

DEVELOPMENT OF CERAMIC GLAZE COMPOSITIONS WITH BACTERICIDAL AND FUNGICIDAL PROPERTIES

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ABSTRACT

Techniques have been developed in recent years that allow the synthesis of materials that are, at least in one of their dimensions, of nanometre size (1-100 nm), and thus display significantly different properties and functions from those observed in traditional materials of micrometre size. Nanomaterials have a wide range of potential applications, particularly in electronics, materials science, communications, and biological systems. Economic analyses predict that the nanotechnology market will turn over between 750000 million and 2 billion Euros by 2015.

In the ceramic sector, however, work has not yet begun with nanomaterials, which is why it has not been possible appropriately to evaluate their potential advantages. Such is the case with the antimicrobial properties that certain nanomaterials can contribute to ceramic tiles.

The appearance of this new generation of materials can enable ceramic products with bactericidal and fungicidal properties to be obtained, whose surfaces are able to prevent pathogenic microorganisms from growing or to eliminate them, thus maintaining improved environmental hygiene and safety conditions. The ceramic sector could thus develop innovative products of greater quality and high added value to enhance its competitiveness.

1. INTRODUCTION

At present, public health is an issue of social interest. The news on pollution by pathogenic microorganisms in critical areas, such as hospitals, slaughter houses, restaurants, industrial facilities, etc., raises alarm and concern in society.

Antimicrobial materials and products are being increasingly demanded by an ever-larger market. Thus, glasses, plastics, paints, varnishes, etc. have recently appeared with antimicrobial characteristics.

Among the metal ions that exhibit antimicrobial properties, silver in the form of Ag(I) is well known for its biocidal effect in relation to a broad spectrum of microorganisms [1-3]. For that reason, various attempts have been made in the ceramic sector in the past to provide tiles with antimicrobial characteristics [4-11], mainly using this element.

Recent studies have demonstrated that nanometre-sized particles of silver (1-100 nm) also display antimicrobial properties [12-19]. Rong has established that silver nanoparticles exhibit greater antimicrobial activity, in fact, than silver nitrate at the same concentration [20]. This finding, together with their low toxicity, suggests that silver nanoparticles could be antimicrobial agents of interest.

This study presents, for the first time, a systematic examination of the bactericidal properties of silver nanoparticles on ceramic tiles.

2. MATERIALS AND EXPERIMENTAL METHOD

2.1. Materials.

The following materials were used: colloidal silver, with 73% Ag, and 'silvered' kaolin, which contained 22% Ag.

The colloidal silver contained silver particle of nanometric size and a protein as a stabiliser, which were used to prepare aqueous suspensions of silver nanoparticles. These were examined by transmission electron microscopy (TEM) (figure 1), the existence of silver nanoparticles smaller than 20 nm being observed.

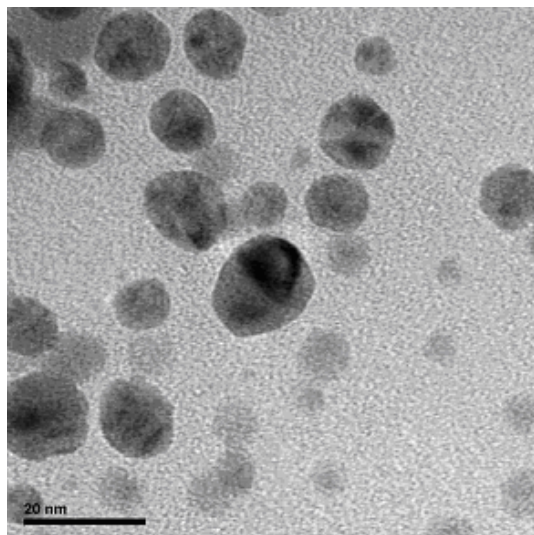


Figure 1. TEM micrograph of colloidal silver.

In the silvered kaolin, the kaolin mineral acted as an inorganic substrate, on which silver nanoparticles had been deposited by an adsorption process.

