Disciplinarum Scientia. Série: Naturais e Tecnológicas, Santa Maria, v. 17, n. 3, p. 397-405, 2016.
Recebido em: 22.08.2016. Aprovado em: 09.11.2016.

ISSN 2176-462X

TiO_2 THIN FILMS FOR PHOTOCATALYTIC OXIDATION OF PHARMACEUTICAL COMPOUNDS[1]

OXIDAÇÃO FOTOCATALÍTICA DE FÁRMACOS UTILIZANDO FILMES FINOS DE TiO_2

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ABSTRACT

Degradation of amoxicillin was investigated in aqueous solution by photocatalysis on TiO_2 thin film under UV (365 nm) radiation. The TiO_2 thin film is a pure anatase phase as shown in the X ray diffraction analysis. Enhancement of photocatalysis kinetic rate by addition of NaOH was also evaluated. No significant degradation occurred by UV radiation per se and a low adsorption affinity between the antibiotic molecule and TiO_2 surface was observed. pH had a significant effect on antibiotic degradation and the photocatalytic reactions followed a zero-order kinetics and the rate constants (k) were 8.02×10^{-4} mol L^{-1} min^{-1} to 7.45×10^{-3} mol L^{-1} min^{-1} for amoxicillin in pH 6 and 11, respectively.

Keywords: amoxicillin, photocatalysis, nanostructures.

RESUMO

*Foi investigada a degradação da amoxicilina, em solução aquosa, por fotocatálise em filme fino de TiO_2, sob radiação ultravioleta em 365 nm. Análise de difração de raios X do TiO_2 confirmou apenas a fase anatase. Avaliou-se também a influência do NaOH na fotocatálise. Os resultados mostraram que não ocorreu degradação significativa pela radiação UV, e observou-se uma baixa afinidade de adsorção entre a molécula do antibiótico e a superfície do TiO_2. O pH teve um efeito significativo sobre a degradação do antibiótico e as rea*ções fotocatalíticas segu*iram uma cinética de ordem zero. As constantes de velocidade (k) foram $8,02 \times 10^{-4}$* mol L^{-1} min^{-1} *e $7,45 \times 10^{-3}$* mol L^{-1} min^{-1} *para a amoxicilina em pH 6 e 11, respectivamente.*

***Palavras-chave**: amoxicilina, fotocatálise, nanoestruturas.*

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INTRODUCTION

Pharmaceutical compounds including antibiotics, sunscreen and hormones have been observed in different aqueous samples (CARBALLA et al., 2004; ELMOLLA; CHAUDHURI, 2010; IVETIC et al., 2014; KLAVARIOTI et al., 2009; MIRZAEI et al., 2016; RIVERA-UTRILA et al., 2009) due to the high consumption rate by humans and in veterinary medicine. The presence of antibiotics in the environment leads to the development of antibiotic resistant bacteria, creating a public health problem. The limitations of microbiological treatment for effluents with antibiotics can be overcome by using an advanced oxidation process.

The photocatalytic oxidation of numerous organic substances has been widely investigated over the last few decades, mainly by the use of titanium dioxide (TiO_2) (SAMADI et al., 2016). Due to its high gap energy, the TiO_2 in anatase structure requires illumination with UV light at a wavelength of λ=413nm for the TiO_2 in anatase structure is necessary for photoexcitation and the subsequent generation of highly reactive oxidizing species such as OH radicals. These radicals are capable of oxidizing a wide range of organics regardless of their molecular structure and in the presence of other organic and inorganic components (DOLL; FRIMMEL, 2004; TOEPFER et al., 2006; ZIEGMANN et al., 2006). Generally, two forms of TiO_2 have been widely used in photocatalysis: dispersed particles in liquid media and thin films supported on solid materials (MALATO et al., 2009). When TiO_2 dispersion is used in photocatalysis, the suspended TiO_2 has to be separated by centrifugation upon completion of each reaction cycle. However, this problem could be avoided by using the TiO_2 films on different types of substrates (MALATO et al. 2009). The preparation of TiO_2 thin films is one of the major research interests in the photocatalysis field in order to identify the optimum condition for coating of TiO_2 films on various substrates. Several methods have been employed to fabricate TiO_2 films, including reactive sputtering, chemical vapor deposition and sol-gel process (AKPA; HAMEED, 2010; DHANDAVUTHAPANI et al., 2016; LAN et al., 2013).

