Preparation of modified paints with nano-structured additives and its potential applications

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Abstract
Recently, an increase in the production of intelligent nanomaterials has been reported for the application of solid surface coating. These nanomaterials provide a wide number of functionalities such as anticorrosive, antibacterial, and self-cleaning properties. Hence, titanium dioxide (TiO₂) and zinc oxide (ZnO) nanoparticles were synthesized using a green chemistry approach. These nanoparticles were fully characterized by scanning electron microscopy, energy-dispersive X-ray, high-resolution transmission electron microscopy, X-ray diffraction, ultraviolet (UV)–visible spectroscopy, Brunauer–Emmett–Teller test, and nitrogen adsorption–desorption isotherm. Then, a commercial enamel-type paint was modified by using different concentrations (2, 3.5, and 5 w/v%) of nanoparticles. These nanofilled paints were then brushed onto the surface of different types of materials such as carbon steel sheets, wood sheets, and aluminum disks. Anticorrosive, self-cleaning, and antibacterial properties of the nanofilled paints were evaluated, with the aim to determine the capability for this application. According to the characterization results, TiO₂ and ZnO nanoparticles exhibited similar physicochemical properties compared to those synthesized using traditional methods. The anticorrosion results revealed that nanofilled paints provide a barrier using low concentrations of nanoparticles, due to the decrease of agglomerates on the surface avoiding the presence of high porosity. In the case of self-cleaning, a proposed mechanism of degradation demonstrated that the presence of both nanoparticles in the paint provided high degradation of methylene blue due to the high surface area offered by the nanoparticles. On the other hand, antibacterial activity under UV light was observed only for ZnO nanoparticles, which may be related to the diffusion of nanoparticles into the cell membrane of the bacteria, affecting the normal function. These results showed to be promising for the modification of paints with TiO₂ and ZnO nanoparticles, and the application on solid surfaces for the construction, and even in textile fields.

Keywords
Nanoparticles, paint, self-cleaning, antibacterial, anticorrosion

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Introduction
The growing research focused on the synthesis and modification of materials in the nanoscale has increased their applicability in different fields such as biomedicine, electronics, optics, computing, solar thermal energy, construction, and intelligent coatings.1–6 Among the multifunctional properties of these nanocomposites are

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Titanium dioxide (TiO$_2$) and zinc oxide (ZnO) nanoparticles have been extensively studied for the application as self-cleaning, anticorrosive, and antibacterial additives in construction materials, especially in external surfaces, due to the improvement offered to the aesthetic quality of buildings, leading to a reduction in maintenance cost.

The incorporation of nanomaterials in paints may lead to the inhibition activity of a wide number of Gram-positive and Gram-negative bacteria, which is very hard to prevent nowadays.

Titanium dioxide (TiO$_2$) and zinc oxide (ZnO) nanoparticles have been extensively studied for the application as self-cleaning, anticorrosive, and antibacterial additives in construction materials, especially in external surfaces, due to the improvement offered to the aesthetic quality of buildings, leading to a reduction in maintenance cost.

Among the properties of these mesoporous photocatalytic nanomaterials are those to improve the surface characteristics of a limestone building such as adhesion efficiency, mechanical resistance, and hydrophobic behavior, as well as the degradation by solar radiation of other compounds such as methylene blue (MB) and carbon soot for self-cleaning purposes.

TiO$_2$ and ZnO production has been focused in the use of green chemistry with the aim to reduce the high energy consumption, toxic chemical, and high cost, needed for the synthesis using traditional methods. Hence, natural sources such as plants, organic, and agricultural wastes are considered as raw material environmentally friendly, in which concentrated extracts can be obtained allowing the reduction of metal precursor without using hazardous chemicals.

Different species of plants have been used to prepare leaf extracts for the synthesis of TiO$_2$ and ZnO nanoparticles, including Phyllanthus niruri, Trigonella foenum-graecum, Psidium guajava, Sesbania grandiflora, Azadirachta indica, Typha latifolia, Averrhoa bilimbi, and Chamaecostus cuspidatus. Current study proposed the use of Cymbopogon citratus (commonly known as lemongrass) leaf extract as reducing of metal precursors and capping agent, due to the high content of phytochemicals such as neral, citral, geranial, pinito, allantoin flavonoids, hydrocarbons, waxy esters, sterol esters, ketones, aldehydes, terpenoids, phenols, fatty alcohols, fatty acids, among others.

