Cerium oxide thin films: synthesis, characterization, photocatalytic activity and influence on microbial growth

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ABSTRACT
The resistance of surfaces to biofouling remains a significant advantage for optical devices working in natural conditions, increasing their lifetime and reducing maintenance costs. This paper reports on the functionalities of transparent CeO₂ thin films with thicknesses between 25 and 600 nm deposited by reactive magnetron sputtering on the glass substrate. The CeO₂ photocatalytic performance exhibited an efficiency of 30% on imidacloprid degradation under 6 h of UV radiation and increased linearly with the irradiation time, suggesting a complete degradation within 48 h. The films did not alter the growth rate of the green algae *Chlorella vulgaris* after 72 h short-term exposure. The tested CeO₂ films proved to efficiently inhibit with high efficiency the *Staphylococcus aureus* biofilms and planktonic growth (reducing the counts of bacterial cells by 2 to 8 logs), demonstrating the promising potential of these materials for obtaining antimicrobial and antibiofilm surfaces, with broad applications for the biomedical, ecological and industrial fields.

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Introduction
Photocatalysis is an emerging technology for wastewater treatment that can function under the influence of sunlight in the presence of catalyst material. The free electrons and holes generated in the catalyst under the influence of sunlight, UV lamps, xenon lamps, etc., migrate to form oxidising species such as hydroxyl (·OH) or superoxide (O²⁻) radicals that exhibit strong oxidation of pollutants leading to their degradation (Rueda-Marquez et al. 2020). Semiconductors are materials that possess both light-absorbing and catalytic properties. Although many narrow bandgap materials such as Si, CdS, CdSe possess advanced sunlight absorbing properties, they are electrochemically unstable. On the other hand, wide-bandgap metal oxides such as TiO₂, ZnO, WO₃, V₂O₅, etc., are stable, low cost, abundant, and non-toxic, but they absorb only UV light.

Because of some unique features, such as the wide bandgap between 2.7 and 3.19 eV (Hogarth and Al-Dhhan 1986; Guo et al. 1995; Shih et al. 2010), 4f energy levels playing an important role in electron transfer (Azimi et al. 2013), high stability in the reaction medium and environmentally friendly properties, CeO₂ became attractive materials for catalysis (Shen et al. 2020), solid oxide fuel cells, wastewater treatment, antimicrobial (Guo et al. 1995; Li et al. 2019; Rueda-Marquez et al. 2020; Wang et al. 2021) etc., applications. Previous studies have proved the applications of CeO₂ nanocrystals for wastewater treatment applications (Zheng et al. 2017), such as the methylene blue degradation under UV-light irradiation with efficiency >80%. In addition, nitrogen-doped mesoporous CeO₂ was reported (Shen et al. 2020) as an efficient visible-light-driven catalyst for CO₂ photoreduction that can be used in CO and CH₄ production. CeO₂ could also degrade pharmaceuticals (for example, ciprofloxacin) released in surface and ground waters from hospitals, farming and
aquaculture thus preventing their adverse effects on the ecosystem (Kolpin et al. 2002; Xing et al. 2019).

There is a need to fully understand the ecotoxicological impact of cerium oxide thin films on the aquatic environment. Conflicting reports are published (Pelletier et al. 2010; Kuang et al. 2011; Leung et al. 2015) about CeO₂ nanoparticle toxicity. Several groups report toxicity toward bacteria (Pelletier et al. 2010; Kuang et al. 2011), algae (Rodea-Palomares et al. 2011), plants (Cassee et al. 2011), soil nematodes (Roh et al. 2010), and epithelial and cancer cells in human lungs (Lin et al. 2006). It is also proposed (Asati et al. 2010) the possibility of controlling of toxicity of CeO₂ by modulating the surface charge with a polymer coating. Due to their high chemical activity and stability, CeO₂ was an excellent catalyst for the photodegradation of ciprofloxacin, widely used fluoroquinolone antibiotics (Liu et al. 2016; Oropesa et al. 2018). However, it should be noted that the above studies related to toxicity and antimicrobial properties of CeO₂ have been done for nanoparticles only. No such study related to thin films CeO₂ would be important in the photovoltaic and window applications.

