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Antimicrobial effect of cotton fabric functionalized with a kaolinite-titania nano-hybrid composite

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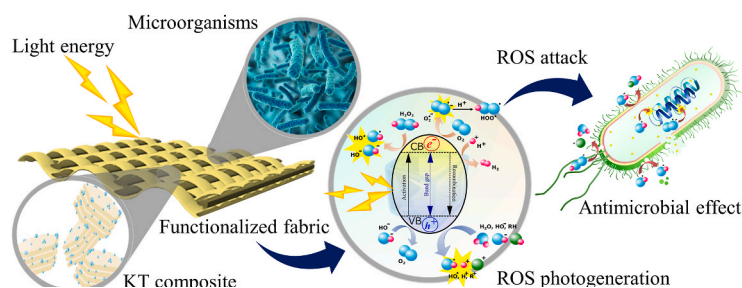
ABSTRACT

It is well known that certain diseases can be transmitted through contact with contaminated surfaces. Due to the structural characteristics and composition, textile products are favorable media for the retention, growth, and propagation of pathogens, making them potential vehicles for contamination. The current health and humanitarian crises have highlighted the urgent task of exploring effective antimicrobial agents that help prevent and combat emerging microbiological diseases. Based on this, the present work investigated the antimicrobial activity of a cotton fabric functionalized with kaolinite-titania nano-hybrid particles. The antimicrobial activity was evaluated against *Escherichia coli* (Gram-negative) and *Bacillus cereus* (Gram-positive) bacteria. Results show that the composite can enhance the photoactivity of the immobilized TiO₂, inducing the complete disinfection of the medium in contact with the treated fabric.

HIGHLIGHTS

- The treated cotton fabric exhibited excellent antibacterial property.
- The samples showed better bactericidal performance against *Bacillus cereus*.
- The multifunctionality of the kaolinite-titania composite was attested.

GRAPHICAL ABSTRACT



Keywords:

Cotton fabric
Antibacterial activity
Kaolinite-TiO₂
Photocatalytic disinfection
Antimicrobial textiles

1. Introduction

A wide variety of pathogenic microorganisms can be transmitted

through water, air, and contaminated surfaces. In recent years, the disease caused by COVID-19 has made evident the usefulness of textile masks in retaining the viral pathogen and has highlighted the

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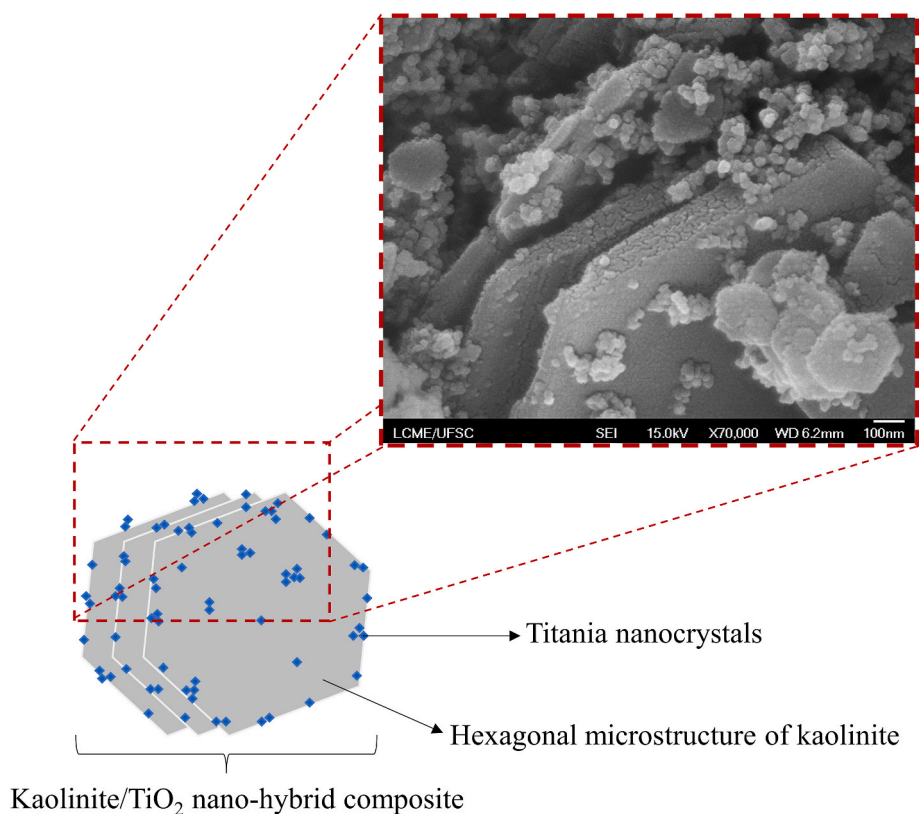


