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# Biofouling resistance of titanium dioxide and zinc oxide nanoparticulate silane/siloxane exterior facade treatments

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ABSTRACT

This paper presents the evaluation of zinc and titanium nano-oxide silane/siloxane emulsions and their resistance to biofouling by algal colonisation. A culture streaming study was conducted to evaluate each treatment using mortar samples. Characterisation of the treatments included assessment of the porosity, surface roughness, sorptivity, hydrophobicity, treatment depth and visual alteration. The results showed that nanoparticulate incorporation did not adversely alter treatment penetration. Nanoparticulate treatments improved water repellence significantly while effectively conserving the morphology of the substrate. Treatments had negligible impact on visual aesthetics of the substrate making them ideal for future retrofit and heritage schemes. It was concluded that the reduced bioreceptivity observed primarily stemmed from the nanoparticulates ability to photocatalytically breakdown contaminants.



## 1. Introduction

Chlorophytes (green algae) and Cyanophytes (blue-green algae) are the most abundant colonisers of facades where moisture is present [1]. They produce green, red and black stains depending on species, which in turn severely alter the aesthetics of a structure. Once these organisms take hold, they also help establish lichens, bryophytes and larger vegetative matter [2]. This increases water retention by the substrate accelerating various degradation mechanisms [3–5], while reducing the energy efficiency of the building [6–8]. In addition, moisture ingress may cause structural decay, as well as both physical and mental health problems for residents [9,10]. Retrofitting of the existing housing stock is a key necessity in reducing UK carbon dioxide emissions to meet the 2008 Climate Change Act, which requires a 34% carbon dioxide reduction by 2020 and 80% by 2050 relative to the 1990 output [11]. It has been estimated that 75% of dwellings existing in 2050 would have already been built, implying that there is a strong need for retrofitting of the existing housing stock to meet UK government targets [12].

Silane/siloxane based water repellents incorporated into oil-in-water (o/w) emulsions are currently the new trend in facade remediation. Silane and siloxane form three-dimensional interpenetrating networks and bond to substrates such as masonry and wood [13,14]. These emulsions are water-based; reducing volatile organic compound (VOC) emissions. They also exhibit shear-thinning properties allowing for more control during application compared to conventional solvent borne solutions. Many of these emulsions use the water present as a catalyst for curing; eliminating the need for harmful peroxides. This is beneficial for the phasing out of unnecessary hazardous materials in accordance with European legislation [15].

Due to their small molecular size, silanes have the potential to allow water vapour to permeate through a structure providing a drier internal environment. Conversely, conventional paints seal these pores stopping humidity from dissipating, increasing the potential for biological propagation and degradation. Siloxanes are often used in these systems to help silane retention during curing and enhance the water beading characteristics at the facade interface. These treatments do not effectively alter the aesthetics of a building unlike conventional coatings, allowing these emulsions to be potentially used nationwide by governments in an effort to reduce green house gas emissions by improving thermal envelope efficiency [16,17].

Green and blue-green algae require light for photosynthesis and cannot survive without it. The interior of a porous substrate thus would not provide favourable conditions for growth. It makes sense

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therefore to use photocatalytic materials requiring UV light to control growth [18]. Thus, in order to further enhance these novel emulsions, two highly effective photocatalytic nano-sized metal oxides were incorporated into the treatments; titanium dioxide (∼15 nm) and zinc oxide (∼20 nm). Since the discovery of water photo-splitting by titanium dioxide in a photochemical cell, photocatalytic oxidation has received significant interest [19]. The two main advantages of incorporating photocatalysts into construction materials and surface treatments with regard to biofouling are twofold. Firstly, alteration of the metal oxide structure by UV irradiation produces a 'super-hydrophilic' interface that allows water to form a thin film on the surface. Better wetting of the contaminants can thus be achieved making removal by runoff and evaporation easier. Secondly, photo-induced oxidation of biofouling contaminants denatures them and destroys bonds formed with the substrate. Water, oxygen and UV irradiation are all required for the production of the super oxides and hydroxyl radicals used during this process [18]. It should be noted that this process is reversible and hence photocatalytic surfaces are amphiphilic in nature.

It is considered that sanitisation of bacteria (*Escherichia coli*) by photo-oxidation occurs due to hydroxyl radicals degrading cell walls and thus interfering with processes such as growth and division [18,20]. Since blue-green (cyanobacteria) algae share similar traits, it seems plausible that this is the key denaturing mechanism in this study although information in this field is sparse [21]. The photocatalytic treatments in this study therefore may help inhibit biofouling, reducing retained water and increasing the longevity and energy efficiency of the structure. However, since silane/siloxane treatments are conventionally noted for their UV resistance and water repellent nature it was unclear to what extent this photocatalytic process would influence bioreceptivity [22]. This study therefore looks into the mechanisms that influence bioreceptivity and thus tries to determine the contribution made by such particulates in these particular treatments.