This paper aims to study CeO₂ thin films focus on imidacloprid degradation and antimicrobial activities and clarify whether they exhibit toxicity in the natural environment. Imidacloprid is a systemic neonicotinoid insecticide available in the global market used for its insecticidal activity to control pests. The imidacloprid was detected in soil, surface water, and groundwater, affecting the aquatic environment (Hogarth and Al-Dhhan 1986). Chlorella Vulgaris has been considered to address the ecotoxicity study.

**Method**

**Synthesis and characterisation**

Thin films of cerium oxide (CeO₂-x) were deposited onto microscopic glass substrates (size 76–26 mm², thickness of 1 mm) using a reactive magnetron sputtering unit from Leybold Optics (Model A550V7). Deposition parameters are described in Table 1. The substrate carrier was operated in the oscillation mode before the fixed Ce target during the deposition to obtain CeO₂ films with a homogeneous composition across the whole sample volume. The target was a 99.9% purity metallic Ce plate of dimensions 125 × 600 × 10 mm. A mixture of argon and oxygen gases (ratio of 160/50, 160/24 and 160/11) was used for reactive sputtering.

The crystallographic texture was determined with X-ray diffraction (XRD), based on Cu-Kα radiation, in the Bragg–Brentano setup using a Bruker D2 Phaser diffractometer with XE-T detector. The surface morphology and thickness of the sputtered coatings were determined with scanning electron microscopy (SEM) using JEOL JSM-7900F unit. The XRD patterns for thin films were measured and then analysed in the range of 2θ angle from 20 to 60 degrees. Grain sizes were calculated using the Scherrer equation. The optical properties of thin films were determined with UV-vis-NIR transmittance spectrum using a spectrophotometer Ocean Optics QE65000, with a wavelength range from 250 nm to 950 nm. The thicknesses of the synthesised CeO₂ films, as measured using the Step-200 profilometer, were 25–600 nm (Figure S1 in Supplementary Information).

**Photocatalytic activity and toxicity of thin films**

The photocatalytic activity was measured in a photocatalytic reactor equipped with ten fluorescent black light tubes of 18 W each (emitted in the range 380-480 nm with a peak wave at 365 nm) placed in a circle at a distance of 40 cm from the aqueous solutions of imidacloprid with an initial concentration of 20 ppm. First, each film with an area of 1 × 1 cm² was placed in a 50 mL IMD solution and left in the dark for 30 min to ensure the adsorption-desorption equilibrium. The solution was then irradiated for up to six hours, 500 μL aliquots removed, and the residual

### Table 1. Deposition parameters and algae growth percentage.

| Sample code | Thickness (nm) | [O]/[Ar] | Pressure (Pa) | Deposition rate, nm/min | Growth (percentage of control) |
|-------------|----------------|----------|---------------|-------------------------|--------------------------------|
| A. The influence of the O/Ar ratio | | | | | |
| 63 | 25 | 50/160 | 0.5 | 5 | 100.73 |
| 64 | 25 | 24/160 | 0.5 | 5 | 98.97 |
| 65 | 25 | 11/160 | 0.5 | 5 | 100.66 |
| B. The influence of thin films thickness | | | | | |
| 63 | 25 | 50/160 | 0.5 | 5 | 100.73 |
| 60 | 50 | 50/160 | 0.5 | 5 | 90.19 |
| 58 | 100 | 50/160 | 0.5 | 5 | 83.18 |
| 59 | 200 | 50/160 | 0.5 | 5 | 75.45 |
| 55 | 400 | 50/160 | 0.5 | 10 | 69.98 |
| 56 | 600 | 50/160 | 0.5 | 10 | 68.54 |
concentration was determined by HPLC consisting of a Shimadzu LC-20ADsp chromatograph, equipped with a Nucleosil C18- Macherey Nagel, Nucleosil® 5μm C18 100 A, LC Column 250 × 4.6 mm, and a UV detector SPD-20A at an absorption wavelength of 270 nm. The column thermostat was maintained at 45 °C. The mobile phase was a mixture of 70%v acetonitrile and 30%v ultrapure water—the flow rate was 1.2 mL/min with a 20 μL sample injection volume. The retention times were 2.76 min. For quantification purposes, calibration curves from 0.5 to 40 mg/L were validated using nine concentration levels with a correlation coefficient R² = 0.9999. The limit of detection (LOD) and quantification (LOQ) of the imidacloprid were 0.7848 and 2.378 mg/L, respectively. The residual concentration of imidacloprid was measured for 360 min. The degradation rate of imidacloprid pollutant was calculated as degradation efficiency using Equation 1:

