Materials Research. 2017; 20(Suppl. 2): 426-431
DOI: http://dx.doi.org/10.1590/1980-5373-MR-2016-1116

TiO_2 thin Films for Biofouling Applications

Viviane Lilian Soethe[a]*, Rafael Gallina Delatorre[a], Eder Marlon Ramos[a], Moisés Luiz Parucker[b]

[a]Universidade Federal de Santa Catarina, Campus Joinville, Rua Dr. João Colin, 2700, Bairro Santo Antônio, Joinville, SC, Brazil
[b]Universidade Federal de Itajubá, Campus Itabira, Rua Irmã Ivone Drumond, 200, Distrito Industrial, Itabira, MG, Brazil

Received: December 22, 2016; Revised: May 31, 2017; Accepted: September 15, 2017

This work presents a study of TiO_2 thin films prepared by sputtering, for using as protection for biofouling action on marine structures. Titanium oxide thin films were prepared with different amount of oxygen on the surface of regular 1020 steel, a structural material for marine technology. The cristalline structure analysis evidenced the formation of anatase and rutile phases, as well as an amorphous phase of titanium oxide. Roughness measurements shown that the surface finish can contribute to the fixation of microorganisms. The crystalline TiO_2 thin films was evaluated as a potential biofouling protective coating. Contact angle measurements revealed that under UV-C light, the material evidenced a changing in wettability from hydrophobic to hydrophilic behavior, what is associated to the activation of photocatalytic reactions that is nocive for living beings on its surface. The effect of marine ambient on sample corroborates this conclusion, where after 6 months of exposure it was not sufficient for growing of biofouling on surface.

Keywords: *Titanium oxides, biofouling, thin films, triode magnetron sputtering*

1. Introduction

Biofouling is defined as the process resulting in the accumulation of microscopic organisms, plants and animals on abiotic surfaces, both natural (rock and wood) and artificial structures (piers, platforms, ship hulls, etc), when immersed in liquid environment like rivers, lakes and the ocean[1,2,3].

The biofouling process has negative impact in various marine activities, highlighting product contamination, energetic losses related to increase of friction, resistance added to heat transfer and pressure losses, leading to significant losses for global industry[4,5].Besides that, the biofouling process is harmful also for oil platforms, marine pipes and cooling systems in nuclear power plants.

The strategies for biofouling prevention in marine industry are traditionally dominated by the fields of chemistry, with the use of biocides in antifouling paints, which retard biofouling by the use of toxic substances[4]. Between those substances, the most efficient are the paints based on Tri-Butil-Tin (TBT), that besides its very high efficiency there is a highly toxic component, leading to several damages to the environment nearby[4,6]. Those paints are currently forbidden by the International Maritime Organization (IMO) for using in marine structures in general[7]. Due to this, environmental friendly solutions that minimize the effects of biofouling, or facilitate its removal, becomes potentially favorable for applications in the marine industry.

Recent research points to titanium dioxide (TiO_2) for the reduction or control of the growing of microorganisms. Such materials, when exposed to ultraviolet (UV) light irradiation decompose organic matter, following a photocatalytic process, exhibiting bactericidal characteristics[8,9,10]. Studies demonstrates that the level of irradiation that reaches the material interferes in the solution employed for the biofouling process. Marine structures in general are naturally exposed to UV light irradiation from de sun light, mainly near the surface, preferential region for biofouling accumulation. Beside the high interest on the bactericidal effect of TiO_2, very few or none attention is devoted for application as antifouling in marine industry. This work has the main goal to evaluate the antifouling characteristics of TiO_2 thin films, prepared as coating for marine structure materials. For that, TiO_2 thin films were obtained by the triode magnetron sputtering process with different argon (Ar) and oxygen (O2) flow, on the surface of AISI 1020 steel. The thin films were characterized structure and morphologically, as well as its bactericidal action and biofouling prevention were initially analyzed.

2. Experimental Procedure

The substrates were conventional AISI 1020 steel, obtained from a 1 inch cylindrical bar sectioned in approximately 0.6 cm thick discs. Previously of the deposition of thin films, the surface of substrates passed through a polishing procedure, consisting of a sequential steps in sandpaper with sizes 80,

---

*e-mail: viviane.s@ufsc.br

120, 320, 600 e 1200, and a finishing step with diamond paste of 3 µm and 1 µm.

