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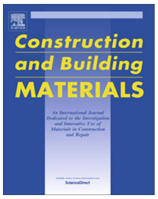

Nanoparticles surface treatment on cemented materials for inhibition of bacterial growth

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HIGHLIGHTS

- Bactericidal characteristics of cementitious materials treated with nanoparticles is reported.
- Untreated zinc oxide and PVP-capped silver nanoparticles have been compared.
- A range of surface pH of mortar samples and bacterial cell densities have been investigated.
- After the seven-day period, more than 60% reduction of viable cells was observed.
- Stabilisation of nanoparticles reduced aggregation and favoured a consistent long-term performance.

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ABSTRACT

Bacterial growth on cemented materials such as concrete can cause degradation and early ageing. This paper explores the bactericidal characteristics of cementitious materials surface treated with zinc oxide (ZnO) and silver (Ag) nanoparticles. The growth of gram positive *Bacillus cereus* and gram negative *Escherichia coli* has been monitored. The growth inhibitory performance of nanoparticles against two model bacteria was further examined at different surface pH of mortar samples and different bacterial cell densities. After the seven-day experimental period, more than 60% reduction in the number of viable cells of both model bacteria was obtained at all tested pH values when nanoparticles with a concentration of 250 mg/l were added at the beginning of culturing time. However, delayed addition of nanoparticles at the mid-logarithmic growth phase, i.e., higher cell densities, resulted in less growth inhibition. Ag nanoparticles showed the highest inhibition due to the high degree of nanoparticle stability and uniform particle size. On the other hand, the stability of ZnO nanoparticles in the experimental mixture was significantly influenced by the pH change and aggregation, which resulted in lower inhibition efficiencies. Gram-positive *Bacillus cereus* was found to be less sensitive to both tested nanoparticles, compared with Gram-negative *Escherichia coli.* The experiment demonstrates the efficacy of nanoparticles in inhibiting bacterial growth on cementitious materials.

1. Introduction

Concrete is a major contributor to the economy of most countries as it is the most widely used manufactured material for construction of buildings, roads, sewer systems, marine structures, bridges, and tunnels. However, the durability of concrete is considered as a major challenge in sustainable construction of infrastructures. Loss of structural integrity and reduced durability of concrete occurs due to a variety of reasons such as corrosion of reinforcing steel, alkali-aggregate reaction, freezing and thawing, sulphate attack, and biodeterioration [1]. Susceptibility of concrete to biological agents been revealed more recently and it can be serious in structures such as sewer systems, subsea pipelines, bridge piers, oil and gas pipelines, and offshore platforms [2,3]. Biodeterioration caused by the growth of microorganisms such as bacteria, fungi, algae and lichens on concrete and mortar surfaces, can result in undesirable changes in concrete properties due to the release of corrosive metabolites and creation of an environment that stimulates steel corrosion or loss of original aesthetic quality due to the formation of biological stains [4,5]. Severe deterioration of concrete in oil storage tanks and legs of offshore platforms has been observed due to sulphate reducing bacteria [6]. The growth of microorganisms such as sulphur oxidising, nitrifying, and ammonia oxidising bacteria on the surface of reinforced concrete in highway bridges was also reported [7]. Active sulphur-oxidising

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bacteria were detected in concrete samples derived from a bridge site in Texas [8], and a positive correlation between the bacterial activity and the degree of deterioration was observed.

Although the high alkalinity of concrete and mortar was considered a major deterrent to microbial growth, colonisation, and growth of microorganisms on or within concrete has been reported after surface neutralisation has progressed [9]. Penetration of carbon dioxide into the surface of concrete and its subsequent reaction with the alkaline components of cement paste ($Ca(OH)_2$) can reduce the pH value of the pore solution to values as low as 9 [10]. This drop in the pH can stimulate the growth of different groups of microorganisms on the surface of concrete [11]. For example, in sewer systems, colonisation of *Thiobacillus thioparus*, a sulphur oxidising bacteria, on the surface of concrete pipe crown at pH 9 was reported [12]. The growth of *T. thioparus* via oxidation of thiosulphate lowers the pH of the surface to moderate or weakly acidic conditions and initiates the successive colonisation of *Thiobacillus novellus*, *Thiobacillus neopolitanous*, and *Thiobacillus intermedius*, which contribute to further reduction of pH. At pH of less than 5, the rapid abiotic or biological conversion of thiosulphate to elemental sulphur enhances the sulphur oxidation pathway by vigorous colonisation and growth of *Acidithiobacillus thiooxidans*. The accelerated formation of sulphuric acid reduces the pH to the values as low as 1.5 [12,13]. Severe damages of sewer pipes due to the reaction of produced sulfuric acid with the calcitic binding material of the concrete and loss of structural integrity has been reported [9].

In order to protect concrete against biodeterioration, surface coatings and incorporation of biocides, either within the coating system or concrete matrix, were commonly used for inhibition of microbial growth and metabolism [14]. Embedment of calcium format, a growth inhibitory compound, in the concrete mix was reported to protect concrete pipes against bacterial degradation in sewer systems [15]. Nonetheless, the effectiveness of biocides is generally temporary and in high dosages, they might affect the structural properties of concrete [16]. Protective materials such as epoxy coatings have also shown excellent initial performance in protecting concrete from chemical and biological deterioration. However, delamination or poor bonding of coatings to the concrete substrate can dramatically reduce their protective performance [17].