2.2. Preparation of the bactericidal film for application on to fired glazed tiles.

Screen printing inks were prepared by adding the necessary quantity of silvered kaolin to a certain quantity of frit and screen printing vehicle and, then, subjecting the mixture to stirring until total homogenisation of the solid in the liquid medium was achieved. The screen printing vehicle used was a mixture of alcohols and cellulose thickeners, such that the resulting inks displayed the appropriate conditions for screen printing application on to fired glazed tiles. Specifically, porcelain tiles with a matt glaze coating were used.

After the screen printing, each sample was dried in a laboratory oven at 110°C for 30 min.

Finally, the samples were fired in an electric laboratory kiln using the following cycle:

- Fast rise to 500°C.
- Heating at a rate of 25°C/min from 500°C to peak temperature ($T_{\max}$).
- Residence at $T_{\max}$ for six minutes.
- Fast cooling from $T_{\max}$ to 590°C.
- Cooling at 5°C/min from 590°C to 540°C.
- Fast cooling to room temperature.
- The peak firing temperature was 1040°C.

2.3. Preparation of the bactericidal film for application on to unfired glazed tiles.

In this case, ink preparation was carried out by adding the necessary quantity of colloidal silver to a certain quantity of screen printing vehicle and, then, subjecting the mixture to stirring until total homogenisation of the solid in the liquid medium was achieved. The screen printing vehicle used was a mixture of alcohols and cellulose thickeners, such that the resulting screen printing inks displayed the appropriate conditions for screen printing application on to unfired glazed tiles. Specifically, unfired porcelain tile bodies were used on to which glaze compositions had been applied that are customarily used on this type of product.

After screen printing, each sample was dried in a laboratory oven at 110°C for 30 min.

Finally, the samples were fired in an electric laboratory kiln using the following cycle:

- Fast rise to 500°C.
- Heating at a rate of 25°C/min from 500°C to peak temperature (T_{max}).
- Residence at T_{max} for six minutes.
- Fast cooling from T_{max} to 590°C.
- Cooling at 5°C/min from 590°C to 540°C.
- Fast cooling to room temperature.
- The peak firing temperature was 1180°C.

2.4. Measurement of antimicrobial efficiency.

Antimicrobial efficiency was determined according to the method described in standard JIS Z 2801 in a test laboratory accredited by ENAC (EN ISO 17025). Standard JIS Z 2801 has been internationally adopted as a reference for evaluating the antimicrobial efficiency of ceramic, plastic, and other surfaces.

According to this standard, antimicrobial activity is determined by comparing the results obtained on a treated surface and on a control surface (blank), after a microorganism incubation time of 24 h at optimum temperature for microorganism growth (figure 2).

