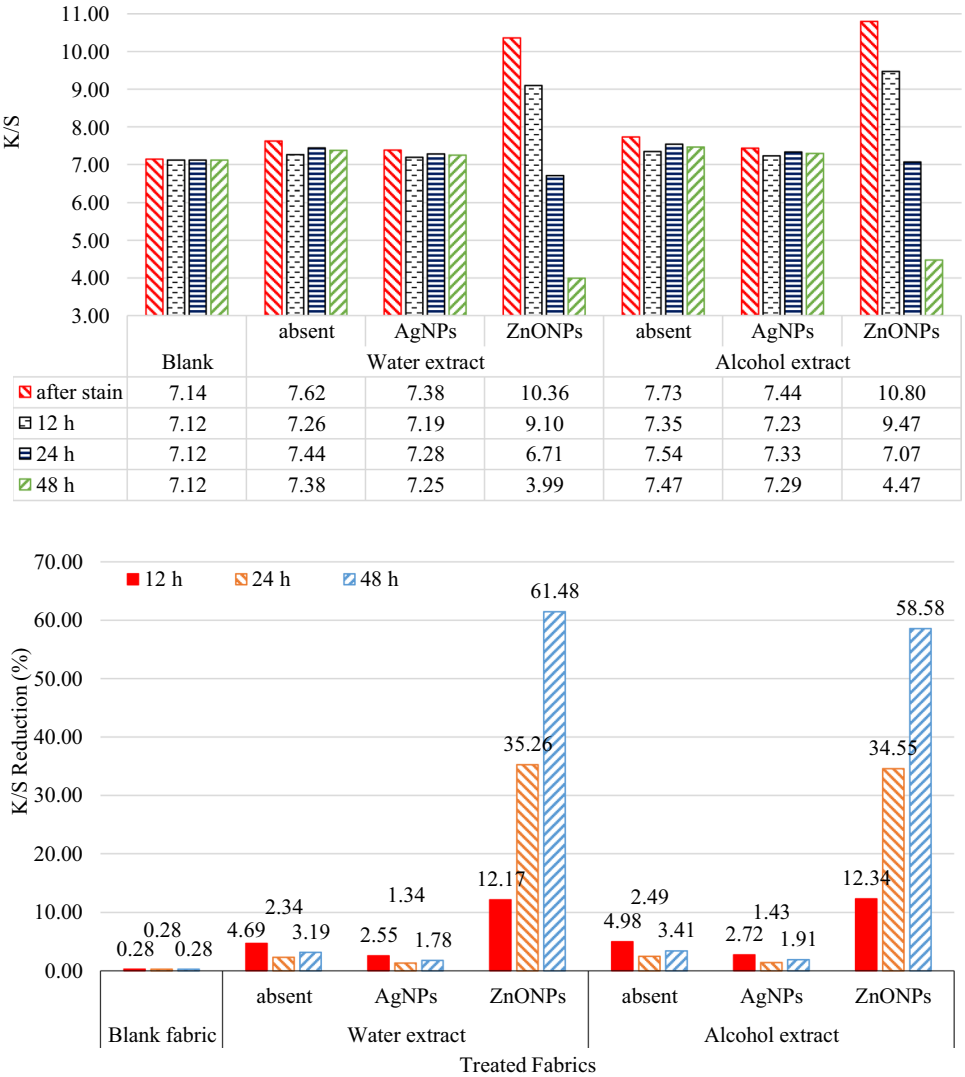

Fig. 10 Self-cleaning activity expressed as *K*/*S* (**a**) and *K*/*S* reduction (%), (**b**) for treated fabrics with *orange peel* extracts and synthesized AgNPs and ZnONPs after UV exposure for 12, 24, and 48 h

surface. The MB stains were readily visible on the surface of the untreated cloth. The properties of photocatalytic degradation were determined by the presence and formation of biopolymer used for ZnONPs impregnation.

Antimicrobial properties

The cotton-treated fabrics were subjected to examine their antimicrobial activity against three microbes, namely Escherichia Coli (*E. Coli*), Staphylococcus aureus (*S. Aureus*), and Candida Albicans (*C. Albicans*). The qualitative and quantitative antimicrobial results are described in Fig. 11 and Table 4.