Before the thin film deposition procedure, the surface of the substrates were ultrasonically cleaned in acetone and dried in heat air. The thin films were prepared with a Triode Magnetron Sputtering (TMS) equipment[11], using as process parameters a voltage of 400 V to 500 V, an electric current of 1,0 A, a substrate temperature of 200 ± 5°C, and total pressure of working gas of 3.0 mTorr. The control parameter was argon and oxygen flow rates inside the chamber, expressed in standard centimeter cubic per minute (sccm), used to prepare coatings at 5 different conditions. In order to modify the oxygen content in each film, and therefore the film properties, the O_2 and Ar flow inside the chamber were changed. The individual value of flux for each gaseous material was controlled in order to keep constant the total pressure of working gas. No other special control was performed with respect on the gas flow. The deposition time in all depositions was 900 s. Table 1 shows the details of the flow rate used in this study.

It can be observed from Table 1 that the condition S2 and S5 have similar ratio between the gases. However, in the S5 condition the oxygen flow rate is higher in the deposition chamber, leading to high deposition rates.

The crystal structure identification of thin films was realized by Grazing Incidence X Ray Difraction (GIXRD) technique, in a Panalytical X'Pert PRO diffractometer, with monochromatic radiation Cu-Ka, at θ-2θ configuration. The spectra were identified using databases of Crystallography Open Database (COD), International Centre for Diffraction Data (ICDD), and published papers[12-14]. In order to investigate topography of surfaces and roughness, a Confocal Microscope, Leica DCM 3D, was employed. Contact angle and surface energy were performed with goniometer Ramé-Hart InstrumentCo, using distilled water and di-iodomethane as working drops, with 1 µl volume. The contact angle was measured with and without the incidence of light in the UV-C region for the observation of photocatalytic activities.

The biofouling tests were performed by visual analysis of samples exposed in marine environment. The samples were allocated in a natural ambient with brackish water, about 30 cm deep from the surface, at a pier located at Marina Cubatão, in the city of Joinville, Brazil. Water parameters like salinity, dissolved oxygen, pH and temperature were monthly monitored during all the experiment, which took 6 months.

3. Results

Figure 1 shows images of the samples prepared in different conditions, described in Section 2. It can be seen that samples has a common pattern, with blue to yellow appearance and variable intensity along the surface, that was attributed to thickness variation associated with relative position of sample and the titanium target inside deposition chamber. Such non uniformity in thickness is a regular feature for vacuum techniques, and usually result in color variations for oxide thin films. The only exception is sample S5, which has a black appearance.

X-ray diffraction patterns spectra for samples S1, S2, S3 and S5 are shown in Figure 2. With exception of sample S5, the spectra reveals small peaks at 25° e 55° associated to anatase phase of TiO_2, and at 27° associated to rutile phase of TiO_2, as well as peaks associated to iron, main material of substrate[12-14]. Sample S5 presented only the pronounced peak associated to the substrate, and a broad peak for the thin film, that was associated to the formation of amorphous titanium oxide[15]. This last result is attributed to the higher content of O_2 in the chamber during deposition procedure, leading to higher deposition rates and the formation of the amorphous phase[12].

In order to visualize the topography and evaluate the roughness of coated surfaces, relating it to the pining of microorganisms by mechanical anchorage, optical confocal microscopy was performed on everyone 5 samples. Figure 3 shows the images obtained by this technique, at a region of 300 µm. The images illustrates the topographies of samples, that exhibited some rough morphology, but uniform. In some cases it's possible to notice the action of final polishing of substrate, like in samples S1 and S4.

Confocal Microscopy analysis allows to measure the mean roughness of region. Figure 4 shows the values of mean roughness for entire surface of images in Figure 3 (Ra). The values measured, around tenths of mm, show roughness much higher than the expected ones for the total thickness of deposited thin films, around 500 nm, what indicates that the observed topography is a reproduction of substrates surface, and the deposited thin film has no influence in this parameter.

Table 1. Argon and oxygen flow and ratio during depositions of TiO_2 thin films on steel.

Gas Flow (sccm)		Ratio Ar / O_2	ID
Ar	O_2		
0.28	2.23	0.125	S1
0.43	2.11	0.204	S2
0.93	1.05	0.886	S3
1.18	0.81	1.457	S4
1.39	4.93	0.282	S5

Figure 1. Images of TiO_2 thin films deposited at different oxygen flow rates.