This plant is widely available in tropical and semitropical environment zones throughout Asia, Africa, and South America. Therefore, lemongrass leaves were proposed to be part of the raw material in the synthesis of TiO$_2$ and ZnO nanoparticles since they are easily found in the Department of Bolivar (Cartagena, Colombia) and are no part of the food chain.

Modification of paints with nanomaterials has been recently investigated, as was reported by Zhou et al., in which a self-cleaning transparent coating based on fluorocarbon and semicrystalline colloidal particles of TiO$_2$-SiO$_2$ was prepared, achieving 96% of methyl orange discoloration using a concentration of 1.5%.

Truppi et al. studied the self-cleaning and photocatalytic properties of TiO$_2$/AuNRs-SiO$_2$ nanocomposite for application in construction materials. Wang et al. developed a pseudo alloy Zn-Al-Mg-TiO$_2$ coating by cold spraying technique on a Q235 substrate, in which the performance of Zn-Al-Mg-TiO$_2$ coating on marine metallic equipment was studied using saltwater dynamic corrosion tests, electrochemical tests, and wear and tear tests. The results reported by Wang et al. revealed that the Zn-Al-Mg-TiO$_2$ coating provided excellent anticorrosion and wear resistance, providing a stable and long-term protection for the metallic substrate, due to the nanoparticle content acted as a physical barrier, preventing the penetration of O$_2$ and H$_2$O. On the other hand, the antibacterial activity of TiO$_2$ and ZnO nanoparticles was widely studied and reported in the scientific literature.

Shankar et al. used three types of ZnO nanoparticles to manufacture a PLA/PBAT-ZnONP composite film, offering a good inhibition activity against Escherichia coli and Listeria monocytogenes. In a similar study, Thakur et al. investigated the green synthesis of TiO$_2$ nanoparticles and their antibacterial activity against several bacteria such as E. coli, Bacillus subtilis, Salmonella typhi, and Klebsiella pneumoniae, in which the results indicated a high inhibition.

Additionally, recent research has also studied the mechanical properties, thermal stability, and weather resistance for resin-based coatings and paints modified with nano- and microscale particles such as SiO$_2$, Ag, CeO$_2$, TiO$_2$, and ZnO. Hence, adhesion tests have been applied using the ASTM D3359 (cross-cut), ISO 2409 (cross-cut), and ASTM D4541-09 (pull-off) standards. The durability of the paints after irradiation can be obtained using a test widely known as weathering durability.

Results from these tests may provide details about the effect on the adhesion and durability with the incorporation of nanoparticles in paints, in which no significant impact has been evidenced in most of the cases. Nguyen et al. analyzed the effect of Rutile (R-TiO$_2$), and ZnO nanoparticles on ultraviolet (UV) shielding efficiency of a water-based acrylic coating. The adhesion and weathering durability tests were performed using a UV/condensation weathering chamber equipped with UV-B-313 fluorescent radiation.
lamps. After 60 cycles of UV/condensation weathering chamber exposure, no significant changes of the color were evidenced, and the adhesion values slightly decreased from 2.5 and 2.4 N/mm² to 2.3 and 2.1 N/mm² for paints modified with R-TiO₂ and ZnO nanoparticles, respectively.

We hereby report a green approach for the synthesis of TiO₂ and ZnO nanoparticles using lemongrass extract as a capping agent for the control size of synthesized nanoparticles. We found that the phytochemical content of extract, promoted the formation of nanoparticles as was observed through the morphologic information obtained from the microscopy images. The physicochemical properties of the as-prepared nanoparticles are similar to those nanoparticles synthesized using the traditional techniques. Finally, the influence of TiO₂ and ZnO nanoparticles in paints was evaluated to determine the efficiency of the anticorrosive, antibacterial, and self-cleaning.

Materials and methods

Materials

Fresh lemongrass leaves (C. citratus) were collected from Cartagena, Colombia. Titanium (IV) isopropoxide (C₁₂H₂₈O₄Ti) solution (95%) and anhydrous zinc chloride (ZnCl₂, >97%) were purchased from Sigma-Aldrich (Burlington, MA). All reactions were carried out using ACS Reagent chemicals. The commercial enamel paint for exteriors was supplied by the brand Kolor®, which is basically made from polyester (alkyd resin) modified with fatty acids and sometimes contains glass powder or tiny metal flake fragments instead of pigments. Varsol (100%) produced by ALGRECO® was acquired in order to increase the shine and hardness of the paint, which is mainly made from distillates of petroleum (aliphatic hydrocarbons).