$$\eta = \frac{c_0 - c}{c_0} \times 100$$  \hspace{1cm} (1)

where: c₀ is the initial concentration of solutions (ppm), and c is the concentration of solutions (ppm) at a time t.

The stability and recyclability of the thin films were proven through three consecutive experiments. First, the photocatalysts were washed thoroughly with distilled water to remove residual substances. Then, after the materials were dried, another photocatalytic process was carried out in the same experimental condition.

The comparative toxicity of the thin films with a surface of 0.25 cm² was carried out using Chlorella vulgaris (CCAP211/11B, cultured by the Algae and Protozoa Culture Collection of the Scottish Marine Institute, Dunberg, Scotland). A standard Bold Basal medium (BB) contained all nutrients: NaNO₃ (25 g/L), CaCl₂·2H₂O (2.5 g/L), MgSO₄·7H₂O (7.5 g/L), K₂HPO₄·3H₂O (7.5 g/L), KH₂PO₄ (17.5 g/L), NaCl (2.5 g/L), and traces elements were used in the growth experiments. A trace element solution based on 0.75 g Na₂EDTA, 0.097 g FeCl₃·6H₂O, 0.041 g MnCl₂·4H₂O, 0.005 g ZnCl₂, 0.002 g CoCl₂·6H₂O, and 0.004 g Na₂MoO₄·2H₂O relative to a 1 L solution was used to complete the need for nutrients. One litre of BB medium contains the following volumes of the solutions listed above: 30 mL NaN₂O₃, 10 mL of each solution of CaCl₂, MgSO₄, K₂HPO₄, KH₂PO₄, NaCl, and 6 mL of trace element solution.

The algae at an initial concentration of approximately 10⁴ cells/mL, with an exposure period of 72 h in Bold’s Basal Medium at 25.0 °C under 16:8h light: dark cycles (5 fluorescent tubes F18/T8 Sylvania aquastar, each 18 W, 900 lux) under 60–70 mol m² s⁻¹. Although the same solution was used in all our tests, the culture was not fed during the toxicity test, and temperature and light conditions were identical for culture maintenance. All flasks were shaken daily and covered with plastic while randomly shifting their place.

Exponentially growing cells (after growing for 72 h in Bold Basal medium) were exposed to the CeO₂ thin films for 72 h, and growth inhibition was analysed by measuring cell concentration compared with the control batch. Green algae growth was measured primarily by cell count, the most commonly monitored parameter. The cell concentration was determined using an Improved Neubauer cytometer (Marienfeld). A 10 μL volume of the suspension containing the algae was considered after an initial dilution (1 mL algae:9 mL BB). A detailed protocol was previously described (Adochite and Andronic 2021a; Adochite and Andronic 2021b). All measurement was performed in duplicate. The growth rate (μ) expressed as day⁻¹ was calculated using Equation 2. Growth was measured as the increase in cell density over 72 h of the toxicity test period, considered exposure endpoints.

$$\mu = \frac{\ln N_t - \ln N_0}{t}$$  \hspace{1cm} (2)

Where N₀ is initial cells density at time 0 (cells/mL), Nₜ is the cells density after 72 h (cells/mL), t = time (day).