Chemical processes are one of the most appropriate technologies to prepare oxide coatings in solid substrates. This methodology has several advantages including good homogeneity, ease of composition control, low processing temperature, production of coatings with a large area, low cost equipment and production of photocatalysts with high quantum efficiency.

The aim of this study is to prepare TiO_2 (anatase) highly transparent thin films supported by glass substrate using the polymeric precursor dip-coating method and to analyze the correlation between surface topography using atomic force microscopy (AFM) as well as the photocatalytic performance on the degradation of amoxicillin antibiotic including the effects of sodium hydroxide content on the solution.

MATERIALS AND METHODS

CHEMICALS

The chemicals used in this experiment were all of analytical grade and used as received. Nanocrystalline titanium dioxide thin films were prepared via polymeric precursor method (RONCONI et al., 2008) using titanium tetraisopropoxide ($Ti(OC_3H_7)_4$ 97% from Aldrich Chemicals). Analytical grade amoxicillin (AMX) was purchased from Sigma and used to obtain a spectrophotometric analytical curve for the determination of the antibiotic concentration.

PRECURSOR SOLUTION PREPARATION

The precursor solution was prepared by dissolution of the precursor salt (titanium tetraisopropoxide) in an aqueous solution of citric acid (Merck), at 80 °C. After complete dissolution and homogenization by magnetic stirring, the polymerization (polyesterification) of the obtained Ti citrate was performed by adding ethylene glycol (Merck). A molar ratio of 1:8:32 (titanium tetraisopropoxide: citric acid: ethylene glycol) was used to prepare the solution (RONCONI et al., 2008).

PREPARATION OF THE THIN FILMS

The TiO_2 thin film coatings were deposited on soda-lime glass plates (30 X 20 X 1.5 mm) used as the substrates for thin films. The substrates were previously cleaned with acetone and rinsed with osmose reverse purified water and dried at room temperature. For the coating, the glass substrates were withdrawn from the precursor solution at room atmosphere (Relative Humidity < 60%) at a rate of 10 cm min^{-1} and the samples were subsequently dried in air at room temperature and then thermally treated at 100 °C for 1h and 450 °C for 2h.

CHARACTERIZATION OF TiO_2 THIN FILM

The TiO_2 X-ray diffraction (XRD) was recorded on a DMAX 2500 diffractometer (Rigaku) using Cu $K\alpha$ radiation and a step size of 0.028 in the range of 10-80°. The step time was 1 s which is adequate to obtain a good signal-to-noise ratio in the mean reflections of the studied TiO_2 crystalline phases (1 0 1) related to the anatase phase ($2\theta = 25.178°$).

The size of the TiO_2 crystallites, d, was estimated from XRD peak broadening by the Scherrer formula, according to equation (1):

$$d = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where β is the full-width at half maximum after correction of the instrumental broadening, λ the CuKα wavelength (λ= 0.15406 nm) and θ the Bragg angle (rad) (WEST, 1984). Specific surface area of samples was determined on a surface area analyzer model.

The Brunauer-Emmett-Teller (BET) specific surface area was measured using nitrogen adsorption-desorption isotherms conducted at - 196 °C using an ASAP 2020 adsorption apparatus (Micromeritics, USA). The surface morphology and roughness of the films were characterized using amplitude modulation atomic force microscopy imaging (Tapping mode) using an atomic force microscope (AFM) Agilent model 5500.

PHOTOCATALYSIS EXPERIMENT

The experimental apparatus consisted of a quartz tube (internal diameter 25 mm) and a 45 W medium pressure Hg lamp with a nominal wavelength of 365 nm. The system was maintained at 25 °C, by a thermostat. The volume of AMX aqueous solutions in all experiments was 10 mL.

The TiO_2 films were placed inside the quartz tube and immersed in a solution of AMX (1.0×10^{-3} mol dm^{-3}). The solution pH was adjusted with HCl or NaOH. After being stirred in the dark for 60 min to achieve adsorption-desorption equilibrium the system solution with the glass/TiO_2 film was irradiated. During illumination, sample aliquots were taken at pre-determined time intervals and analyzed for the residual concentrations of antibiotic by using spectrophotometric method, with a Shimadzu UV 1650 PC spectrophotometer.

RESULTS

The polymeric precursor method led to production of transparent TiO_2 thin films with high reproducibility, acid and alkali corrosive resistance, and high capability of adherence to glass substrates. The resulting coating after one dip was transparent and homogeneous without any cracks.