Green synthesis of TiO₂ and ZnO nanoparticles

The procedure for the preparation of aqueous extract of lemongrass, and then the green synthesis of TiO₂ nanoparticles, was according to the methodology reported previously.71 Lemongrass leaves were cut, washed, and dried to remove impurities, and then crushed manually. One hundred grams of biomass was added in cloth bags for further solvent extraction using 500 mL of distilled water for 6 h. The lemongrass extract thus prepared was then placed in a storage at 4°C. Afterward, 100 mL of this extract was mixed with 20 mL of the precursor C₁₂H₂₈O₄Ti by dropwise addition in a 250 mL beaker. The solution was placed in an ultrasound processor (ultrasonic processor, WiseClean WUC-A06H, Acinterlab (Miami, Florida), 60 Hz), allowing to react for 30 min approximately. The nanoparticles were washed using distilled water and ethanol reagent grade, and then collected by centrifugation at 5000 r/min for 30 min, repeating the procedure several times to remove unreacted precursor. Calcination at 550°C for 3 h was performed with the aim to obtain the anatase phase of TiO₂ nanoparticles.

For the ultrasound-assisted green synthesis of ZnO nanoparticles, a procedure reported by Mohammadi et al.,72 with minor modification was performed. Twenty grams of ZnCl₂ were dissolved in aqueous lemongrass extract (400 mL) with a ratio of 80:320 v/v under magnetic stirring at room temperature for 20 min. In order to adjust the pH = 12 of the solution, 15 mL of sodium hydroxide solution (5 M) was slowly added at 500 r/min. Subsequently, the suspension was placed in an ultrasonic processor (WiseClean WUC-A06H, 60 Hz) for 15 min, then followed by centrifugation at 4000 r/min for 10 min. The resulting precipitate was collected and washed four times with distilled water and twice with ethanol, and finally calcined at 500°C for 5 h.

Characterization

The morphology of TiO₂ and ZnO nanoparticles was studied by using a high-resolution transmission electron microscope (HRTEM) FEI Tecnai F20 Super Twin TMP (Thermo Fisher Scientific, Hillsboro, Oregon). Additionally, an elemental analysis was performed using energy-dispersive X-ray (EDX) spectroscopy. Solutions of 10 μg/mL of TiO₂ and ZnO nanoparticles in absolute ethanol were prepared by using an ultrasound bath, with the aim to obtain a good dispersion of nanoparticles in the medium. Then, a micropipette was used to place a drop of nanoparticle solution onto a carbon-coated grid and let dry for 5 min. Finally, the grid was placed in the holder, which was then introduced inside the microscope. Scanning electron microscopy (SEM) images were acquired using a Phenom XL tabletop (Thermo Fisher Scientific, Hillsboro, Oregon) with an operating voltage of 15 kV. X-ray diffraction (XRD) of the samples was performed in standard reflection (2θ: 5–60°) using an X-ray diffractometer XPert PANalytical Empyrean Series II—Alpha1, Model 2012 (Malvern Pananalytical, Malvern, UK) equipped with copper anode (copper K alpha 1 (CuKα1), λ = 1.5406 Å) and operated at 40 kV and 40 mA. On the other hand, the specific surface area was measured by nitrogen (N₂) adsorption–desorption analysis at −196°C using a Micromeritics (Norcross, GA) ASAP 2020 surface area and porosity analyzer. Prior to N₂ adsorption–desorption analysis, the samples were degassed at 300°C for 2 h in a vacuum. Finally, ultraviolet–visible diffuse reflectance (UV-vis-DRS) was carried out in a spectrophotometer Thermo Scientific (Madison, WI) Evolution-600, with BaSO₄ as a reference and using a scanning speed of 240 nm/min.

Modification of enamel paint with TiO₂ and ZnO nanoparticles

Different concentrations (2, 3.5, and 5 w/v%) of the as-synthesized TiO₂ and ZnO nanoparticles were used to modify a commercial enamel-type paint, according to the
procedure reported by Amorim et al. Initially, the nanoparticles were added into 1 mL of Varsol and then dispersed by placing the solution in an ultrasound bath for 2 min. Then, 3.5 mL of enamel paint was added into the previous solution and stirred for 1 min using a metal stirring rod. The effect of the nanoadditive-modified paints on the anticorrosion, self-cleaning, and antibacterial properties was evaluated by brushing the paints on the surface of rectangular carbon steel sheets (10 x 15 x 0.3 cm$^3$), rectangular wooden sheets (5 x 7.5 x 0.5 cm$^3$), and thin aluminum disks with a thickness and radius of 0.1 mm and 1 cm, respectively. The samples were then dried completely for 72 h at room temperature prior to the evaluation of the as-mentioned paint properties.