Recent advances in nanotechnology revealed that decreasing the particle size to nano scale significantly increases the surface area-to-volume ratio and therefore, alters the physical, chemical and biological properties of nanomaterials, compared to the bulk material of origin [18,19]. In particular, reducing the size of antimicrobials can result in superior properties due to the greater interaction with the surrounding microorganisms (as a result of the larger surface area to volume ratios) or the enhanced release of toxic ions or reactive oxygen species (ROS) from their surface [20]. As a result, nano sized antimicrobial compounds may exhibit multiple mechanisms of action, compared to their bulk forms. In general, the antimicrobial properties of nanomaterials have been attributed to several mechanisms including damage of the cell membrane by either direct contact with nanoparticles or photocatalytic production of reactive oxygen species, release of toxic ions, interruption of electron transport, protein oxidation, and modification of membrane charges, degradation of DNA, RNA and proteins by ROS; and lowering the production of adenosine triphosphate (ATP) due to acidification and ROS production [21]. Furthermore, the addition of nanoparticles to coatings such as epoxy has been found to improve their protective performance [22,23]. Due to their small size, nanoparticles can fill the cavities, and hence increase the integrity and durability of the coatings [24]. In recent years, application of nanomaterials such as TiO_2 nanoparticles in protective coatings to prevent stone materials from the chemical and biological attack has been studied [25,26]. TiO_2-based cementitious materials were reported to eliminate both organic and inorganic air pollutants [27].

Application of nanomaterials for the development of antimicrobial mortar and concrete surfaces can be achieved through two different approaches: incorporation of nanomaterials within the concrete mix, as new building material, and surface treatment over partially deteriorated concrete structures [28,29]. The former approach, i.e., surface coated concrete, provides larger NP-microorganism contact area than concrete with embedded nanoparticles. A common challenge in the application of nanomaterials for antimicrobial purposes is uncontrolled aggregation that dramatically changes the original size and shape of nanoparticles and greatly influences the cell–particle interactions. The aggregation-disaggregation behaviour of nanomaterials depends on several factors including medium pH, ionic strength and also the presence of proteins in the biological systems [30,31]. As cement materials have a high initial pH that greatly varies with time, the efficacy of the nanoparticles on concrete surface needs investigation. The growth inhibitory efficiency of nanoparticles was also shown to be dependent on the bacterial cell concentration [32], and therefore can be influenced by the time of application over either fresh or partially deteriorated surfaces, where a certain level of bacterial growth has developed.

Despite promising developments in nano-enhanced cemented products, the release of nanomaterials into the medium in contact, i.e. air or water, has raised environmental and health concerns. Susceptibility of these products to physical and chemical stress such as mechanical abrasion, chemical degradation under UV light and moisture, and biodegradation may stimulate the release of embedded nanomaterials [33]. Although various toxicological and ecotoxicological studies have examined the dose-response characteristics of a few nanoparticles on single species under laboratory conditions, the lack of material specifications for engineered nanomaterials further limits the development of handling and safety standards [34]. In this regard, adopting principles of industrial ecology and pollution prevention can be considered as a high priority to minimise the environmental and health risks of manufactured nanomaterials [35]. Moreover, the green manufacturing process can be applied to develop re-engineered and less hazardous nanomaterials.

This study reports the effectiveness of two types of antibacterial nanoparticles, silver and zinc oxide when applied on cementitious materials. Both ab initio and retrofit treatments with nanoparticles have been studied. Furthermore, the effects of surface pH and bacterial cell density (i.e., bacterial population in partially deteriorated structures) on the antibacterial activity of the selected nanoparticles were examined.

2. Materials and methods

Bacillus cereus, a gram positive bacterium with thick peptidoglycan layer in the bacterial cell wall, and *Escherichia coli*, a gram negative bacterium with thin peptidoglycan layer, were used as model bacteria. Metal oxide ZnO and metallic Ag nanoparticles were used as antimicrobial agents as they were shown to demonstrate an effective antimicrobial activity against a wide range of microorganisms in both microscale and nanoscale formulations. Nanoparticles with an approximately similar particle size (25–30 nm) were used in this study. To investigate the effect of nanoparticles stability on their performance, a commercially stabilised suspension of silver nanoparticles was used in antibacterial tests; whereas ZnO suspensions were made in the laboratory and were subjected to ultrasonication to provide a homogenous dispersion.

The general methodology to evaluate the effectiveness of nano-treated mortar surfaces in inhibiting the bacterial growth consisted of two stages, as schematically represented in Fig. 1.

At the first stage, Kirby-Bauer disk diffusion test was used to visually monitor the growth of model bacteria in the vicinity of mortar disks treated with antimicrobial nanoparticles (Fig. 2). This technique involves the growth of microbial species on Mueller-Hinton agar in the presence of antimicrobially treated disks. The presence or absence of growth around the disks can be used as a measure of the ability