Antimicrobial activity

The Gram-positive Staphylococcus aureus ATCC 25923 was used to evaluate the antimicrobial activity of thin films of CeO₂ materials. Prior to the photoinactivation experiment, a bacterial inoculum of 10⁶ colony-forming units per mL (CFU/mL) density was
obtained in sterile phosphate buffer solution (PBS) from a fresh S. aureus culture. The materials were distributed to 24 multi-well plates over which 1 mL of microbial suspension was added. The samples were incubated for 24 h at 37°C. After incubation, the films were washed lightly to remove unadhered cells and placed in sterile tubes containing 1 mL sterile saline. They were gently stirred for 2 min to detach the adhered cells from the surface of the materials. From both the resulted microbial suspension and the one in which the materials were incubated, successive tenfold serial dilutions were made, and 10^L of each dilution was spotted on Muller-Hilton agar (Sigma-Aldrich, 70191) to determine the logarithmic reduction of CFU/ml. The results were expressed for both working variants, according to the determination of the number of viable microbial cells, applying the relation:

\[ \lg(CFU/mL) = \lg(N \times 1/D \times 10^2) \]  

where: \( N \) = average of the colonies counted at the level of the three spots, \( 10^2 = \) correction factor of volume, \( 1/D = \) dilution at which the counted was performed.

### Results and discussion

#### SEM measurements

The obtained sputtered films were studied through scanning electron microscopy (SEM). The surface image of the cross-section of the CeO2 coating with profilometer thickness of 100 nm prepared at the deposition pressure of 0.5 Pa and O/Ar flow ratio 50/160 is shown in Figure 1. Since cerium dioxide retains low electrical conductivity, providing a sink for the incident electrons is necessary to avoid accumulating the surface charge during the measurements for better contrast. A thin carbon layer was deposited on top of the CeO2 coating with a total thickness of 3-5 nm. The sputtered CeO2 films possess a columnar structure with a high degree of homogeneity seen in Figure 1(a). The single column’s typical size was around 30-50 nm. The film thickness remains the same over the sample and is found from the cross-sectional image at around 100 nm, as shown in Figure 1(b), which agrees with the result from profilometer measurements. It was seen that the film of CeO2 coating remains compact and with low porosity during production with magnetron sputtering. Despite the columnar structure identified in Figure 1(a), no film substructure can be identified in the cross-sectional image represented in Figure 1(b).

#### The optical properties of CeO2 thin films

The obtained reflectance and transmittance spectra for cerium dioxide thin films with different thicknesses are shown in Figure 2. Compared with bare soda-lime glass (black solid curve), samples with thin films possessed relatively higher reflectance (Figure 2(a)) and less average transmittance (Figure 2(b)) over the UV-vis-NIR range. A lower bandgap can be observed from such behaviour for CeO2 (absorption edge is shifted towards a bigger wavelength) as well as a higher refractive index due to enhanced reflectance between Air-thin film and thin film-glass interfaces.

Absorption spectra for the thin films with different thicknesses were calculated using the expression [27]:

\[ \alpha(\lambda) = \frac{1}{d} \ln \left( \frac{(1 - R(\lambda))^2}{2T(\lambda)} + \sqrt{R(\lambda)^2 + \frac{(1 - R(\lambda))^4}{4T(\lambda)^2}} \right) \]  

where \( d \) – film thickness, \( R(\lambda) \) and \( T(\lambda) \) are...
reflectance and transmittance for the given wave-length $\lambda$. Tauc plots for films of different thicknesses and band gap dependence on thin-film thickness are plotted in Figure 3, fitted with (4) data evidence of the low absorption of cerium dioxide for photon energies up to 3.0 eV. The optical band gap for different thicknesses (Figure 3b) was determined using the Tauc-plot method, assuming ceria to show direct transition (Murugan et al. 2015). The sputtered CeO$_2$ experience shrinkage of the band gap with the film growth. The trend of $E_g$ decrease with the film thickness is observed for other rare-earth containing materials prepared with magnetron sputtering (Moldarev et al. 2020). Lesser values for $E_g$ in CeO$_2$ is usually attributed to the presence of Ce$^{3+}$ species in material that generate defect levels in the band gap (Choudhury et al. 2015). Formation of the columnar structure during magnetron sputter deposition seemingly provided additional defectiveness, compared with the bulk film, due to oxygen vacancies located at the column surfaces. With the films growth, the defect levels were accumulated in the band gap, pushing $E_g$ to the lower levels. In order to verify that the sputtered thin films were able to maintain the photocatalytic process, a spectrum was measured for the dark light bulbs used for the photocatalysis experiment. The obtained spectrum (dashed curve in Figure 3 (b)) indicated a good absorption by CeO$_2$ thin films during the process, since the most of the incident light possesses photon energies above the optical band gaps.

