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SURFACTANT INFLUENCE ON THE SYNTHESIS OF ZINC OXIDE NANOPARTICLES AS POTENTIAL ANTIMICROBIAL TREATMENT FOR TEXTILES

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The abundance of the scientific literature reporting the performances of the metal and metal-oxide nanoparticles promoted further studies regarding the new synthesis strategies that combine the advantages of low costs and environment-friendly methods. Herein, the synthesis of zinc oxide nanoparticles (ZnO NPs) is presented, using different ratios of zinc precursor and a tension-active compound, sodium dodecyl sulfate (SDS). The fabricated dispersions were used as antimicrobial treatment for a textile fabric consisting of a knitted 95% cotton / 5% elastane. The deposition was performed using the padding method. The treated fabrics were evaluated in terms of antimicrobial activity, against *Escherichia coli* and *Staphylococcus aureus*, and physico-mechanical properties (mass per unit area, horizontal and vertical density, air permeability and hydrophilicity). The antimicrobial efficiency was correlated with the critical micelle concentration (CMC) of the surfactant used. The satisfactory effect was obtained when the concentration of SDS was above this concentration. The size of the inhibition zone varied in accordance with the zinc precursor content, in the case of gram-negative bacteria and showed disorderly behavior for the gram-positive bacteria. The mass per unit area and the horizontal and vertical density did not suffer significant modifications after treatment deposition. However, the air permeability decreased due to the presence of the long hydrocarbon chains from the surfactant molecular structure, while its ionic part led to an improved hydrophilicity.

Keywords: textiles, nanoparticles, antimicrobial.

INTRODUCTION

The increasing progress in nanoscience research provided a solid fundament for exploiting the properties of nanomaterials in different fields and for different applications (Baig *et al*., 2021). Metal and metal-oxide nanoparticles are the subject of many studies evaluating their potential in areas such as medicine (for drug delivery, diagnostics, tissue engineering, antimicrobial properties), environment bioremediation (as pollutants removers, sensors, catalysis), agriculture (as pesticides and herbicides, food safety, water purification), material science (as protective coatings) electronics (for energy storage) etc. (Altammar, 2023). In textiles science, nanomaterials have been applied for textile finishing (manufacturing antimicrobial and self-cleaning textiles), on the one hand (Vats *et al*., 2023; Dejene & Geletaw, 2023), and for environment bioremediation (textile wastewater treatment), on the other hand (Al-Araji *et al*., 2023; Munir *et al*., 2023). Among metal nanoparticles tested for their antimicrobial properties, silver nanoparticles (AgNPs) are the most popular, due to their versatility and high efficiency at low cost. Moreover, by synthesizing AgNPs using *green* methods, the environment-friendly property is added to the list of their advantages (Lite *et al*., 2022; Lite *et al*., 2023). Gold nanoparticles have been also studied for their antimicrobial properties and environment-friendly fabrication. However, despite their high efficiency, the high cost of the gold precursor (gold salts), represents a disadvantage (Si *et al*., 2020). The antimicrobial mechanism consists of disrupting the membrane of the

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microorganism by producing reactive oxygen species and by binding the -SH groups of the constituent proteins (Abdul-Reda Hussein *et al*., 2024). In addition to their metal homologues, the metal-oxide nanoparticles present also the photocatalytic effect. Titanium nanoparticles (TiO_2 NPs) (Anbumani *et al*., 2022), magnesium oxide nanoparticles (MgO NPs) (Khan *et al*., 2022), calcium oxide nanoparticles (CaO NPs) (Jadhav *et al*., 2022), zinc oxide nanoparticles (ZnO NPs) (Jayachandran *et al*., 2021; Kim *et al*., 2020), copper oxide nanoparticles (CuO/Cu_2O NPs) (Shehabeldine *et al*., 2023) were reported to exhibit antimicrobial properties and are promising candidates for producing antimicrobial treatments for textile finishing. For this work, the synthesis of ZnO NPs was performed, using different ratios between the surfactant and the zinc precursor. The resulting dispersions were deposited on textile fabrics and the antimicrobial effect was evaluated. Moreover, it was determined how the physico-mechanical properties of the treated textile fabric were altered by the obtained dispersions.