Anticorrosion, self-cleaning, and antibacterial evaluation

Anticorrosion test was performed in a salt fog chamber (Renault (Strongsville, Ohio D17 1058J) using the ASTM B117:16 for 200 h. The dimensions of the samples were adjusted to 10 x 15 x 0.3 cm$^3$ (width, height, and thickness) and were then painted on both sides using an insulating tape for coating the edge.

The self-cleaning capacity of the samples coated with nanofilled paints was evaluated through the degradation of MB organic dye stain, as a function of the accumulated solar radiation (0, 3000, and 4000 J/m$^2$). This test was measured using an HD 2102.2 Photoradiometer (Delta OHM, Padova, Italy) equipped with an LP 471 UVA probe (315–400 nm) (Delta OHM, Padova, Italy). Accordingly, an MB with a concentration of 20 mg/L was prepared, and 0.1 mL (a drop) was then placed in the middle of the wood samples coated with nanofilled paint, and finally, the samples were exposed to solar radiation. Samples were photographed in order to appreciate visually the decolorization (Padova, Italy) degree, and then compared using a sample coated with unmodified paint (target). To quantify the decolorization percentage, four solutions (5, 10, 15, and 20 mg/L) of MB were prepared, a drop of each solution was deposited on a rectangular wooden sheet coated with paint without nanomaterials and dried for 72 h at room temperature and darkness. Finally, the cyan composition of each spot was determined using the eyedropper tool of Adobe Illustrator CS6 software.

On the other hand, the antibacterial test was carried out by using aluminum disks coated with nanofilled paints for inhibition of E. coli. Fourteen grams of nutritive agar (OKOID, CM0003) were weighed following a typical formula: 1 mg/L of “Lab-Lemco” powder, 2 g/L of yeast extract, 5 g/L of peptone, 5 g/L of sodium chloride, and 15 g/L of agar. These nutrients were dissolved using a base volume of 500 mL of distilled water, which was then stirred at 500 r/min and heated up until boiling temperature was reached. The solution was cooled down to decrease the temperature up to 30°C, and the pH was then measured and adjusted to 7.35. The nutrient agar was sterilized at 121°C and 2 atm or 75 min (15 sterilizing and 60 drying). Aluminum disks of 1 cm of diameter were cut in order to perform the test by duplicate. The disks were then coated by using unmodified paints and nanofilled paints with TiO$_2$ and ZnO nanoparticles. The antibacterial activity test against E. coli was carried out in sterile petri dishes, in which 20 mL of sterile culture medium was poured and left to solidify for 1 h. Finally, the disks were placed into the petri dishes and incubated at 37°C for 24 h.

Figure 1. SEM images of (a) TiO$_2$ and (b) ZnO nanoparticles. SEM: scanning electron microscopy; TiO$_2$: titanium dioxide; ZnO: zinc oxide.
Results and discussion

Characterization

The morphology of the as-prepared TiO$_2$ and ZnO nanoparticles was studied by SEM, as shown in Figure 1(a) and (b), respectively. For both types of nanoparticles, the same agglomeration behavior can be easily observed using a magnification of $\times$500 at 100 $\mu$m, which is a typical result for the synthesis using a green approach.

HRTEM images of TiO$_2$ nanoparticles are shown in Figure 2(a) to (d). Figure 2(a) shows an agglomerated system of nanoparticles with a similar shape of a sphere, obtaining an average size particle of 12.34 ± 1.52 nm. From Figure 2(b) the lattice spacing can be clearly evidenced, which represents the interplanar space (101) of the anatase phase with a value of 0.353 nm. In addition, rings corresponding to planes (101), (004), (200), and (105) were identified in Figure 2(c), revealing the polycrystalline character of TiO$_2$ nanoparticles synthesized using green ultrasound-assisted chemistry. The purity of the sample was also confirmed using the EDX spectrum, the results of which are shown in Figure 2(d) and indicate the presence of Ti atoms.