**The crystallographic texture of the photocatalysts**

Figure 4 shows XRD patterns for the thin films of CeO$_2$ of different thicknesses. At the initial stage of the sputter deposition, the films of CeO$_2$ possessed a disoriented grain structure, as is shown for films with 25 nm thickness. However, as film thickness increased, a preferential orientation towards [100] crystallographic direction of CeO$_2$ was observed, accompanied by the consequent formation of the [200] dominant peak in the XRD patterns with film thickness. Figure 5 displays lattice parameters and crystalline sizes for the films with different thicknesses estimated by Bragg’s condition and Debye-Scherrer equation, respectively. For the latter, the full width half maximum for the peaks $\beta$ can be derived from the relation:

$$\beta = \frac{k \cdot 2 \theta}{D \cdot \cos \theta} \quad (5)$$

where $k = 0.9$ – dimensionless factor of the crystalline shape, $\lambda$ – wavelength of the incident X-ray beam (Cu-K$_{\alpha}$ radiation), $D$ – crystalline size.

The crystalline size of CeO$_2$ increased with coating thickness, achieving a maximum value at 400 nm (Figure 5). On the other hand, variation of the lattice parameter for films with a thickness of 50-600 nm remained insignificant; the high difference of that parameter for 25 nm thick ultrathin film is seemingly caused by low signal-to-noise level.

The growing process of newborn crystallines was controlled by choosing the deposition parameters during the magnetron sputtering process. For example, for the sputtered CeO$_2$ on the glass substrate, the oxygen partial pressure variation while film production leads to the switch in the preferential direction for the crystallines (Van Steenberge et al. 2014). This change in the orientation of the grain can modify the surface properties of CeO$_2$, including the wetting ability (Tam et al. 2018). Besides the partial pressure of the reactive gas, important parameters controlling the crystallographic structure of the sputtered CeO$_2$ include the substrate material (Wang et al. 2021), energy density of the plasma during the deposition process (Murugan et al. 2015), applied substrate bias.
(Inoue et al. 2004) and following heat treatment of the film (Inoue et al. 2004).

For determining the effect of the thin film crystallography on the photocatalytic properties of CeO$_2$, a series of coatings were produced with different partial oxygen pressure. The films prepared at chamber pressure 0.5 Pa and O$_2$/Ar flow ratio of 50/160 are labelled as ‘high oxygen level’, and samples produced at $p = 0.25$ Pa and O$_2$/Ar $= 6.5/160$ are labelled as ‘low oxygen level’. The film thickness of both types of CeO$_2$ was found as 50 nm. Figure 6 presents the XRD patterns for the thin films. Samples prepared in high oxygen levels show unusual CeO$_2$ behaviour with a dominant peak (200) and a weak peak (111), with a preferential grain orientation, and thin films are textured. Similar results have been obtained earlier in gadolinium oxyhydride (Baba et al. 2020). On the other hand, cerium dioxide thin films prepared in lack of oxygen (low level) show crystallographic texture (111). In both cases, the peaks are shifted towards lower angles compared with the reference pattern (JCPDS No. 34-0394), which implies non-stoichiometry of CeO$_2$ thin films and increased Ce$^{3+}$/Ce$^{4+}$ ratio (Kossoy et al. 2006; Phokha et al. 2020). This effect might be eliminated by annealing in an...
oxygen vacancies across the material (Phokha et al. 2020).

**Photocatalytic activity and aquatic toxicity evaluation of CeO$_2$ thin films**

At the lower pressure below 1.0 Pa, Yamagishi et al. (2003) demonstrated poor photocatalytic activity of the films synthesised by reactive magnetron deposition due to the generation of the surface defects that can be recombination centres of electrons and holes generated under UV irradiation (Yamagishi et al. 2003). Compared to powders, the thin CeO$_2$ layers obtained by reactive magnetron sputtering have the advantage that they can be used in pesticide removal processes without requiring an additional step to retain photocatalysts in powder form. However, the thin films have a significant disadvantage of moderate efficiency of imidacloprid degradation due to the low BET-specific surface area of thin films compared to powders. For this reason, the tests were carried out short-term (up to 6 h) and long-term (up to 72 h).