Fig. 1. SEM-FEG micrograph of KT composite at 70000x.

importance of hygiene and correct sanitation of clothing and textile accessories as preventive care. Textile products, as they are organic, fibrous, and absorbent materials, in addition to being constantly exposed to human touch and atmospheric dirt, are conducive to microorganisms' adhesion, proliferation, and transmission. For these reasons, the development of textiles with antimicrobial activity that can help fight and prevent diseases has been a hot topic nowadays.

Various mineral particles and organic compounds were evaluated as antimicrobial additives for textiles [1,2]. Among them, titania (TiO_2) is considered a promising antimicrobial agent due to its high effectiveness in inactivating various types of bacteria. In addition, TiO_2 is a non-toxic and low-cost compound with high chemical stability and photocatalytic properties [3]. Even under mild ultraviolet radiation, TiO_2 can show sufficient photocatalytic activity to eliminate xenobiotic compounds [4]. Akhavan et al. [5] synthesized carbon-nanotubes/ TiO_2 immobilized on Si (0 0 1) wafers for *E. coli* inactivation. Kalaiarasi et al. [6] prepared a Polyaniline- TiO_2 nanocomposite, which exhibited antimicrobial activity against *K. pneumoniae* and *P. mirabilis*. Hebeish et al. [2] developed silver-doped TiO_2 nanowires, which they used to functionalize a PVP-treated cotton fabric and tested against *S. aureus*, *B. cereus*, *E. coli*, *P. aeruginosa*, and *C. albicans*.

The present research investigated the antimicrobial activity of a cotton fabric functionalized with a kaolinite-titania composite against gram-positive and gram-negative bacteria. This composite was recently successfully synthesized and exhibited excellent performance when applied in powder form to photocatalytic degradation of methylene blue in aqueous media, as reported in our previous work [7]. In another work [8], the same composite applied to cotton fabric exhibited superior fire-retardant behavior decreasing flame propagation due to its mineral nature when combined with phosphorus and nitrogen compounds. The present work shows that our composite also exhibited antimicrobial activity in addition to the photocatalytic and fire-retardant properties. Therefore, the results show the versatility of the applied treatment, proving the multifunctionality of the composite and the treated fabric.

2. Experimental

2.1. Preparation of functionalized fabric

A woven fabric (cotton 100%) was functionalized with a kaolinite-titania nanohybrid composite (denoted as KT) by solvothermal synthesis [8]. The KT composite consists of kaolinite microparticles containing TiO_2 nanocrystals adhered to its surface [7]. Details on the preparation method of the KT composite and the treated fabric were elucidated in the Supplementary Materials section.

2.2. Antimicrobial test

The antibacterial efficacy of the functionalized fabric was investigated under dynamic contact conditions on *Escherichia coli* and *Bacillus cereus* cells using ASTM E2149-13a (2014) with minor modifications explained as follows.

Both microorganisms were isolated from the biological sludge of a textile industry, which means that they were already used to textile chemicals. Bacterial cells were cultured in Tryptic Soy Broth (TSB) at 35°C and agitation of 100 rpm for 18 h. After, the culture was diluted with sterile buffer solution (0.3 mM KH_2PO_4 pH 7.2) until it reached an absorbance of 0.16 ± 0.02 and 0.67 ± 0.02 at 600 nm for *E. coli* and *B. cereus*, respectively. These absorbances represent concentrations of approximately 3.0×10^8 colonies forming units (CFU) $\times \text{mL}^{-1}$. The solutions were then properly diluted to obtain the working solution containing a final concentration of about 3.0×10^5 CFU $\times \text{mL}^{-1}$. The bacterial concentration of the working solution was determined by a serial dilution and plate count technique. For this, 0.1 mL of the different dilutions were spread on the surface of Tryptic Soy Agar plates and incubated at 35°C for 24 h.