## 2. Experimental

### 2.1. Emulsion preparation

n-isooctyltriethoxysilane 95% (ITES), polydimethylsiloxane and a non-ionic polyoxyethylene stearate (POE) was purchased from ABCR Gmbh & Co. KG. Distilled water was obtained from ReAgent Chemical Services Ltd. Titanium dioxide (anatase) 99% and zinc oxide 99.5% were purchased from Nanostructured & Amorphous Materials, Inc. The emulsions were prepared by phase inversion and high shear mixing with <0.5%wt of POE used as the emulsifier. This was then followed by the introduction of the respective nanoparticulate dispersion produced by a technique developed by the APC Research Group of the University of Portsmouth. Oil to water volume ratio was kept at approximately 8:2. Emulsion details are given in Table 1.

### 2.2. Mortar preparation

Testing was carried out on mortar slabs (17 cm × 27 cm × 2 cm). Due to easier mould removal and better surface finish a 3:1 sand-to-cement mortar was selected over a 4:1 mortar. Water/cement weight ratio was relatively high, 0.6, as a study conducted by Giannantonio et al. [23] showed that higher ratios produce more porous substrates, making them potentially more susceptible to biofouling. The mortar was put in wooden preforms using a float and left for three days to cure. The samples were then removed and left to dry for a week. Each sample was treated using a pre-wetted brush with 40 g of emulsion and allowed to cure for another week. Additionally, plastic rods were attached to the top rear of each culture streaming test sample using epoxy resin so that these could be mounted inside the rig; samples were left for 24 h before installation.

### 2.3. Culture streaming test

Water containing algal culture was pumped onto mortar samples placed on a rack (inclined at a 45° angle) inside a tank. The culture that was not retained by the mortar was collected in the tank's base and then recycled. Prior studies were used as the basis for the test design [5,6,24–26]. The system consisted of a 179 cm × 60 cm × 70 cm acrylic tank containing a pitched acrylic rack. A 45° angle allowed increased contact time between the culture and the mortar. Internal parts of the tank were joined together by polycarbonate glue first and then sealed using marine sealant containing no biocides. Two 36 W 150 cm fluorescent lights (Kengo F58 T8/835; Luen yick Electrical Mfg. Co. Ltd.) were bolted to the tank sides at a point where light would be equidistant from the surface of the samples to be tested. Above these, two 36 W 120 cm UV-B lights (F40-BLB-EX; GE Lighting) were added to represent UV influence on fouling and the treatments to be tested. The top of the tank was not hermetically sealed; however it was covered in aluminium foil to help focus light on the samples. Two 300 W aquarium heaters were placed in opposing corners of the tank and set to maintain the temperature at ∼25 °C. Two magnetic stirrers were placed approximately 45 cm from each end of the tank to help reduce settling and consolidation of algal matter. Figs. 1–3 show rig set up and mortar sample placement.

5 mortar samples of each type were hung on the rack. Above the samples an 8 mm diameter plastic rail containing 1.5 mm holes every 20 mm was mounted on plastic supports attached to the rack. The distance from the rails to the sample surface was approximately 15 cm and designed to allow water to fall approximately 2–3 cm from the top of the sample. The tank contained two 1400 L/h 24 W water pumps. Each pump was attached to both rails at either end using T-connectors. At one end two remote probes of a data logger (TR-74Ui; T&D Corporation) were mounted onto one of the rail stands. The remote data logger measured; light illumination, UV irradiance, temperature and humidity during testing. This was set up to record data every 10 min over the eight week testing duration. Water was sprayed for 90 min every 12 h for the duration of testing. The lights for this period were turned on at the start of the first streaming cycle and turned off at the finished of the second. The rig was set up in a large wooden frame that was covered with black-out cloth to reduce external influence. Every week periodic scans were conducted using an Epson 1250 Photosmart scanner. These images were then used to assess changes in colonisation kinetics of each sample. Scanned images were transformed into 8-bit greyscale images containing a range of 0–256 possible intensities, relating to dark to light respectively. A histogram of each image was then calculated using imaging software (IRIS; Christian Buil) which helped identify any change in colour during the study. Changes in colour would alter the

**Table 1**
Emulsion descriptions.

| Abbreviation | Treatment description | Nano-particulate incorporation (%wt) |
|---|---|---|
| TC | Mortar control (no treatment) | N/A |
| EC | Control emulsion (no nanoparticles) | N/A |
| EZ | Zinc oxide emulsion | <0.1 |
| ET | Titanium dioxide emulsion | <0.1 |