These results are in agreement with those reported by Liang et al.,$^{26}$ in which TiO$_2$ nanoparticles were synthesized through the sol-gel method using acetylacetone as the hydrolysis control agent, and with a calcination temperature of 500°C. Equation (1) was used to identify the planes of TiO$_2$ nanoparticles corresponding to each ring obtained in the selected area electron diffraction (SAED) pattern.

$$\frac{1}{d_{(hkl)}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$ (1)
where $h$, $k$, and $l$ are the Miller indices, $a$ and $c$ the lattice parameters, in which $a = 3.7852 = b \neq c = 9.5139$ and $d_{hkl}$ are the lattice spacing values for tetragonal structures.$^{73,74}$

ZnO nanoparticles were also studied by HRTEM, as shown in Figure 3(a) to (d). Figure 3(a) reveals that the green ultrasound-assisted chemistry method generates semispherical and rod-shaped nanoparticles with average particle sizes of $137.41 \pm 15.80$ and $54.81 \pm 12.57$ nm, respectively. Additionally, a wide size distribution was observed and is similar to that reported by Begum et al.$^{75}$ in which ZnO nanoparticles were synthesized using *Eryngium foetidum* L. The lattice spacing showed in Figure 3(b) was determined for the Wurtzite phase (100) with a value of 0.29 nm. Figure 3(c) indicates the ring corresponding to the plane (102). Finally, high purity of Zn atoms contained in the sample was confirmed in the EDX spectrum as shown in Figure 3(d). Equation (2) was used to identify the planes of ZnO nanoparticles in the SAED pattern, which presented a hexagonal structure according to the values of $a = 3.2506$ and $c = 5.2075$.\textsuperscript{76}

$$\frac{1}{d_{(hkl)}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

The structural information of the as-synthesized nanoparticles was performed through XRD. Figure 4 shows patterns for TiO$_2$ and ZnO nanoparticles prepared through the green ultrasound-assisted chemistry. The tetragonal structure of the anatase phase of TiO$_2$ nanoparticles is attributed to the temperature and calcination time (550°C during 3 h, respectively) used during the green synthesis. Hence, the diffraction pattern revealed different peaks located at 25.37°, 37.12°, 37.90°, 48.22°, 54.12°, 55.21°,
and 62.91°, corresponding to the Miller index (hkl) of (101), (103), (004), (200), (105), (211), and (204) planes, respectively. According to the pattern of the ZnO nanoparticles, several peaks can be observed between 5° and 60° corresponding to the characteristic planes of the hexagonal structure (Wurtzite), which are represented by the angles at 31.71°, 34.31°, 36.31°, 47.51°, 56.51°, 62.81°, and 66.31°. These results are in agreement with the Joint Committee on Powder Diffraction Standards (No. 79-2205). The average crystal sizes were determined using the Debye–Scherrer formula (equation (3)):

$$D_{hkl} = k\lambda(\beta \cos \theta)^{-1}$$  \hspace{1cm} (3)

where $D_{hkl}$ is the size of the crystal in nm, $k$ is the crystalline form factor (0.89), $\lambda$ is the wavelength of the X-ray source (CuKα1, $\lambda = 0.15406$ nm), $\beta$ is the angular full width at half maximum (FWHM) of the most intense peaks. The average crystal size was calculated by taking the plane (101) of both nanoparticles, obtaining values of 9.37 and 33.22 nm for TiO$_2$ and ZnO nanoparticles, respectively.

The absorbance UV-vis spectrum of the prepared nanoparticles is shown in Figure 5, indicating the typical curve for the interaction of Ti-O and Zn-O structures. The optical band gap energy ($E_g$) was calculated according to the Kabelka–Munk function by using the following equation:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$  \hspace{1cm} (4)

where $h\nu$ is the photon energy, $\alpha$ is the absorption coefficient, and $A$ is an energy-dependent constant known as the band tailing parameter. Another constant is $n$, which is known as the power factor of the transition mode of the materials. Tauc plot was obtained from this function, assuming an indirect transition between the edge of the valence band and conduction for anatase TiO$_2$, and direct for the case of ZnO nanoparticles.$^{78, 79}$ The calculated values of $n$ according to direct, indirect, direct forbidden, and
indirect forbidden were 0.5, 2, 1.5, and 3, respectively. Accordingly, the \( (\alpha h\nu)^{1/n} \) versus \( h\nu \) graph is shown in Figure 6, in which the band gap energy values were 3.14 and 3.16 for TiO\(_2\) and ZnO nanoparticles, respectively. These results are in agreement with those reported in literature, suggesting that the nanoparticles offer excellent photocatalytic activity.\(^{80,81}\)