Fabric samples of 1.0 ± 0.1 g were used as test specimens; the treated and untreated fabric were tested. Each sample was placed in a 250 mL sterile Erlenmeyer flask and 50 mL of the working solution was added. A

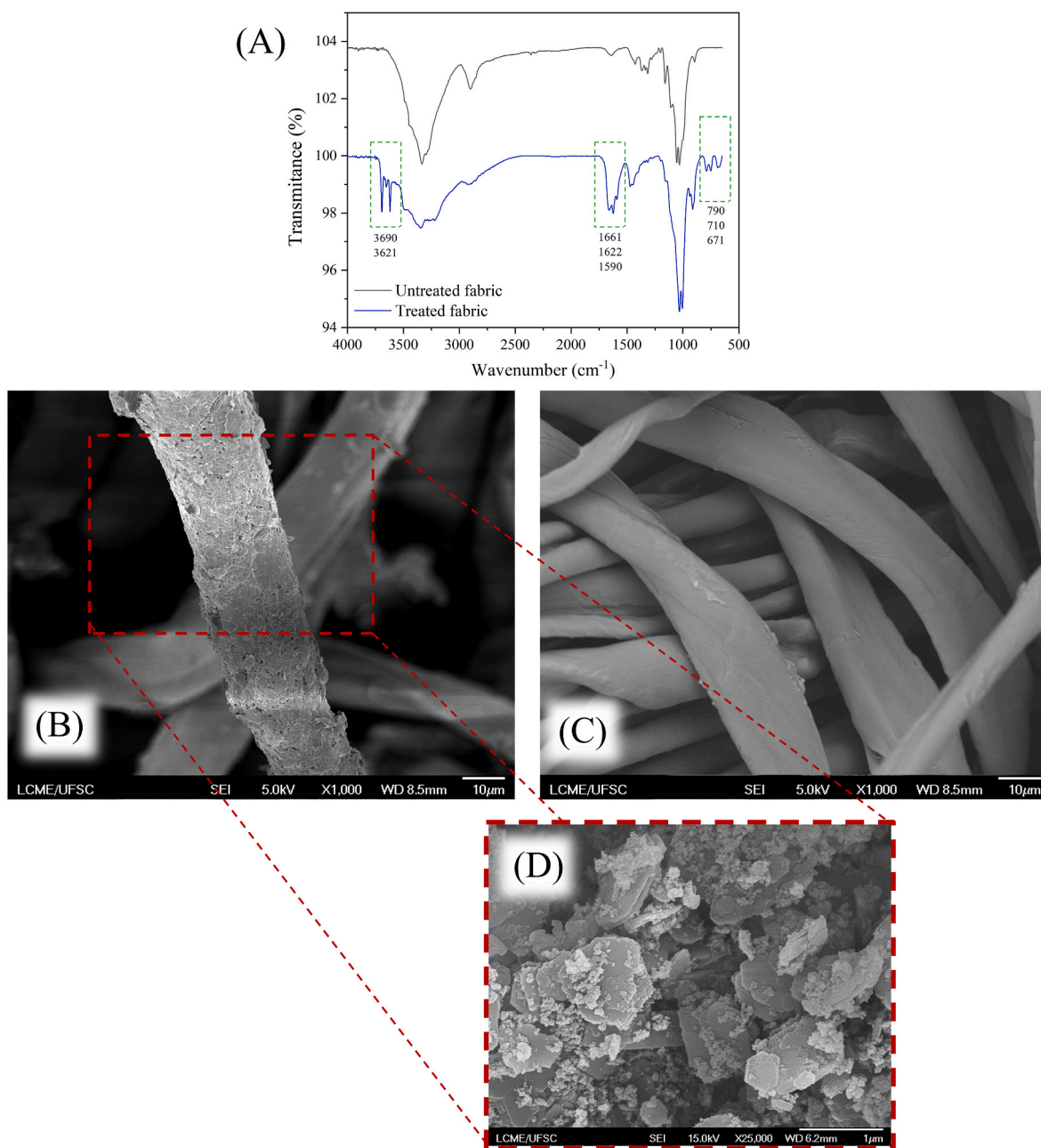


Fig. 2. FTIR analyzes and SEM-FEG micrographs of treated and untreated cotton fabric. (A) - FTIR analyzes of treated and untreated cotton fabric; (B) - Micrograph of treated fabric (it is possible to see the fiber covered by a mineral film); (C) - Micrograph of untreated fabric; (D) - Micrograph of KT composite immobilized on the surface of the fibers.