The inhibition zone of the three microbes onto the treated textile with both orange peels in aqueous and alcoholic extracts confirms the antimicrobial activity of both orange peel extracts (Gao et al. 2021; Pratiwi et al. 2018).

Treated fabric with orange peel extracts in water or alcohol provides a good inhibition zone area (extract in water: 167.06, 137.54, and 108.39; extract in alcohol: 173.81, 102.5, and 179.3 mm^2) for examined microbes *E. Coli*, St. Aureus, and *C. Albicans*, respectively.

In addition, fabrics treated with chitosan/ZnONPs from AgNPs with both orange peel extracts exhibit antimicrobial resistance with excellent values in water extract 186.35, 188.85, 204.38 mm^2 and in alcohol extract 185.85, 137.76, and 238.36 mm^2 for examined microbes *E. Coli*, *S. Aureus*, and *C. Albicans*, respectively.

Furthermore, fabrics treated with both orange peel extracts in the presence of AgNPs exhibit antimicrobial resistance with excellent values in water extract 224.61, 188.85, and 204.38 mm^2 and alcohol extract 205.96, 137.76, and 238.36 mm^2 for examined microbes *E. Coli*, *S. Aureus*, and *C. Albicans*, respectively. This advantageous behavior is because of the inclusion of the phenolic and flavonoid compounds in orange peel extracts. In addition, the treated fabrics are more effective for gram-positive than for gram-negative bacteria since all of the bacteria tested differ in the cell wall structure.

Antimicrobial behavior can be associated with the inhibition function of polyphenolic compounds in microbial RNA and DNA. It is also possible to depolarize the cytoplasmic microbial membrane. The compounds provide even antifungal action as the key component in the cell membrane of fungi is inhibited by ergosterol (Fahmy et al. 2021; Hassabo and Mohamed 2019; Hassabo et al. 2020; Kamel and Hassabo 2021; Khattab et al. 2020).

In contrast, fabric treated with composites based on chitosan/orange peel extract/ZnONPs mixture shows higher