Figure 1 shows the X ray diffraction (XRD) pattern of the nanostructured TiO_2 thin film. A peak at 25.1° corresponds to (1 0 1) reflections of the anatase phase of TiO_2. The anatase phase was the predominant structure of the thin films obtained from the 1:8:32 precursor solution. No traces of TiO_2-rutile phase were found. The material was composed of pure anatase phase consistent with a previous paper (RONCONI et al., 2008). The crystallite size calculated using the Scherrer formula was 18.9 nm.

The glass slide with the TiO_2 film had a geometrical area of 0.5×10^{-2} m^2 and a BET surface area of 0.118 m^2 g^{-1}, a result 20 times higher than that of the TiO_2/glass sample. Greater catalytic activity is expected with this high surface roughness. The surface morphology after the annealing temperature of 450 °C during 2h for the 70 nm-thick TiO_2 film is shown in the AFM images presented in figure 2. As shown in figure 2, the as-grown TiO_2 film demonstrates a high surface roughness and approximately 20 nm diameter protrusions.

Figure 1 - XRD patterns of TiO_2 thin film deposited on glass substrates.

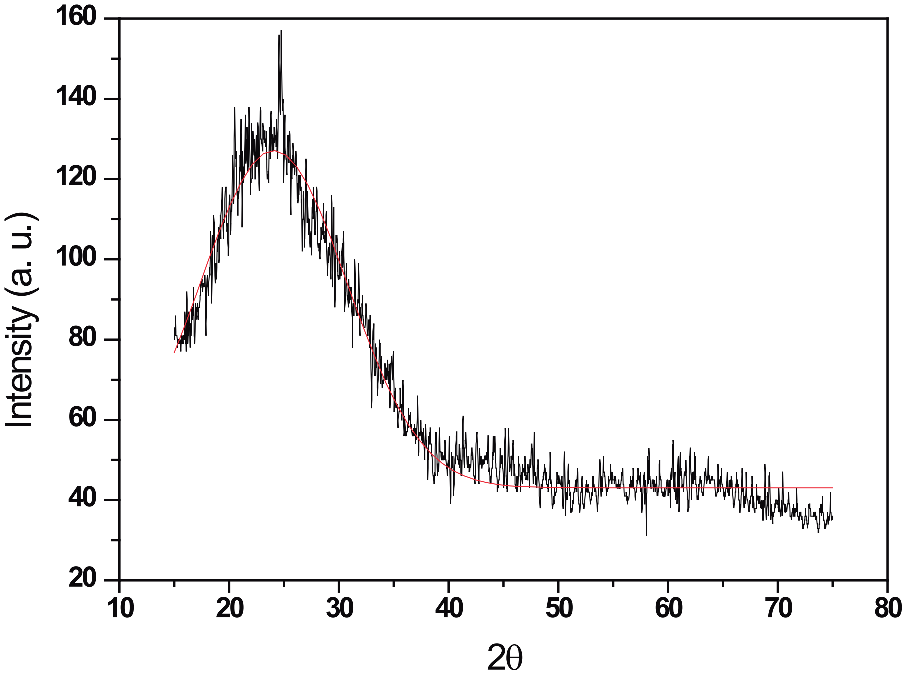
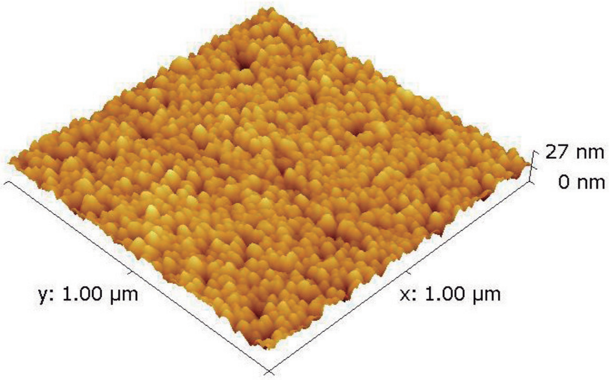


Figure 2 - AFM topography image of TiO_2 thin film surface



The adsorption equilibrium of the AMX onto the TiO_2 thin film was reached within less than 5 minutes, with a decrease of 0.8% in the absorbance of the antibiotic solution. The smaller adsorption rate of AMX on TiO_2 thin films deposited on the glass substrate is associated to the weak interactions between AMX molecules and the TiO_2 surface (FISHER et al., 2009).