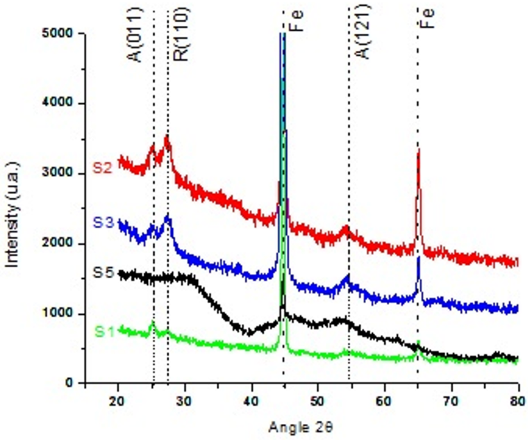

Figure 2. XRD patterns of theTiO_2 thin films deposited at different argon/oxygen flow rates.

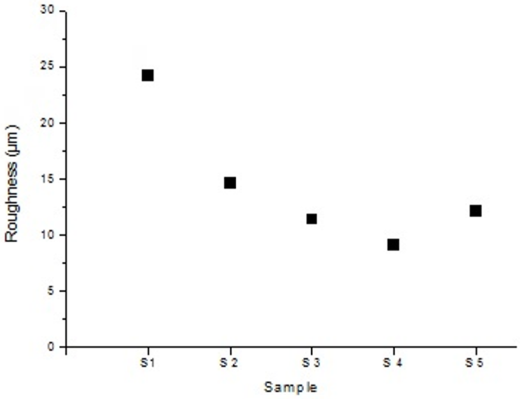

Figure 4. Mean roughness values for TiO_2 thin films on steel substrates.

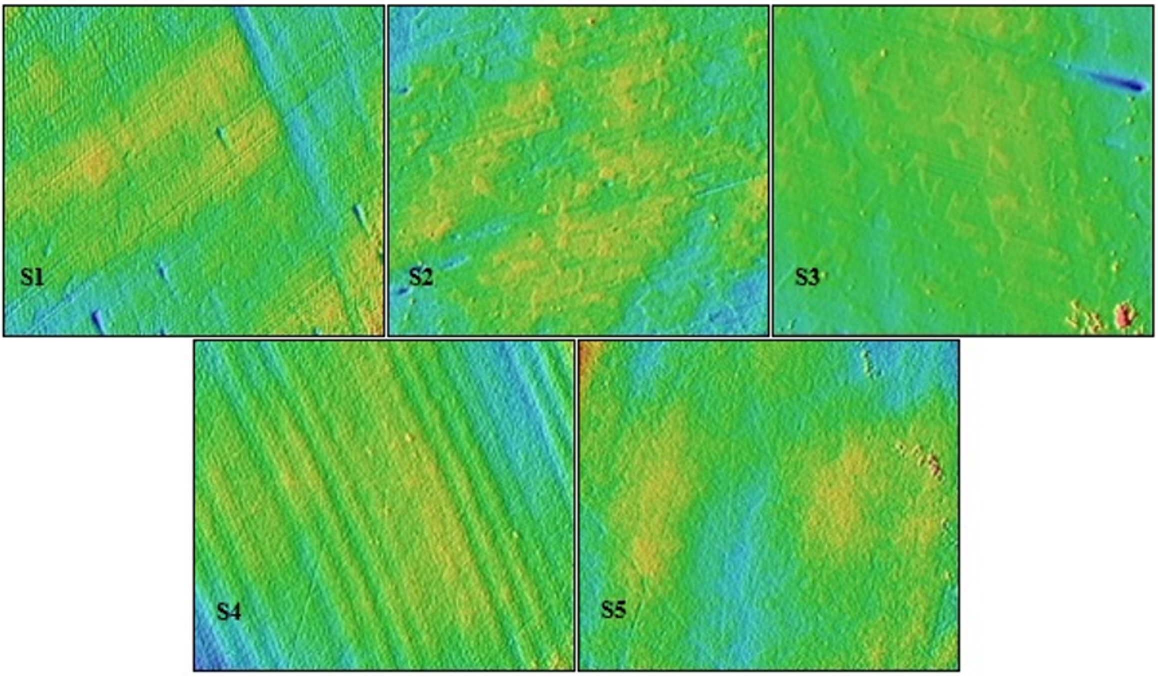

Figure 3. Images of the TiO_2 thin films obtained by Optical Confocal Microscopy, in a region with 300 µm length.