The stability of the thin films in aqueous solutions is important for repeated photocatalysis cycles. Photocatalytic activity and stability of CeO$_2$ films were performed for up to six hours, the photodegradation efficiency of IMD was determined, and EDX analysis of the films after photocatalysis. Table 2 shows that the 100 and 200 nm films have a constant Ce/O ratio of 0.33 and are stable after 6 h of immersion in water.

| Samples | Thickness (nm) | O/Ar flow ratio | Element (at.%) | Ce/O ratio |
|---------|----------------|-----------------|--------------|-----------|
| 63      | 25             | 50/160          | 10 68 15 7   | 0.147     |
| 60      | 50             | 50/160          | 2 69 18 11   | 0.028     |
| 58      | 100            | 50/160          | 25 75 – –    | 0.33      |
| 59      | 200            | 50/160          | 25 75 – –    | 0.33      |

It should be noted that only cerium oxide film was exposed to the incident beam for those samples since only cerium cations were detected during the measurements. The enhanced amount of oxygen detected for the films with thicknesses of 100 and 200 nm suggests the chemical composition of CeO$_3$ in the pre-surface layers of the coatings. This surface over-stoichiometry compared with the regular cerium dioxide material is a feature of the films prepared by magnetron sputtering method (Khan et al. 2015; Miran et al. 2018; Kabir et al. 2018). For the thinner films (25 and 50 nm), traces of Na and Si appear due to the high penetration depth of the incident beam of electrons during the measurements with EDX. Furthermore, CeO$_2$ passed into solution by dissolution, and it was confirmed by the visual observation for Sample 63 and Sample 60. The higher IMD photodegradation efficiencies of these layers (Figure 7a) are due to the detachment of CeO$_2$ powders from the thin layers due to the increase in the contact surface between the CeO$_2$ powders and imidacloprid solution during UV irradiation.

Additionally, it should be mentioned that CeO$_2$ potentially is able to form the glass-ceramic hetero-junction on the substrate surface. The lower size for the undetached particles then would be preferential for the photoinduced charge carriers separation to the enhanced photocatalysis process.

The possibility of using the photocatalyst after several cycles of photocatalysis and its stability in aqueous solutions are strong arguments for its potential application on an industrial scale, thus avoiding secondary pollution. The stability of the obtained photocatalyst having 100 nm (Sample 58) and 200 nm (Sample 59) thickness by a cycling degradation experiment were evaluated. First-order kinetic behavior was observed in the photocatalytic degradation of imidacloprid under UV excitation and using CeO$_2$ catalysts in 3 cycles (Figure 8a). The reusability was studied by repeating the experiment three consecutive cycles toward the photodegradation of IMD solution, and the first-order kinetics of each cycle for two different thicknesses, 100 and 200 nm, respectively, are illustrated in Figure 8a. The catalyst as the thin film was stable, and it was regenerated by washing with double-distilled water and stored in the dark. The reusability results showed an increase after the second cycle, suggesting the photocatalyst’s activation due to UV irradiation and a decrease in photodegradation efficiency in the third cycle with no apparent catalyst deactivation after three cycles further demonstrates the excellent efficiency of the photocatalyst. After three consecutive cycles, the photocatalytic performance of photocatalysts can also be maintained at a high level, indicating the good photostability of the as-prepared samples. Furthermore, the imidacloprid kinetic rate (k) after three cycles is not influenced by the thickness of the layer.

The CeO$_2$ thin films ecotoxicity evaluation on C. vulgaris shows a correlation between the 72 h growth rate and the thickness of thin films, where the growth rate decreased with the thickness increase. The growth rate did not differ from the control for thin films with a thickness of 25 nm (Figure 8b). Inhibition of algae growth in the presence of 200—600 nm thick
layers can be explained by the presence of Ce$^{4+}$ ions in the algae medium, which most likely induce the reactive oxygen species (ROS) production in the algal cells (Pulido-Reyes et al. 2015).