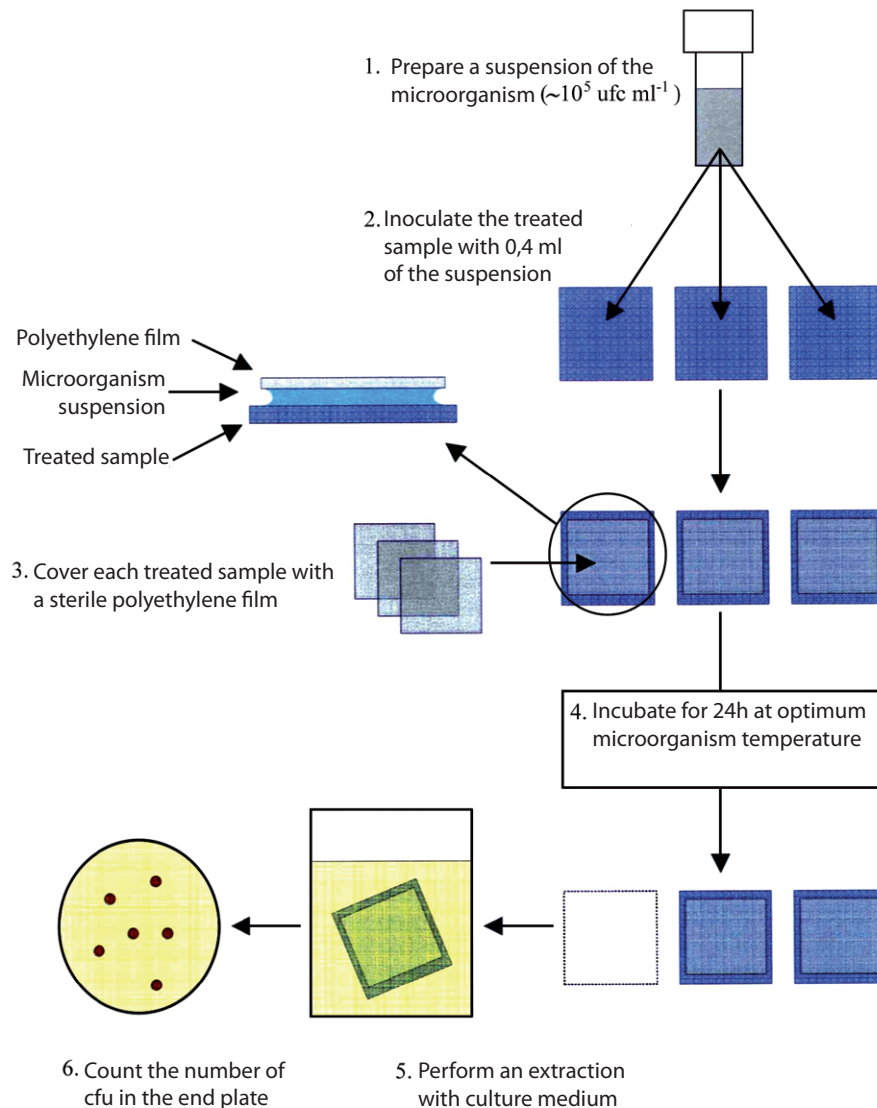


Figure 2. Schematic illustration of the method described in standard JIS Z 2801.

3. RESULTS

Figure 3 shows the reduction of the number of colony-forming units (cfu) per ml in the treated samples, in relation to a blank, after 24 hours. The values that appear in Figure 3a correspond to the application of an ink that contained silvered kaolin (Ag concentration in the ink: 0.3% by weight), while the values shown in figure 3b correspond to the application of an ink that contained colloidal silver (Ag concentration in the ink: 3% by weight).

It may be observed that the number of cfu in the treated samples is much smaller than in the respective blanks, which indicates the bactericidal efficiency of the applied films.