Wettability is an important property for the characterization of adhesion in surfaces, obtained by contact angle measurements, and allows the calculation of surface energy. The surface energy is directly related to the capability of material to interact to other materials, being them in solid, liquid or gas phase. Figure 5 shows the values of contact angle measured using distillate water. Also in Figure 5, surface energy values calculated using the contact angle measured both with distillate water and di-iodomethane. The contact angle values, around 95°, seems to doesn't change for films prepared in different conditions, and can be associated to a hydrophobic characteristic for the surfaces.

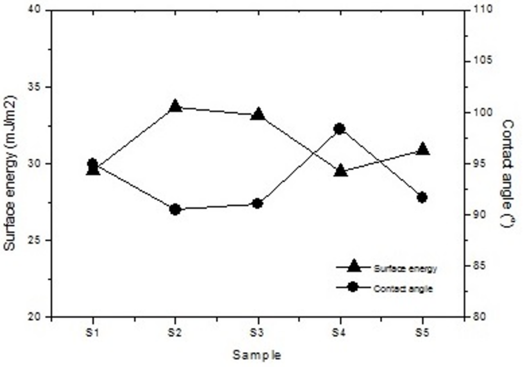

Figure 5. Contact angle and surface energy values of surfaces coated with TiO_2 thin films.

The evaluation of photocathalitic properties of TiO_2 films can be observed by wettability measurements as a function of incidence of UV light irradiation. Figure 6 shows the values of contact angle measured after an exposure in UV-C light irradiation at different times, obtained using distilled water, on the surface of sample S3. The experiment was performed at 3 different positions on the surface of sample, leading to the presented error bars. The values of contact angle undergo a changing after 60 minutes of exposure to UV-C light, stabilizing at around 50° after 180 minutes of exposure, equivalent to a hydrophilic behavior, in opposite to the initial hydrophobic condition.

The wettability changing with UV incidence, for a hydrophilic state, is a consequence of the activation of photocatalytic reactions in TiO_2, as commonly observed in literature[8]. Titanium dioxide is a semiconductor with band gap around 3,0 eV, where light irradiation in UV region is used to excite electrons from valence band (vb) to conduction band (cb), and leading to two types of charge carriers, the electrons (e_{cb}^-) and holes (h_{vb}^+). Those carriers are the responsible for the activation of chemical reactions as follows[16,17].

The water molecules in contact to the excited material undergo a chemical reaction that forms hydroxyl radicals ($\cdot OH$), following equation 1. Actually, oxygen molecules exhibit affinity to electrons, reducing its character to reactive oxygen (O_2^-), following equation 2. The formation of hydroxyl molecules on the surface of material is the responsible for the contact angle variation, making it hydrophilic, and is directly related to the incidence of UV-C light irradiation[8,17,18].

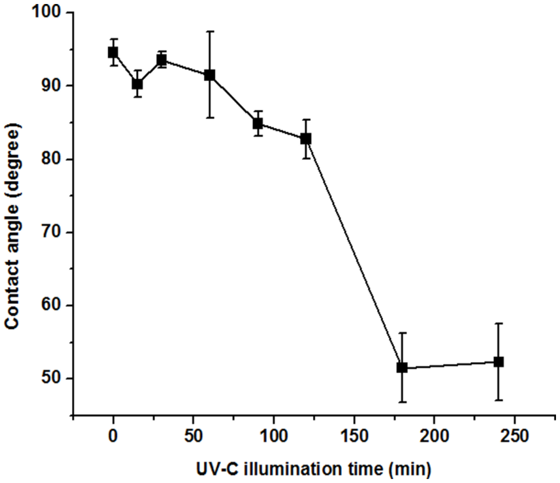

Figure 6. Contact angle measurements as a function of UV radiation exposure, for sample S3 ($Ar/O_2 = 0.886$).

$$h_{vb}^{+} + H_2O \rightarrow \cdot OH + H^{+} \qquad (1)$$

$$e_{cb}^{-} + O_2 \rightarrow O_2^{-} \qquad (2)$$

The bactericide action of TiO_2 rises from the existence of those reactive molecules on its surface, mainly hydroxyl. The reaction of reactive species of oxygen, like $\cdot OH$ and O_2^-, with organic compounds results in its decomposition. This mechanism is the responsible of biocide action on TiO_2 irradiated surface, and to its bactericidal action, that could lead to decrease of the biofouling during aquatic immersion[19].