**Antimicrobial activity of materials**

Figure 9 displays the difference between log CFU/mL of the control cultures (i.e. the *S. aureus* grown in the absence of the cerium oxide coatings) and the *S. aureus* strain grown in the presence of the cerium oxide samples represented by thin films of different thicknesses. *S. aureus* strain was selected, because this species is one of the most frequent etiological agents of biofilm related infections (Zheng et al. 2018) and exhibits drug resistance phenotypes of clinical and epidemiological significance (e.g. methicillin resistant *S. aureus* – MRSA, vancomycin intermediate/resistant *S. aureus* – VRSA/VISA). The list of the most dangerous resistant superbugs such as ESKAPE (*Enterococcus faecium*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Acinetobacter baumannii*, *Pseudomonas aeruginosa*, and *Enterobacter* spp.) included *S. aureus* as priority 2: high group (Rice 2008; Savoldi et al. 2020).

In order to evaluate the potential release of antimicrobial species from the tested coatings, the number of viable cells adhered on the surface of the tested samples and the number of viable bacterial cells in the suspension in which the *S. aureus* cells were incubated with the samples for 24 h at 37°C were quantified. In both cases, similar growth inhibition rates were obtained, demonstrating that the tested films exhibit local antibacterial effects but also seem to release antibacterial species that act on the free bacterial cells floating in the liquid medium. Regarding the antibacterial efficiency of different samples, the inhibition of *S. aureus* growth ranged from 2 to 8 logs. The lowest antibacterial efficiency has been exhibited by samples 63, 64, 65 and 59, represented by films with thicknesses of 25, respectively, 200 nm, while the highest efficiency was obtained by sample 58, followed by samples 60, 55 and 56.

Our results suggest that these films could find potential applications in the biomedical field for improving the surfaces of medical devices and
preventing bacterial adherence, biofilm development and occurrence of biofilm-related infections. These materials could thus help prevent the disastrous consequences of medical device-associated infections (Darouiche 2001; Zimmerli et al. 2004), such as high mortality, longer hospital stays, higher costs and the need for device replacement.

Besides their negative impact on the biomedical field, bacterial biofilms could represent a problem in food, beverage, cosmetic and pharmaceutical industries, the bacterial cells, including pathogenic and resistant ones such as \textit{S. aureus}, being can form biofilms inside processing facilities, leading to products spoilage, and endangering consumer’s health (Galié et al. 2018; Muhammad et al. 2020). Furthermore, biofilms may also cause biofouling, biocorrosion of pipes, ship hulls and oil or gas installations (Dobretsov et al. 2013; Prest et al. 2016; de Carvalho 2018). Therefore, obtaining improved materials or coatings for industrial facilities could decrease the health-associated risks and the economic and ecological burdens posed by biofilms development.

**Conclusion**

The photocatalytic performance and safety of CeO$_2$ thin films for applications in photocatalysis and beyond, in the medical, industrial, and ecological fields, to prevent the negative consequences of biofilm development were emphasised.

The thin layers were obtained by magnetron sputtering, a method in which deposition parameters were rigorously controlled and reproducible for industrial applications. The low roughness of the coatings generally obtained by magnetron sputtering lead to a relatively low photocatalytic activity compared to powders with a larger specific surface area, but the use of thin layers has several advantages. For example, the photocatalyst was activated after the first run cycle, and the degradation rate constant increased two times after the first run cycle and 1.7 times after the third. Another example is that these layers are not toxic to green algae, demonstrated by the control of green algae growth compared to the control sample.

The tested surfaces proved to inhibit \textit{S. aureus} biofilms and planktonic growth with high efficiency, reducing the counts of bacterial cells by 2 to 8 orders-of-magnitide. These features, correlated with the lack of ecotoxicity, demonstrate the potential of cerium oxide films to be used for obtaining antimicrobial and antibiofilm surfaces with broad applications in different fields.

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**Conflict of interest disclosures and other ethics statements**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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