flask containing only the working solution was also prepared as a control sample. The flasks were incubated in an orbital shaker at 30 °C and 155 rpm for 1 h. After this steep, serial dilutions of the samples (supernatant) were plated on TSA and incubated at 35 °C for 24 h to determine the number of surviving CFU. The tests were performed in triplicate. The results were expressed in terms of percentage reduction of the number of CFU (R%), comparing the CFU of the initial solution (I) with the CFU at the end of the tests (F) according to Equation (1).

$$R\% = \frac{(I - F) \times 100}{I} \quad (1a)$$

To determine if the antimicrobial agent was leaching from the fabric, the parallel streak method AATCC 147 (2011) was used with minor modifications. *E. coli* was chosen as test organism. The bacterial inoculum was prepared by transferring 1.0 mL of a 24 h broth culture (grown

in TSB) into 9.0 mL of sterile distilled water. Using a 4 mm loop loaded with the inoculum, five streaks of approximately 6 cm in length and spaced 1 cm apart were made on the surface of TSA plates. Rectangular pieces (2.5 × 5.0 cm) of coated and untreated fabrics were then placed transversely across the streaks, ensuring the contact between the microorganisms and the material. Subsequently, the plates were incubated at 37 °C for 24 h. After that, the plates were visually examined to observe if a clear zone of inhibition was formed beyond the fabric's edge. The test was performed in triplicate.

3. Results and discussion

3.1. SEM-FEG analyzes

Fig. 1 shows the micrograph of the KT composite on an image with

Table 1

Quantification of antibacterial activity of the untreated and treated fabric against *E. coli* and *B. cereus*.

Microorganism	Sample	Initial	Final	Reduction (%)
		(CFU × mL ⁻¹)	(CFU × mL ⁻¹)	
<i>E. coli</i>	Control	2.99 × 10 ⁵	2.77 × 10 ⁵	7.57 ± 4.65
	Untreated fabric	2.99 × 10 ⁵	8.13 × 10 ⁴	72.83 ± 4.76
<i>B. cereus</i>	Treated fabric	2.99 × 10 ⁵	3.33 × 10 ³	98.89 ± 4.83
	Control	3.49 × 10 ⁵	3.10 × 10 ⁵	11.09 ± 2.77
	Untreated fabric	3.49 × 10 ⁵	7.00 × 10 ⁴	79.92 ± 2.99
	Treated fabric	3.49 × 10 ⁵	0	100.00 ± 1.95

70000× magnification. It is possible to observe the details of the kaolinite crystal (structure of stacked hexagonal lamellae) containing the titania nanoparticles well distributed and adhered to the surface [9]. The image showed the immobilization of nanoparticles in the basal and lateral planes of the clay mineral, as already reported in the literature [10,11].

Fig. 2 shows the KT composite immobilized on the fibers' surface of the treated fabric (2B) and untreated fabric (2C). Untreated fabric fibers showed a smooth appearance containing slight twists, befitting the natural look of cotton. In contrast, the treated fabric fibers containing the mineral composite particles have a rough and irregular surface appearance. The micrographs confirmed the success of the composite synthesis [7] and its immobilization on cotton fibers [8].

EDX analysis of the treated sample was performed by SEM-FEG, using a JSM-6701F (Jeol) equipment with an EDS NanoTrace™ X-ray detector (Thermo Scientific) device. The qualitative result is shown in Fig. S2, and the estimated proportions of the elements present in the sample are shown in Table S1.