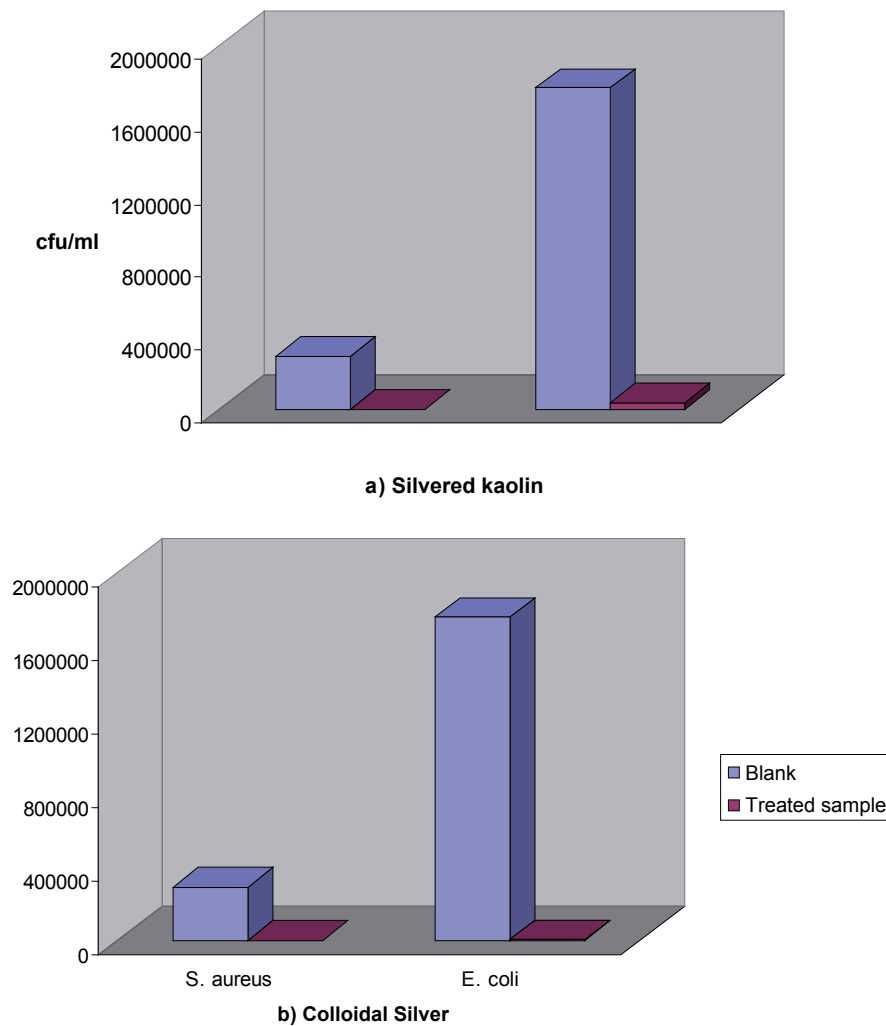


Figure 3. Number of cfu/ml in the samples treated with a) silvered kaolin and b) colloidal silver in relation to a blank, for each microorganism.

Standard JIS Z 2801 defines the antimicrobial activity of a surface, R , as the difference between the number of bacteria in the control sample (blank) and the number of bacteria in the treated sample, according to equation 1.

$$R = \log B - \log C$$

Equation 1.

where, B is the number of cfu per ml in the control sample (blank) after 24 hours.

C is the number of cfu per ml in the treated sample after 24 hours.

The number of cfu in the treated samples and in the control samples were used to calculate the antimicrobial activity, R , from equation 1. Table 1 details the values of R obtained for each microorganism and for each material.

Material	Ag in the ink (%)	Firing	Standard JIS Z 2801			
			Staphylococcus aureus		Escherichia coli	
			R	Relative reduction (%)	R	Relative reduction (%)
Silvered kaolin	0.3	Third fire	2.6	-99.7	1.7	-98.0
Colloidal silver	3	Single fire	4.3	-99.99	2.9	-99.9

Table 1. Antimicrobial activity, R, and reduction percentage in the resulting bacteria for the studied materials.

It should be noted that the silver used is effective at very low concentrations (< 0.3%), while higher concentrations do not significantly enhance its antimicrobial activity, which, together with the cost of the silver, advises against working with high concentrations.

4. CONCLUSIONS

The present study demonstrates the feasibility of the industrial application of silver nanoparticles for providing ceramic tiles with bactericidal and fungicidal properties, which are two functionalities with high added value.

The deposition of silver nanoparticles in the form of screen printing ink on ceramic tiles requires no changes in the ceramic tile manufacturing process: the same glaze and ink application systems and the same firing cycles that are currently employed can be used. In addition, the application allows all the design possibilities of current ceramics to be applied.

The integration of silver nanoparticles in an organic or inorganic matrix suppresses or minimises their aggregation, favouring their stability during ink preparation and application, as well as during subsequent thermal treatment. This means that a bactericidal effect can be obtained with very small quantities of silver and, therefore, a reduction in manufacturing costs.

On the other hand, the use of matrices containing silver nanoparticles minimises the occupational risk associated with the use and handling of nanometric size particles.

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