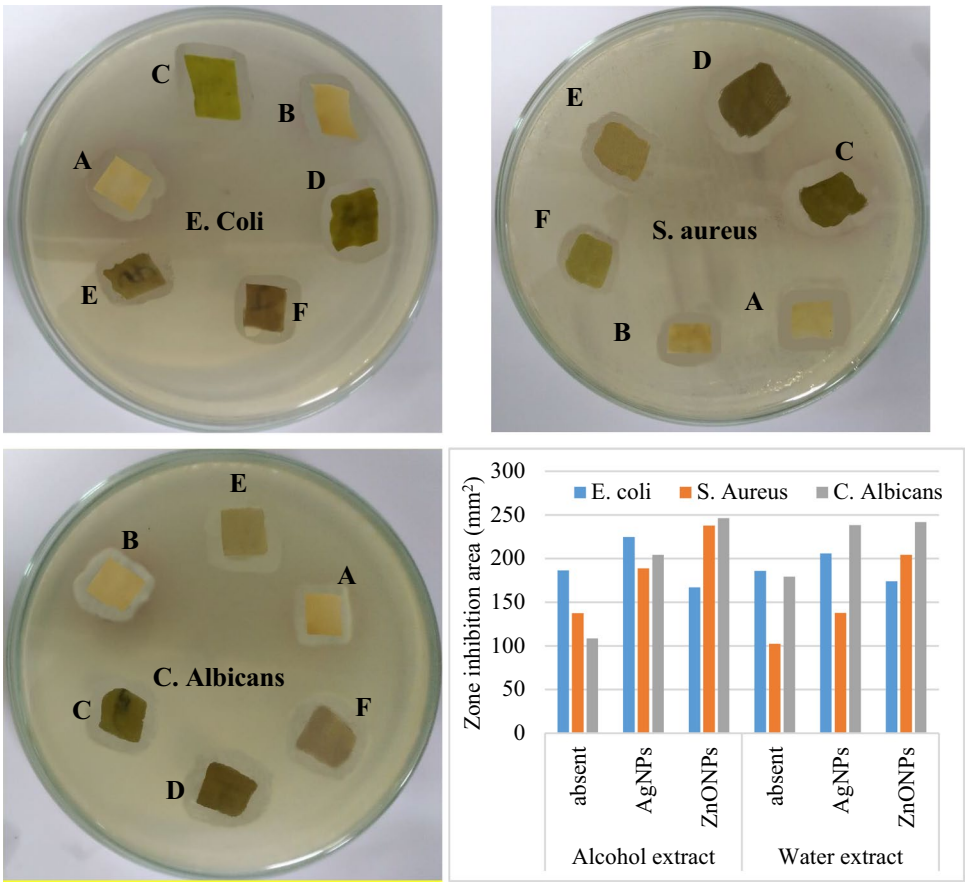

Fig. 11 Antibacterial activity of treated fabrics with orange peel extracts in water and alcoholic solution in the presence and absence of metal nanoparticles against three microbes: **a** *E. Coli* as a gram-negative bacterium, **b** *S. aureus* as a gram-positive bacterium, and **c** *C. Albicans* as fungus 1) untreated fabric: **A** treated fabrics with orange peel in water extract, **B** treated fabrics with orange peel in alcoholic extract, **C** treated fabrics with synthesized AgNPs (water extract), **D** treated fabrics with synthesized AgNPs (alcoholic extract), **E** treated fabrics with synthesized ZnONPs/chitosan emulsion (water extract) F) treated fabrics with synthesized ZnONPs/chitosan emulsion (alcoholic extract)

Table 4 Zone inhibition area and microbial reduction % for treated fabrics with orange peel extracts in water and alcoholic solution in the presence and absence of metal nanoparticles

Extraction process	Metal-NPs	*E. coli* (ATCC 25,922)						*S. Aureus* (ATCC 29,213)						*C. Albicans* (ATCC 10,231)					
		ZI* (mm^2)	Bacteria reduction %					ZI* (mm^2)	Bacteria reduction %					ZI* (mm^2)	Bacteria reduction %				
			Before washing	After washing cycles					Before washing	After washing cycles					Before washing	After washing cycles			
				5	10	15	20			5	10	15	20			5	10	15	20
Blank fabric	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Water extract	Absent	167.06	57.09	41.2	30.47	29.02	27.56	137.54	69.13	49.87	36.86	35.1	33.34	108.39	51.31	37.03	27.39	26.09	24.78
	AgNPs	186.35	75.44	54.42	40.22	38.3	36.39	188.85	82	59.19	43.78	41.69	39.61	204.38	67.66	48.83	36.11	34.39	32.67
	ZnONPs	224.61	95.79	92.77	86.57	82.65	78.52	237.64	98.58	95.95	93.54	91.45	86.88	246.38	95.31	93.98	92.76	91.04	86.48
Alcohol extract	Absent	173.81	60.6	47.31	39.35	37.47	35.6	102.5	79.14	66.77	61.14	58.22	55.31	179.3	55.64	46.96	43.01	40.96	38.91
	AgNPs	185.85	84.51	65.97	54.85	52.23	49.62	137.76	89.14	74.61	67.69	64.47	61.24	238.36	75.92	63.54	57.63	54.89	52.14
	ZnONPs	205.96	98.36	94.82	90.2	87.58	83.2	204.17	99.5	98.88	97.96	97.24	92.37	241.85	98.18	97.3	95.39	93.65	88.96

Zone inhibition (mm^2) = (total area – fabric area)

inhibition zone values than fabrics treated with orange peel extracts in the presence of AgNPs. It was also shown that the inhibition area values of composite-treated fabrics based on the alcoholic extract of orange peel were higher than the findings of composite-based aqueous extract from orange peel.

Chitosan/ZnONPs or AgNPs communicate successfully with bacterial cells in the coating process (Aboelnaga et al. 2018; Hassabo et al. 2018; Ibrahim et al. 2017; Mohamed et al. 2017b).