3.2. FTIR analyzes

Fig. 2 (A) shows the FTIR analyzes of the treated and untreated fabric samples. In both spectra, vibrational modes characteristic of cellulose were observed. In this case, the intense peak in the region of 3330 cm⁻¹

corresponds to structural OH groups stretching vibration [12], which reveals the continuity of the hydrophilic characteristic of cotton in the treated sample. The broader peak at 3260-3240 cm⁻¹ in the treated sample can be ascribed to the formation of some intermolecular bonded OH stretching after the fiber treatment [8]. The peaks in the region between 1300 and 1400 cm⁻¹ are related to the wagging vibration in the CH bond plane and the axial deformation mode of CH bonds [13]. The absorption band around 1461 cm⁻¹ may be related to the vibrational elongation of the -CN bonds, possibly coming from the free ends of the APTES molecules [8]. The band around 1000 cm⁻¹ is characteristic of OH bonds and CO elongation.

The spectrum of the treated fabric showed peaks at 3690 and 3621 cm⁻¹, corresponding to structural OH (internal and external) vibration of aluminol groups (Al-OH) [11], which indicates the presence of kaolinite. The peak at 1590 cm⁻¹ may be related to the stretching vibration of Si-O bonds [11] from the presence of kaolinite particles and APTES (adhesion agent used in the synthesis of KT immobilization on fibers). The absorption peak at 1622 cm⁻¹ is related to N-H vibrational deformation [14], possibly from the APTES primary amine group. The peak around 900 cm⁻¹ may be related to the vibrational elongation P-OH from the phosphorylation of some hydroxyl groups in the treated fiber [8]. The band observed at 671 cm⁻¹ may be linked to the elongation of the Ti-O-Ti bonds [15-17] due to titania crystals immobilized in the kaolinite.

3.3. Antimicrobial properties

Table 1 shows the microbial activity (CFU quantification) of *E. coli* and *B. cereus* after contact with treated and untreated fabric samples. The fabric functionalized with KT composite showed excellent antimicrobial activity, both for *E. coli* (~99% reduction) and for *B. cereus* (100% reduction) compared to the control sample and the untreated fabric (see Fig. 3). Although mercerized and adequately rinsed, the non-functionalized fabric also showed some antimicrobial action, perhaps due to traces of sanitizing substances (e.g., surfactants) that may have remained in the fibers, even after several pre-washes. Considering that the composite contains TiO₂, it is possible to assume that the antimicrobial action of the functionalized fabric occurs due to the attack of reactive oxygen species (ROS) [18] photogenerated during the conditions of the dynamic test [19].

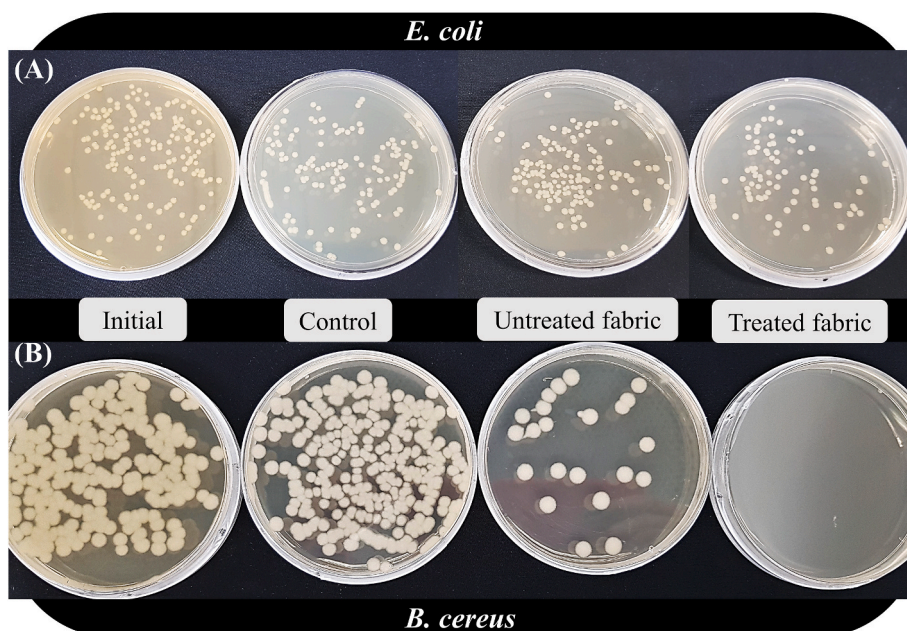


Fig. 3. Results of the dynamic contact test (ASTM E2149-13a) for (A) *E. coli* and (B) *B. cereus*.