EXPERIMENTAL

Reagents, Solutions and Materials

The precursor of the zinc oxide consisted of zinc acetate dihydrate. The surfactant selected for this study was sodium dodecyl sulfate (SDS), an anionic surfactant, with a long hydrocarbon chain. Sodium hydroxide 0.02M was used for pH adjustment. All reagents were purchased from Merck and were of analytical purity. The textile fabric used consisted of a knitted 95% cotton / 5% elastane (navy blue color) – made of threads Nm 50/1 having horizontal density, Ht = 13 threads no./cm and vertically density, Vt = 19 threads no./cm. The binder used in the finishing process was based on acrylic resin (PERMUTEX® RA-9260) and was purchased from Stahl Europe B.V.

Sample Preparation

Synthesis of ZnO NPs Treatment

Solutions of the zinc precursor and surfactant were prepared, to a final volume of 600 mL. Different molar ratios of these elements were used, according to Table 1. The pH of each solution was adjusted to ~11, using NaOH 0.02M, until they turn into milky-white dispersion.

Table 1. Molar ratios zinc precursor/SDS used for ZnO NPs synthesis

Sample code	$Zn(OAc)_2$	SDS
0.5:1	0.5	1
1:1	1	1
2:1	2	1
3:3	3	3
5:5	5	5
10:10	10	10
1:2	1	2
2:2	2	2
1:10	1	10
5:10	5	10

Treatment Deposition on Textile

The textile materials (20 cm × 30 cm) were treated with the obtained dispersions, after 24 h from their preparation, by the padding method. For this process, a laboratory-scale padder instrument BVHP 2 (Roaches, West Yorkshire, UK), equipped with two rollers, was used. Each sample was passed two times through the padder, then, they were subjected to a drying operation, for 4 min, at 100°C, followed by a curing step, for 2 min, at 150°C, using a drying/curing/heat-setting unit, model TFO/S 500 mm (Roaches, West Yorkshire, UK). The binder emulation was prepared up to a concentration of 20 g/L. For each textile sample, 200 mL of the binder emulsion was used, directly in the padder bath.

Sample Characterization

Antimicrobial Assessment

To perform a qualitative antimicrobial assessment, against *Staphylococcus aureus* ATCC 6538 (gram-positive) and *Escherichia coli* ATCC10536 (gram-negative), the agar-well diffusion method was used, according to SR EN ISO 20645/2005. A volume of each strain was spread on the entire Petri dish surface. The textile samples (10 mm in diameter) were placed in the center of the plates, on the surface of the nutrient medium. The plates were incubated at 37°C for 24h. Inhibition zones were calculated according to the following formula:

$$IZ = (D - d)/2 \quad (1)$$

where IZ represents the diameter of the inhibition zone (mm), D – the total diameter of the specimen plus the inhibition zone (mm), and d – the diameter of the specimen (mm).

Physico-Mechanical Properties

The treated fabrics were characterized in terms of mass per unit area (SR EN 12127-2003), density (SR EN 1049-2:2000), permeability to air (SR EN ISO 9237:1999), and hydrophilicity, measured using the drop test method, according to the Romanian Standard SR 12751/1989 standard.

RESULTS AND DISCUSSION

Antimicrobial Assessment

The results of the tested samples are presented in Table 2, for both bacteria strains. According to the standard SR EN ISO 20645:2005, the criteria for inhibition zones are the following: if the size of the inhibition zone is zero and the sample shows visible bacteria contamination, the effect is evaluated as unsatisfactory. When the contamination is minimal, the effect is at the efficiency limit. The effect is evaluated as satisfactory when there is no bacteria growth observed on the sample (even if the size of the inhibition zone is zero). When the size of the inhibition zone is higher than zero, the antimicrobial effect can be further quantified.

The samples evaluated with a satisfactory effect correspond to the ratio precursor:surfactant of 1:10, 5:10, and 10:10. The common aspect of these samples is represented by the high content of surfactant. This phenomenon is related to the behavior of the surfactant at its critical micelle concentration (CMC) (IUPAC). In the case of SDS surfactant, the value of the CMC is $8x10^{-3}$ mol/L (Dominguez *et al*., 1997). The formation of micelles prevents growth and aggregation of the ZnO NPs. Table 3 illustrates the Petri dishes containing the samples evaluated with the satisfactory effect.