The bacteria reduction % for treated fabrics provides the same behavior against examined bacteria and fungi. The bacteria reduction % of treated fabrics after different washing cycles was investigated and provided decrease in the microbial resistance until 10 washing cycles, and any further increase in washing cycles provides a small decrease in bacteria reduction %. These results confirmed that treated fabrics have a good microbial resistance decreased by washing cycle but still prevent the bacterial growth. Additional evidence is that good production would come from these treated fabrics in the medical field.

The inclusion of chitosan in a composite has also been found to give a stronger bacterial reduction because of amine groups, which have a good bactericidal effect as a result of their positive charge, which shows the antimicrobial effect of the treated fabrics. This was because the relationship between the interaction of amines and the more anionic gram-negative cell surface lipopolysaccharides works to prevent nutrient transfer into the cells (Carmona-Ribeiro and de Melo Carrasco 2013).

In addition, the lipophilic properties of the products are increased by this amino group. The antimicrobial effect of the treated materials was thus also proposed to have less impact on the presence in the amino group of the metals and ZnONPs than the presence in AgNPs. As a result, the mode of interaction was disturbed with the bacterial cytoplasmic membrane (Ikeda et al. 1986).

Assessment of mosquito repellent performance

Many insect species are disease vectors. Blood sucks can damage humans and animals and can spread hazardous diseases through insects such as mosquitos, flies, lice, and bedbugs. Malaria kills every year over one million persons. Textiles treated with insecticide will provide the citizens and the environment with an efficient level of protection for risky diseases (Elsayed and Hassabo 2022).

The most effective approach for treating fabric is the incorporation, utilizing the covering or encapsulation techniques of repellent agents on the surfaces of the textile fabric (Abdel-Mohdy et al. 2008, 2009; Hebeish et al. 2008).

The encapsulation technology improved the durability of the treated fabrics (Nelson 2002).

Bio-compounds from natural plants are usually safer for humans with very low levels of toxicity. It is used as a mosquito larvicide and an insect repellent for human use (Rahman et al. 2016). Thereby, it is important to establish safe, non-toxic, environmentally friendly methods to synthesize mosquito repellents textile fabric.

Both extractions of orange peel in the presence and absence of metal oxides were used during this work as a simple green and economical approach for insect-repellent finishing processes.

Table 5 displays the percent of repellence, knockdown, and death obtained; the untreated fabrics showed lower knocking down and death against mosquitoes, while after using different treated cotton fabrics before and after washing with orange peel extracts in the presence and absence of metal nanoparticles providing a good percent of repellence, knockdown, and death. Table 5 indicates that treated cotton fabrics have toxicity against mosquitoes. The values of repellent, knockdown, and death percentage are increasing as the exposure time increased.

Further investigation, after washing cycles, is coated fabrics show a decrease in insecticide activity. This result is especially relevant when these fabrics are used for biomedical application, which was possible in certain cases when safety without washing, such as disposable clothing, is required for several days or weeks.

It should be emphasized that the approach used for recognizing this form of mosquito repellent material is a simple, cheap, reproducible, and desirable technique of green technology that is environmentally friendly. The orange peel extract mechanism of action is not very simple, due to the nervous system's orange peel component (limonene) interfere with people, which gives it its protection (Pavela 2015).

The slower knockdown and immediate killing of insecticidal fabrics are often seen when they are revealed. This means that some of the mosquitoes land directly on the surface of the cloth and are subjected to a high degree of insecticide absorption to rapidly kill the insects. The toxic activity for both treatment fabrics and blank is growing over time, with treating the fabric with orange peel extracts as repellency, knockdown, and death percent.

Furthermore, the effect of washing on the toxic preservation of the treated fabrics was decreased, but still have toxicity effect on the insect more than untreated fabric.

As predicted during the synthesis of both nanometals, as we used a small amount from extract, the activity of treated fabrics with extracts in the presence of both nanometals was decreased compared to treated fabrics with extracts in the absence of nanometals. Besides, the presence of ZnONPs decreases the insect repellency, knockdown, and death percent more than in the case of the presence of AgNPs, which may be because during the synthesis of ZnONPs, a small amount of orange peel was used for reduction, and it was burned and disappeared in calcination step (at 400 °C); therefore, the effect of orange peel component (limonene), which was the mainly responsible for mosquito repellent performance, was disappeared.