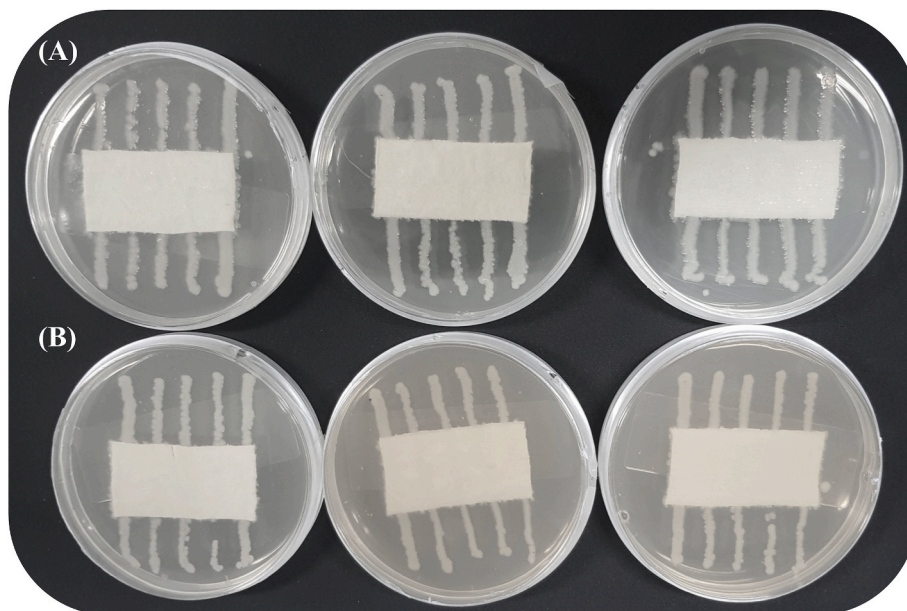


Fig. 4. Results of the parallel streak method for the untreated (A) and treated (B) cotton fabric.

KT particles immobilized on cotton fabric when in a liquid medium, under ambient light radiation for a sufficient time, can undergo photoexcitation and give rise to ROS. Although the dynamic method does not subject the working solution to specific high-energy lighting, it is well known that TiO_2 can be photoactivated even under natural light [20]. In our previous work [7], UV-vis DRS analyzes showed that the absorption energy band of KT (3.17 eV) is superior to that of TiO_2 (2.91 eV) alone (see Fig. S1 (b)). In this context, kaolinite possibly shifts the TiO_2 absorption edge to a higher energy region [10], giving the composite superior optical properties, better redox capacity, and, consequently, better photocatalytic performance, which could explain the observed results.

The death outcome for *B. cereus* was slightly better than for *E. coli*, which may be related to gram-positive bacteria's lower cell wall complexity compared to gram-negative ones. Cell wall destruction depends on several factors, including the gram-positive or gram-negative nature of the bacteria. Many works report that the greater complexity of the cell wall of gram-negative bacteria can make it difficult to kill microorganisms under redox attack conditions, making them more resistant under certain conditions [19]. The bacterial cell wall is a multilayered structure composed mainly of proteins, lipids, and carbohydrates. The Gram-positive cell wall is formed of a thick layer of peptidoglycan (PGN) densely functionalized with anionic glycopolymers. The PGN layer is made up of N-acetyl glucosamine-N-acetyl muramic units cross-linked by pentapeptides [21]. The Gram-negative cell wall contains a thinner layer of PGN located between the cell membrane and the outer membrane. The outer membrane is made up of lipopolysaccharides (LPS) (exclusive to Gram-negative bacteria). It serves as a strong barrier preventing the entry of hydrophobic substances and macromolecules, in addition to porins responsible for allowing the diffusion of selected molecules [19,21]. Due to the low permeability of the outer membrane, Gram-negative bacteria are considered less sensitive, mainly to metal ions and nanoparticles. For these reasons, after the test, CFU quantification for *E. coli* (Gram-negative) was slightly lower than *B. cereus* (Gram-positive). Since TiO_2 nanoparticles are immobilized, and their size is much larger than that of bacterial cells, it is unlikely that the microbial inactivation mechanism is related to the adsorption and penetration of nanoparticles into the cytoplasmic membrane.