Table 1 summarized the surface area of the TiO\(_2\) and ZnO nanoparticles analyzed by using a multipoint Brunauer–Emmett–Teller (BET). The surface area of TiO\(_2\) nanoparticles provided the largest value due to the smaller particle size compared to ZnO. These values were compared with those reported in literature for the same type of nanoparticles synthesized through a green chemistry approach. Furthermore, a single point adsorption total pore volume \( (V_{\text{pore}}) \) showed to be less than 2069 Å radius, which was determined at \( P/P_0 = 0.995 \). In Figure 7, an N\(_2\) physical adsorption–desorption test was performed to determine the surface and pore morphology of the as-synthesized TiO\(_2\) and ZnO nanoparticles. According to the results, TiO\(_2\) nanoparticles presented a mesoporous surface typical for type IV materials. The shape of the hysteresis loop is of type H3 in agreement with the International Union of Pure and Applied Chemistry convention, which is associated with the stack of plate-like particles, generating slit-like pores distributed in the range between micro- and mesopores.\(^{84–87}\) In case of ZnO nanoparticles, the hysteresis loops can be ascribed to H3 type due to the relative pressure of about 0.9–1.0, attributed to the fragile particle agglomerations with three-dimensional network of pores.\(^{88}\) SEM and TEM images are also in agreement with these results, supporting the type of aggregation presented for both TiO\(_2\) and ZnO nanoparticles. These results can be also supported by the calculation of the cumulative and incremental pore volume as shown in Figure 8(a) and (b). According to the curves, a broad pore size distribution between 1.6 nm and 120 nm can be observed, indicating and confirming the presence of micropores, mesopores, and macropores in the structure of the nanoparticle. From Figure 8(a), the major pore volume is evidence below 50 nm, representing a transition from mesopores to macropores, in which a pore disorder in the structure can be inferred as shown in Figure 8(b). Therefore, an increase in the active sites for the potential application of self-cleaning may be attributed to these results, along with those shown from the BET test.\(^{85}\)

**Corrosion, self-cleaning, and antibacterial testing**

Corrosion tests were performed in a salt fog chamber using the ASTM B117:16. Figure 9 shows the photographic record of the carbon steel plates coated with nanofilled paints after 200 h of exposure to accelerated corrosion in a salt solution. The ASTM standard categorizes the degree of oxidation \( (G) \) with a scale between 0 and 10 based on the visible percentage of the corroded surface, in which 0% is the highest value with a percentage of oxidized surface

![Figure 7. Nitrogen adsorption–desorption isotherms of the as-prepared TiO\(_2\) and ZnO nanoparticles. TiO\(_2\): titanium dioxide; ZnO: zinc oxide.](image)

![Figure 8. Calculation of the (a) cumulative pore volume and (b) incremental pore volume for the as-prepared TiO\(_2\) and ZnO nanoparticles. TiO\(_2\): titanium dioxide; ZnO: zinc oxide.](image)
greater than 50%, and 10% is the lowest value with a percentage equal to or less than 0.01%. According to the results, the oxidation of the sample’s surface is in agreement with the values obtained from the oxidation degree test reported in Figure 10. Hence, the optimum concentration of nanoparticles for the modification of enamel-type paints corresponded to 2 w/v%, due to the fact that samples exhibited a significantly low level of corrosion compared to those samples using higher concentrations. Therefore, increasing the concentration of nanoparticles in the paints may produce major oxidation of the substrate, which may be related to the fact that agglomerates avoid good dispersion of nanoparticles in the solvent (Varsol) as can be observed in the SEM images of the nanofilled paints in Figure 11, leading to the formation of porosity in the paint coating, and consequently the appearance of corrosion points.