Besides, the findings from this examination are described as corrected repellence, knockdown, and death. The corrected toxicity of the examined fabrics before and after washing is illustrated in Table 6.

Conclusion

Citrus Sinensis peel (orange peel) consists of several bioactive components such as phenols, limonene, flavonoids, and essential oils. Orange peel can be used to impart multi-functional finishing to textiles because of its active bio-component. In this study, orange peel was extracted using two solvents (water and ethanol). The two extractions were used to treat the cotton fabric and used as a reducing and stabilizing agent in the synthesis of silver nanoparticles and zinc oxide nanoparticles.

Table 5 Insect repellent of treated fabrics with orange peel extracts in water and alcoholic solution in the presence and absence of metal nanoparticles before and after washing

Treatment formulation		Repellency %						Knockdown %						Death %					
		10 min		30 min		60 min		10 min		30 min		60 min		1 h		6 h		12 h	
		B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A
Blank		15	16	6	6	3	3	0	0	0	0	5	5	0	0	0	0	5	5
Water extract	Absent	63	33	80	68	90	84	25	15	74	47	90	66	0	0	48	22	87	63
	AgNPs	41	21	52	44	59	54	16	10	48	31	59	43	0	0	31	14	56	41
	ZnONPs	18	10	23	20	26	24	7	5	22	14	26	19	0	0	14	6	25	18
Alcohol extract	Absent	68	36	88	74	98	91	28	17	80	52	98	72	0	0	53	24	95	68
	AgNPs	44	23	57	48	64	59	18	11	52	34	64	47	0	0	34	16	62	44
	ZnONPs	20	11	26	22	29	27	8	5	24	15	29	21	0	0	15	7	28	20

B: before washing, A: after washing

Table 6 The corrected toxicity of treated fabrics with orange peel extracts in water and alcoholic solution in the presence and absence of metal nanoparticles before and after washing

Treatment formulation		Corrected repellency % (after 60 min)		Corrected knockdown % (after 60 min)		Corrected death % (after 12 h)	
		Before washing	After washing	Before washing	After washing	Before washing	After washing
Water extract	Absent	89.9	83.1	89.7	64.2	86.2	60.7
	AgNPs	57.4	52.9	56.5	39.9	54.2	37.6
	ZnONPs	24.1	22.1	22.5	15.1	21.5	14.0
Alcohol extract	Absent	98.4	90.9	98.3	70.5	94.5	66.7
	AgNPs	62.8	58.0	62.1	44.0	59.6	41.5
	ZnONPs	26.6	24.4	25.0	16.9	23.9	15.8

The UV–Vis spectra of synthesized silver nanoparticles using orange peel extract showed that the synthesis of silver nanoparticles was increased by increasing the pH medium in both extracts, in addition to the formation of silver nanoparticles in alcoholic extraction which is higher than in water extraction. It was found also that the particle size of silver nanoparticles decreases by increasing the pH medium, and the particle size of silver nanoparticles in water extract was higher than those in the alcoholic extract at different pHs (6, 8, and 10). TEM images are shown as a small and spherical form of a good distribution of silver nanoparticles.

The synthesized ZnONPs were also studied at various pHs. The particle size of synthesized ZnONPs was analyzed. It was found that, by increasing the pH medium, the synthesized ZnONPs particles decreased. Moreover, for shaping ZnONPs in both extracts, pH 12 proved to be an excellent medium. TEM images show that thin, spherical nanoparticles are agglomerates of small clusters during synthesis steps by increasing pH (until pH 12).

The treated cotton fabric with orange peel extractions, AgNPs, and ZnONPs impregnated with chitosan, showed that the UPF values and antimicrobial activity for fabrics treated with ZnONPs in the presence of the chitosan are better than those treated with AgNPs only or extractions. The best mosquito repellent effect was obtained when the fabric was treated with alcoholic orange peel extract.

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Declarations

Conflict of interest The authors declare that the data supporting the findings of this study are available within the article. The authors declare that there is no conflict of interest.

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