Fig. 4 shows the result of the parallel streak test. The test did not show the formation of microbial inhibition zone beyond the edges of the

fabric, which corroborates the hypothesis of microbial inactivation by photocatalytic action of the treated fabric and not by leaching of KT particles. The analyzes assume that the antimicrobial activity of the functionalized cotton fabrics occurs by photocatalytic activation of TiO_2 , that is, under conditions of humidity and light radiation (with emission of photons with energy equal to or greater than the band-gap energy [2]), for the formation of ROS (see the Supplementary Materials section).

3.4. Mechanism of microbial inactivation

TiO_2 is widely reported as a semiconductor material with excellent photocatalytic performance when subjected to atmospheric and radiation conditions suitable for its photochemical activation [20,22]. A semiconductor material has two distinct regions between the layers of atoms, called valence band (VB) and conduction band (CB), with a distance between them called a bandgap. The bandgap region has no electronic states, and the bandgap energy can be defined as the minimum energy required for the excitation and promotion (leap) of an electron from a lower energy state (VB) to an unoccupied higher energy state (CB) [20]. When the semiconductor material (in this case, the TiO_2 crystals present in the composite) is exposed to light radiation with an energy equal to or greater than the bandgap energy, an electron (e^-) in the filled VB is promoted to a vacant CB, leaving a positive gap (h^+) in VB (see Eq. (1)). The holes in the VB (h_{vb}^+) give rise to a strongly oxidizing region, while the electrons in the CB give rise to a strongly reducing field. The electrons promoted from VB to CB can generate delocalized fields of energy on the crystalline structure of the material, providing electrical conductivity capacity similar to the presented by metals. Thus, the composite containing TiO_2 acts as a heterogeneous photocatalysis material, mediating a redox process in the bacterial medium, promoting the formation of reactive oxygen species (ROS), such as $\cdot\text{O}_2^-$ (Eq. (2)) and $\cdot\text{OH}$ (Eq. (3)) [2,18]. These species can react to give H_2O_2 (Eq. (4)), hydroxide ions, and hydroperoxyl radicals (Eq. (5)).