Table 2. Antimicrobial assessment

Sample code	*Escherichia coli*		*Staphylococcus aureus*	
	Inhibition zone (mm)	Effect evaluation	Inhibition zone (mm)	Effect evaluation
0.5:1	0	Unsatisfactory	0	Unsatisfactory
1:1	0	Unsatisfactory	0	Unsatisfactory
2:1	0	Unsatisfactory	0	Unsatisfactory
3:3	0	Unsatisfactory	0	Unsatisfactory
5:5	0	Unsatisfactory	0	Unsatisfactory
10:10	3.5	Satisfactory	6	Satisfactory
1:2	0	Unsatisfactory	0	Unsatisfactory
2:2	0	Unsatisfactory	0	Unsatisfactory
1:10	2.5	Satisfactory	3.5	Satisfactory
5:10	3	Satisfactory	2.5	Satisfactory

When comparing the sizes of the inhibition zone (Figure 1), the general trend observed is of direct proportionality between zinc precursor and antimicrobial effect. This effect is in accordance with previous studies (Sirelkhatim *et al*., 2015; Li *et al*., 2020). In the case of *Escherichia coli* (gram-negative bacteria), the values of the inhibition zone size corresponding to the ratio zinc precursor:surfactant 1:10, 5:10, and 10:10 are 2.5, 3, and 3.5 mm, while for *Staphylococcus aureus* (gram-positive bacteria), the values were 3.5, 2.5, and 6 mm. Therefore, the treatment presented higher efficiency for gram-positive bacteria. Moreover, while for *E. coli* the effect was of a slight increase in efficiency with the zinc content increase, for *S. aureus*, the efficiency reached a minimum efficiency for the 5:10 ratio. This phenomenon could be explained based on the cumulative effect of the particles' size and content. While the increase if the content promotes a higher antimicrobial efficiency, the increase in the particle size or the formation of aggregates leads to a decrease in efficiency (Palanikumar *et al*., 2014; Álvarez-Chimal *et al*., 2022).

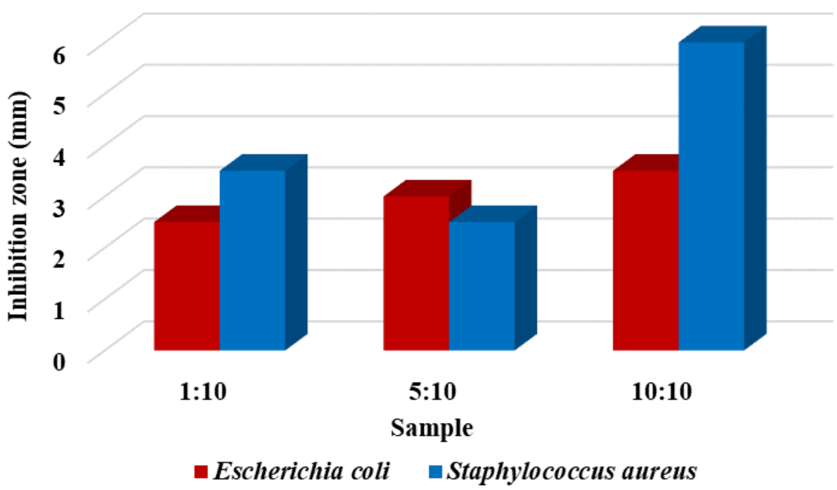
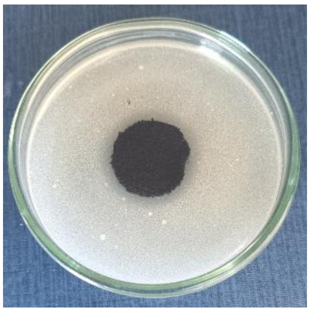
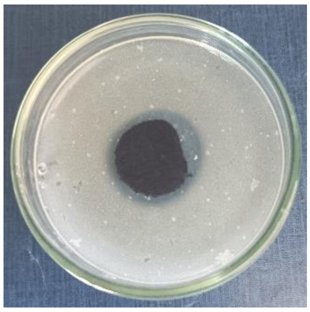
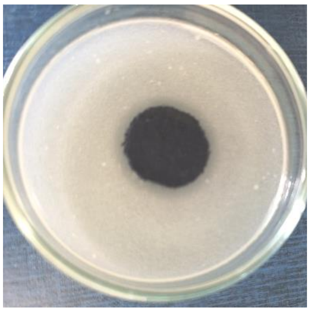
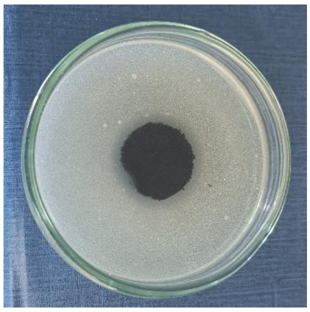
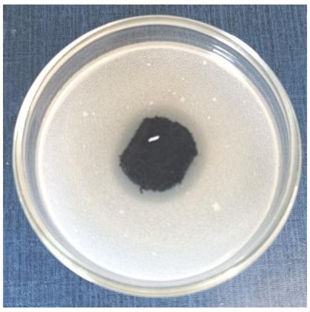
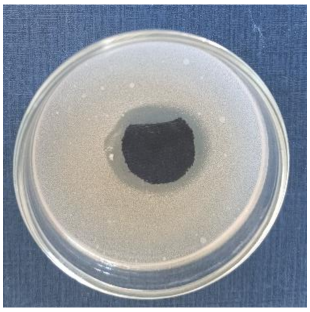