The TiO_2 thin films were studied under marine natural ambient as described in Section 2, during a period of 6 months, searching to visually evaluate antifouling capacity. During this time, the accumulation of fouling was monitored weekly, as well as some parameters of the water. Figure 7 shows images of the sample S3 after a 6 months exposure, from the front of the sample, that contains the TiO_2 coating (Figure 7a), and from the back of the sample, where the surface was a regular plastic protective paint (Figure 7b). The result for other conditions is not shown due to their high state of substrate oxidation, unable to a visual evaluation of biofouling quantity.

Figure 7 can be used to visualize the biofouling protective characteristic of TiO_2 thin films. The thin film face shows a region with the result of corrosion of steel substrate, orange region and another region with no evidence of any growing of biofouling on the surface and no corrosion products, exposing the thin film surface. The corrosion is a result of the oxidation of steel, by forming rust, probably caused by the detaching of film under aquatic ambient. The back face, for comparison, presented a high level of biofouling, in a macrofouling level, with the growing of macroscopic living

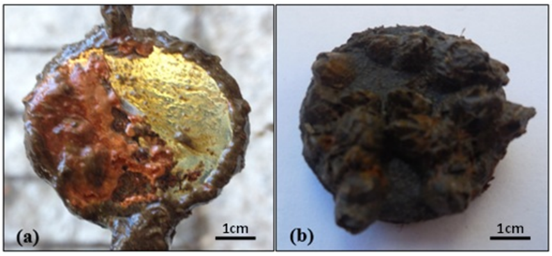

Figure 7. Sample S3 (Ar/O_2 = 0.886) after 6 months of exposure to marine ambient, (a) face coated with TiO_2 thin film; (b) face coated with plastic paint.

beings. This result evidences huge differences in terms of microorganisms attaching between the TiO_2 surface and the regular paint surface.

Table 2 shows some important parameters from the aquatic ambient used in analysis of biofouling. From that, especially for salinity evaluation, it is possible to characterize the ambient as brackish water [20]. The monitoring of such parameters is important to relate the rate of growth of animals as well as the biological species that are growing on surfaces.

Table 2. Physical-chemical analysis of the natural ambient during period of biofouling analysis.

Parameter	Value
OD (mg/L O_2)	6.8
pH	6.52
Salinity (ppt)	1.6
Temperature (K)	291.2

4. Conclusion

The preparation of coatings of titanium oxide on AISI 1020 steel was performed by the deposition of thin films by magnetron sputtering. Structure properties of the final material can be changed by different deposition conditions, involving the relative amount of argon and oxygen inside the deposition chamber, and the total flow of gases. It was possible to prepare two types of titanium oxide depending on the deposition condition that is a crystalline mixture of anatase and rutile phases of TiO_2, and an amorphous phase of titanium oxide. For purposes of biofouling protection, the coexistence of the two phases of TiO_2 can have practical positive characteristics, since there are results on the increase of this activity for a mixture of phases in detriment of single phase materials[16].

The bactericide potential of films is verified with contact angle measurements under UV-C ligth irradiation incidence. The changing of hydrophobic to hydrophilic behavior under radiation, observed in crystalline TiO_2 thin films, informs the activation of photocatalytic reactions, leading to reactive species like OH^-, an usual property of the semiconductor TiO_2. This characteristic allows the material to have bactericidal properties that is indispensable for using as biofouling protection, as the premises of this work.

The protection of samples for biofouling could be verified in an experiment performed in natural marine ambient, with brackish characteristics. For the sample containing crystalline TiO_2, after 6 months immersed in this ambient, no trace of biofouling was noticed on its surface, while a huge amount of macrofouling with natural living species is observed on the surface with plastic paint protection. This result demonstrates the capability of TiO_2 thin films to act as biofouling protection, meaning the activation of photocatalytic reactions under marine water. This activation is attributed to solar radiation, that contains radiation with the UV region of frequency, in range associated to UV-A, UV-B and UV-C. Besides UV-C is predicted to be absorbed in water, radiation in the UV-A is accepted to have transparency properties, and have sufficient energy to overcome the energy gap of TiO_2 as well.

5. Acknowledgements

Authors would like to acknowledge: (i) the Laboratory of Plasma, in the State University of Santa Catarina (UDESC), for the open access to their structure; (ii) the X - Ray Diffraction Laboratory in Physics Department of Federal University of Santa Catarina (UFSC), and Dr. Fabricio Faita, for the XRD analysis; (iii) the Marina Cubatão for the allowing for using their pier for the experiment of immersion of samples in natural marine ambient.