The photographic record of the self-cleaning tests performed on wood sheets coated with nanofilled paints and stained with MB is shown in Figure 9. The reported images correspond to the concentrations of 2 and 3.5 w/v%, in which a high degradation of MB can be clearly observed, as the accumulated radiation and the concentration of nanoparticles increase, allowing the adsorption and subsequent degradation of the dye. A calibration curve was plotted based on the cyan percentage, in order to corroborate and quantify the data collected in the MB decolorization test as shown in Figure 12. In Figure 13, the photodegradation of MB can be clearly evidenced for all samples, including the target (paint without nanoparticles) with a low photocatalytic activity. The presence of TiO$_2$ and ZnO nanoparticles in the paint considerably improved the photocatalytic degradation of MB, even using 2 w/v% as the lowest concentration.
tested. Although TiO$_2$ nanoparticles showed higher degradation of MB, ZnO nanoparticles also offered this self-cleaning property with values slightly less than those obtained for TiO$_2$. These results are related to the surface area, as reported in the BET analysis in Table 1, ZnO presented a surface area four times less indicating that an adsorption process may occur at a lower level compared to TiO$_2$. This degradation behavior is in agreement with the results reported by Guo et al.,$^{23}$ in which TiO$_2$ (P-25) nanoparticles were used to modify white paints for potential application in compacting architectural mortars (SCAM), showing a high self-cleaning capability toward the degradation of rhodamine B under visible light irradiation.

The proposed mechanism for self-cleaning properties of coatings with nanofilled paints using simulated spot with MB is shown in Figure 14. When samples are exposed to solar radiation, processes such as drying, adsorption, and photodegradation may occur simultaneously. Adsorbed water and oxygen play an important role in self-cleaning properties, working as precursors for the generation of reactive oxygen species by interacting with photogenerated electron/hole pairs ($e^-/h^+$). Equations (5) to (10) summarized the reactive oxygen species generated, in which holes can oxidize water molecules or adsorbed hydroxyl groups on the photocatalyst surface by transferring interfacial charge to produce free hydroxyl radicals ($\cdot$OH). Electrons can reduce the adsorbed O$_2$ into an anionic superoxide radical ($O_2^-$), allowing to oxidize organic compounds to smaller molecules. Additionally, this $O_2^-$ species can react with hydrogenations ($H^+$) to generate hydrogen peroxide ($H_2O_2$), which is excited by electrons and transformed into $\cdot$OH. According to equation (11), the holes may attack the dye molecules generating by-products, and equation (12) corresponds to a widespread reaction of the by-products and the mineralization. According to recent research developed by Nguyen et al.,$^{79,89}$ the intermediates generated by photocatalytic degradation of MB are azure B, azure A, azure C, leuco MB sulfoxide, diphenyl sulfoxide, benzenesulfoxide acid, and dimethyl-$p$-phenylenediamine, as can be evidenced in Figure 14(a) to (g), respectively. However, a possible oxidation of the paints can occur due to the organic content in the chemical composition, in which an interaction between the different reactive oxygen species may not be only toward the degradation of MB but also with those organic content of the paints taking into account that these species are not selective.

\[
\begin{align*}
\text{TiO}_2/\text{ZnO} + h\nu & \rightarrow h^+ + e^- \tag{5} \\
\text{H}_2\text{O} + h^+ & \rightarrow \cdot\text{OH} + \text{H}^+ \tag{6} \\
\text{O}_2(\text{abs}) + e^- & \rightarrow \text{O}_2^- \tag{7} \\
\text{H}^+ + \text{O}_2^- & \rightarrow \cdot\text{OOH} \tag{8} \\
\cdot\text{OOH} + \cdot\text{OOH} & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \tag{9} \\
\text{H}_2\text{O}_2 + e^- & \rightarrow \cdot\text{OH} + \text{OH}^- \tag{10} \\
\text{MB} + h\nu & \rightarrow \cdot\text{MB} \tag{11} \\
\cdot\text{MB} + (\cdot\text{OH}, \text{O}_2^-, h^+) & \rightarrow \text{intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \tag{12}
\end{align*}
\]

Antibacterial activity was performed in aluminum disks coated with nanofilled paints against *E. coli* activity, as is shown in Figure 15(a) to (d) and Figure 16 (a) to (d). TiO$_2$ nanoparticles showed no inhibition of bacterial growth for all concentrations, while the incorporation of ZnO nanoparticles generates a protection barrier against the microorganism. Although some inhibition activity could be observed, no significant radius of the inhibition halos was observed when using ZnO nanoparticles, which may be attributed to the low capability to diffuse from the paint into the culture medium, avoiding contact with the cells. Velmurugan et al.$^{90}$ have reported the mechanism of antibacterial action of nanoparticles against several human
The proposed mechanism behind the inhibition of bacteria using nanoparticles can be explained as follows: (1) the nanoparticles may anchor with the bacterial cell wall and then penetrate causing structural changes in the cell membrane, such as the permeability leading to death of the cell; (2) the formation of free radicals by the nanoparticles is considered another mechanism that leads to damage of the cell; (3) the appearance of porosity in the cell membrane which can slowly lead to death of the cell; and (4) the

![Figure 12.](image.png)

**Figure 12.** Photographic record of self-cleaning test carried out on wood sheets coated with unmodified paint (target) and paints modified using TiO$_2$ and ZnO nanoparticles (2 and 3.5 w/v%) under solar radiation. TiO$_2$: titanium dioxide; ZnO: zinc oxide.