Figure 1. Sizes of the zone of inhibition formed on Petri dishes inoculated with microbial strains and incubated with textile samples treated with ZnO NPs

Table 3. Images of Petri dishes inoculated with the tested microbial strains and incubated with textile samples treated with ZnO NPs

Bacteria strain Sample	*Escherichia coli*	*Staphylococcus aureus*
1:10		
5:10		
10:10		

Physico-Mechanical Properties

The physico-mechanical characteristics (Table 4) showed little modification of mass per unit area, density, and air permeability, while the hydrophilicity suffered a decrease to a minimum of 52%.

Except for sample 5:10, the mass per unit area was not modified after depositing the treatment, suggesting that the antimicrobial efficiency is obtained even at a minimum loading of the material. The horizontal and vertical density decreased by 5.4% and 0.5% respectively, and it was maintained for all samples. This might be due to the textile fibers relaxation after applying the treatment and might also explain the lack of increase in mass per unit area (Laureckienė & Milašius, 2017; Li *et al.*, 2021). The air permeability decreased by 30-33%, while hydrophilicity increased by 28-52%. The presence of the tension-active compound sodium dodecyl sulfate contributed to the decrease of air permeability due to its long hydrocarbon chain, while the ionic part of the molecule bonded to the functional groups of the textile material led to an improved hydrophilicity. However, even with these improvements, the material remained hydrophobic, which led to the conclusion that the initial character of the material is not drastically changed after applying the treatment.

Table 4. Physico-mechanical characteristics of the treated textiles compared to reference

Sample	Fabric mass per unit area (g/m^2)	Density		Air permeability, 100 Pa ($l/m^2/s$)	Hydrophilicity (s)
		Horizontal (threads no. /10cm)	Vertical (threads no. /10cm)		
Reference	175	148	191	305.3	105
1:10	175	140	190	203.6	50
5:10	169	140	190	213	75
10:10	175	140	190	204.3	70

CONCLUSION

Textile fabric samples of a knitted 95% cotton / 5% elastane (navy blue color) were treated with synthesized ZnO NPs of different ratios zinc precursor:SDS surfactant. The color of the material was intentionally selected in order to evaluate the effect of the white-milky treatment deposition. The first observation after applying the treatment was that this did not alter the color of the material. By assessing antimicrobial efficiency, a strong relation between the content of the surfactant and the antimicrobial effect of the resulting ZnO NPs dispersion was demonstrated. This behavior was attributed to the critical micelle concentration of surfactant used. In the case of gram-negative bacteria *E. coli*, a general trend of increase in efficiency was observed with the increase of zinc precursor (from 2.5 to 3.5 mm IZ), while for the gram-positive bacteria *S. aureus*, the effect was cumulative between the antagonist antimicrobial effect at the increase of the ZnO particles size and its total content (the minimum IZ was 2.5 mm for the ratio 5:10 and the maximum was 6 mm, for the ratio 10:10). The physico-mechanical characteristics were not significantly modified in terms of mass per unit area and density (horizontal and vertical). However, the air permeability decreased by 30-33% as a result of treatment deposition, while the hydrophilicity was improved.

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