6. Referências

1. Da Gama BAP, Pereira RC, Coutinho R. Bioincrustação marinha. In: Pereira RC, Soares-Gomes A, orgs. *Biologia Marinha.* 2ª ed. Rio de Janeiro: Interciência; 2009. p. 299-318.
2. Yebra DM, Kiil S, Dam-Johansen K. Antifouling technology - past, present and future steps towards efficient and enviromentally friendly antifouling coating. *Progress in Organic Coatings.* 2004;50(2):75-104.
3. Dineshram R, Subasri R, Somaraju KRC, Jayaraj K, Vedaprakash L, Ratnam K, et al. Biofouling studies on nanoparticle-based metal oxide coatings on glass coupons exposed to marine environment. *Colloids and Surfaces B: Biointerfaces.* 2009;74(1):75-83.
4. Schultz MP, Bendick JA, Holm ER, Hertel WM. Economic impact of biofouling on a naval surface ship. *Biofouling.* 2011;27(1):87-98.
5. Fleming HC, Sriyutha Murthy P, Venkatesan R, Cooksey KE, eds. *Marine and Industrial Biofouling.* Berlin: Springer; 2009.
6. Ruffolo AS, Macchia A, La Russa MF, Mazza L, Urzì C, De Leo F, et al. Marine antifouling for underwater archaeological sites: TiO_2 on Ag-doped TiO_2*International Journal of Photoenergy.* 2013;2013:251647.
7. Castro IB, Westphal E, Fillmann G. Tintas anti-incrustantes de terceira geração: novos biocidas no ambiente aquático. *Química Nova.* 2011;34(6):1021-1031.

8. Fujishima A, Rao TN, Tryk DA. Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews.* 2000;1(1):1-21.

9. Tasaka M, Kanno H, inventors; Basf SE, Ricken Technos Corp, assignee. *Paint, adhesive composition, bonding method and laminate.* United States patent US 20130078460. 2013 Mar 28.

10. Tea N, inventor; Irvine Sensors Corporation, assignee. *Wear-Resistant Conformal Coating for Micro-Channel Structure.* United States patent US 20110303404. 2011 Dec 15.

11. Ságas JC, Duarte DA, Irala DR, Fontana LC, Rosa TR. Modeling reactive sputter deposition of titanium nitrite in a triode magnetron sputtering system. *Surface and Coatings Technology.* 2011;206(7):1765-1770.

12. Thamaphat K, Lisuwan P, Ngotawornchai B. Phase Characterization of TiO_2 Powder by XRD and TEM. *Kasetsart Journal. (Natural Science).* 2008;42(5):357-361.

13. Nezar S, Saoula N, Sali S, Faiz M, Mekki M, Laoufi NA, et al. Properties of TiO_2 thin films deposited by rf reactive magnetron sputtering on biased substrates. *Applied Surface Science.* 2017;395:172-179.

14. Scuderi V, Buccheri MA, Impellizzeri G, Di Mauro A, Rappazzo G, Bergum K, et al. Photocatalytic and antibacterial properties of titanium dioxide flat film. *Materials Science in Semiconductor Processing.* 2016;42(Pt 1):32-35.

15. Bharti B, Kumar S, Kumar R. Superhydrophilic TiO_2 thin film by nanometer scale surface roughness and dangling bonds. *Applied Surface Science.* 2016;364:51-60.

16. Luttrel T, Halpegamage S, Tao J, Kramer A, Sutter, E, Batzill M. Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO_2 films. *Scientific Reports.* 2014;4:4043.

17. Banerjee S, Dionysiou DD, Pillai SC. Self-cleaning applications of TiO_2 by photo-induced hydrophilicity and photocatalysis. *Applied Catalysis B: Environmental.* 2015;176-177:396-428.

18. Foster HA, Ditta IB, Varghese S, Steele A. Photocatalytic disinfection using titanium dioxide: spectrum and mechanism of antimicrobial activity. *Applied Microbiology and Biotechnology.* 2011;90(6):1847-1868.

19. Fujishima A, Zhang X, Tryk DA. TiO_2 photocatalysis and related surface phenomena. *Surface Science Reports.* 2008;63(12):515-582.

20. Brasil. Ministério do Meio Ambiente. Conselho Nacional do Meio Ambiente. *Resolução n. 430, de 13 de maio de 2011.* Available from: <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=646>. Access in: 26/09/2016.