![Figure 13.](image.png)

**Figure 13.** MB decolorization using unmodified paint (target) and modified with different concentrations of TiO$_2$ and ZnO nanoparticles. MB: methylene blue; TiO$_2$: titanium dioxide; ZnO: zinc oxide.

| Sample | $S_{BET}$ (m$^2$/g) | Reference $S_{BET}$ (m$^2$/g) | $V_{pore}$ (cm$^3$/g) |
|--------|---------------------|-------------------------------|---------------------|
| TiO$_2$ | 53.591              | 81.5982                      | 0.217               |
| ZnO    | 12.597              | 38.1983                      | 0.065               |

**Table 1.** BET surface area analysis of TiO$_2$ and ZnO nanoparticles.

BET: Brunauer–Emmett–Teller; TiO$_2$: titanium dioxide; ZnO: zinc oxide.

pathogens. The proposed mechanism behind the inhibition of bacteria using nanoparticles can be explained as follows: (1) the nanoparticles may anchor with the bacterial cell wall and then penetrate causing structural changes in the cell membrane, such as the permeability leading to death of the cell; (2) the formation of free radicals by the nanoparticles is considered another mechanism that leads to damage of the cell; (3) the appearance of porosity in the cell membrane which can slowly lead to death of the cell; and (4) the
**Figure 14.** Proposed self-cleaning mechanism of the paints modified with TiO$_2$ or ZnO nanoparticles using simulated spot with MB. MB: methylene blue; TiO$_2$: titanium dioxide; ZnO: zinc oxide.

**Figure 15.** Antibacterial activity of circular disks coated with paint modified using TiO$_2$ nanoparticles at (a) 2, (b) 3.5, and (c) 5 w/v%; compared with the (d) target (coating with paint without nanoadditives). TiO$_2$: titanium dioxide.
inactivation of the cells through electrostatic interaction of thiol groups with vital enzymes.

**Conclusions**

The green ultrasound-assisted chemistry methodology using lemongrass extract allowed to synthesize TiO$_2$ and ZnO nanoparticles with excellent structural, morphological, optical, and photocatalytic properties observed from the characterization results, in which phytochemicals worked as capping and reducing agent, respectively. According to the results in the corrosion test, concentrations of nanoparticles in paints higher than 2 w/v% provide an accelerated oxidation of the carbon steel, due to the occurrence of agglomeration which generates more porosity on the surface. Although using less concentration of nanoparticles for the modification of paints may offer positive economic and environmental impacts, a surface modification of TiO$_2$ and ZnO nanoparticles would possibly improve the dispersion in solvent, allowing to reduce the appearance of agglomerates in paints, and thus, the formation of porosity on the sample’s surface. We found that the same behavior of efficiency was observed in the photocatalytic test, in which the samples painted with a nanoparticle concentration of 2 w/v% were found to degrade MB, indicating this nanocomposite as promising for self-cleaning in the construction field. Although TiO$_2$ nanoparticles are agglomerated, the photocatalytic activity was slightly higher than that for ZnO nanoparticles, which is strongly related to the small particle size, and thus, the surface area. We also found that no antibacterial inhibition for the samples using disks with the paint containing TiO$_2$ nanoparticles. However, the results were the opposite for the samples coated with paint containing ZnO nanoparticles, which was possible to observe an increase in the antibacterial inhibition, indicating the diffusion and further

![Figure 16. Antibacterial activity of circular discs coated with paint modified using ZnO nanoparticles at (a) 2, (b) 3.5, and (c) 5 w/v%; compared with the (d) target (coating with paint without nanoadditives). ZnO: zinc oxide.](image-url)
interaction of some nanoparticles with the bacteria cell. These findings determined that the modification with a low concentration of TiO$_2$ and ZnO nanoparticles offers an enhancement in the physicochemical properties of paints, allowing to be applied in the construction field as a promising nanocomposite.

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