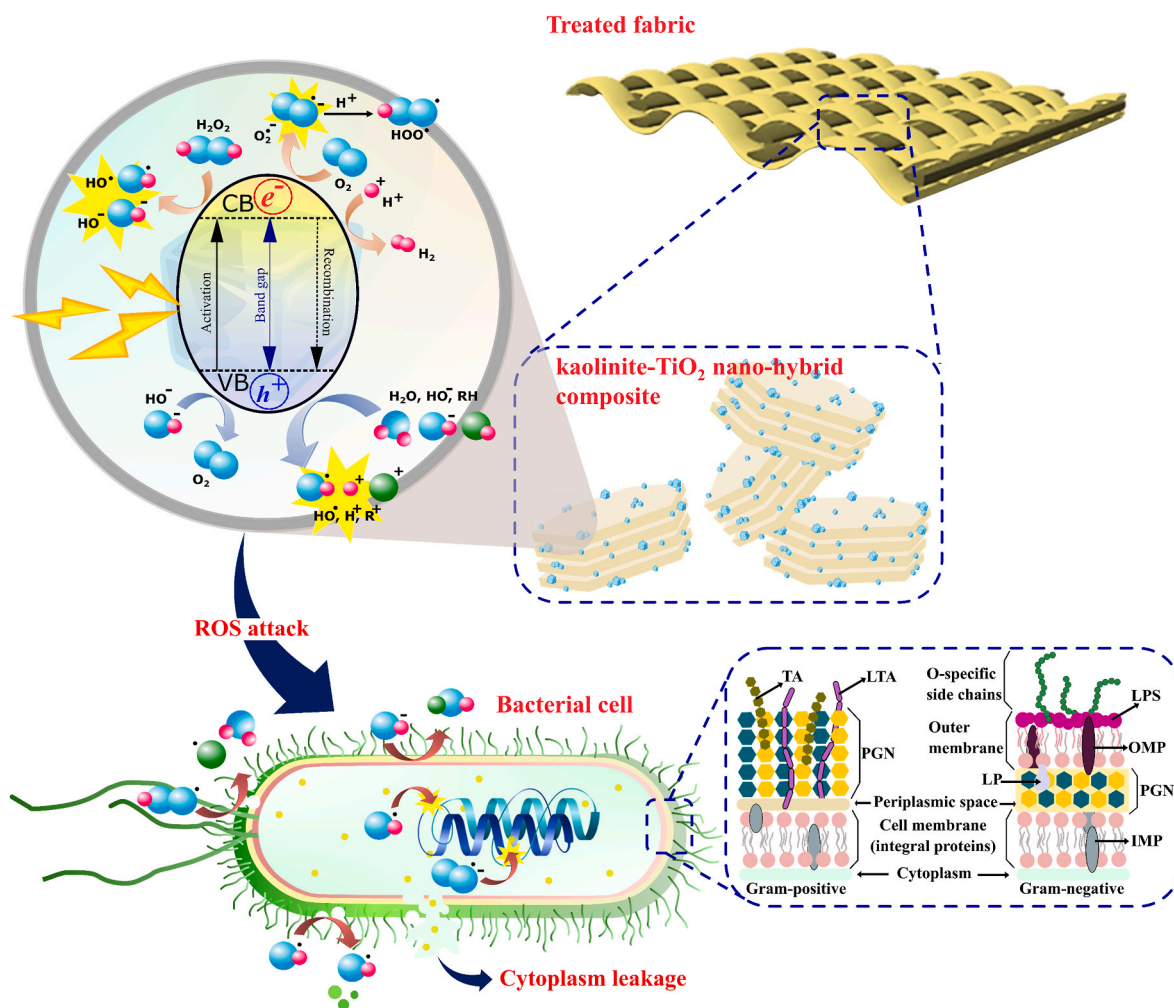


Fig. 5. Mechanism of antimicrobial activity of KT functionalized cotton fabric. The cell wall scheme was adapted from Ref. [19], where, OMP: Outer membrane protein; IMP: Integral membrane protein; LPS: lipopolysaccharide; LTA: lipoteichoic acid; LP: lipoprotein; TA: wall teichoic acid; PGN: Peptidoglycan.



During the analyzes, the chemical species generated by the KT composite came into contact with the bacteria in the medium (working solution). The chemical attack of ROS promotes the oxidative degradation of lipids and proteins that form the cell wall of bacteria, increasing the permeability of ROS to the interior of the cells or causing the rupture of the membrane and leakage of the cytoplasm, culminating in the death of microorganisms [19,22]. Fig. 5 illustrates a possible mechanism of death of bacteria still inside the working solution.

4. Conclusion

The cotton fabric functionalized with the kaolinite-TiO₂ nano-hybrid composite exhibited excellent antimicrobial activity against Gram-positive (~100%) and Gram-negative (~99%) bacteria. The observed microbial inactivation suggested a bacterial elimination mechanism guided by ROS photogenerated on the surface of KT-functionalized fabric while stirring the working solution. Although the method does not directly expose the samples to high energy radiation, previous analyzes of the composite suggest that the material has improved optical and photocatalytic properties compared to TiO₂ alone. In this context, the composite synthesized and immobilized in the cotton fabric seemed to fulfill the antimicrobial action well, even under weak radiation

conditions. These results highlight the multifunctional behavior of the prepared textile which is promising for several applications.

CRediT authorship contribution statement

Carlos Rafael Silva de Oliveira: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization, Writing – review & editing, Project administration. **Jéssica Mulinari:** Methodology, Validation, Formal analysis, Investigation, Writing – original draft, and, Writing – review & editing. **Marcos Antonio Batistella:** Conceptualization, Methodology, Writing – review & editing, and, Supervision. **Antônio Augusto Ulson de Souza:** and, Supervision. **Selene Maria de Arruda Guelli Ulson de Souza:** Resources, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matchemphys.2022.127078>.

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