To observe the effect of direct photolysis on the AMX due to UV irradiation, an experiment was conducted at an initial AMX concentration of 1.0×10^{-3} mol dm^{-3} and pH 5. By 90 min UV irradiation, degradation was 0.8 % for AMX (data not shown). Amoxicillin exhibits an absorption peak at 290 nm and no significant degradation was expected due to UV irradiation at 365 nm. As described in the literature, degradation is associated with the hydrolysis of the antibiotic. The hydrolysis reaction would proceed through the attack of the nucleophile in aqueous solutions to the β-lactam ring followed by ring opening (ELMOLLA; CHAUDHURI, 2010). Consequently, degradation of the studied antibiotic when subjected to TiO_2 photocatalysis will be mainly due to the active species produced during the photocatalytic process (e.g., hydroxyl radical, hole and superoxide ion).

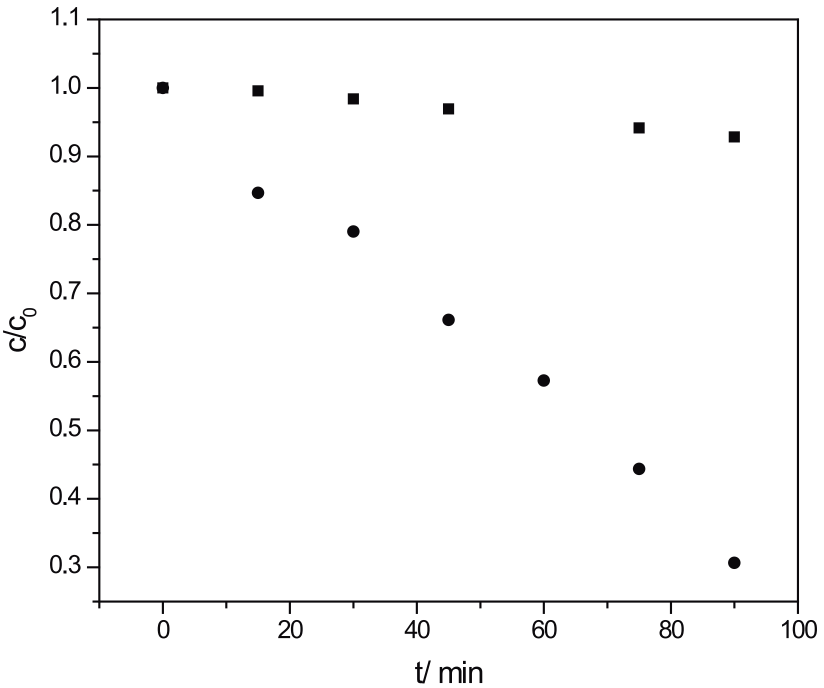
To study the kinetics of the photocatalytic degradation of amoxicillin, experiments were conducted with the TiO_2 thin film, at an irradiation time of 90 min and pH 6. The concentration of AMX, after 30 min dark adsorption was taken as the initial AMX concentration (C_0) for kinetic analysis. Figure 3 shows the plots of (C/ C_0) ratio versus irradiation time for amoxicillin.

The linearity of the plot depicted in figure 3 suggests that the antibiotic photocatalytic degradation follows zero order kinetics.

Addition of NaOH to the TiO_2 film immersed in the antibiotic solution is a well-known procedure and in many cases leads to an increase in the rate of photocatalytic oxidation (LAN et al., 2013). The hydroxyl ion accepts a photogenerated electron from the conduction band of the semiconductor to form the OH radical that increases the antibiotic degradation rate.

The photocatalytic reaction of AMX at pH 11 gave an increase in the rate constant from 8.02×10^{-4} min^{-1} to 7.45×10^{-3} min^{-1}. The presence of high reactive hydroxyl radicals in alkaline medium increases the rate for AMX degradation as described for the degradation of organic compounds (MIRZAEI et al., 2016).

Figure 3 - Kinetics of AMX degradation (■) pH= 6, (●) pH= 11.



CONCLUSIONS

In conclusion, a highly porous, transparent, homogeneous and uniform TiO_2 thin film has been successfully synthesized by polymeric precursor-assisted dip coating technique. The TiO_2 films showed excellent adhesion to glass substrates and a pure anatase phase was obtained as demonstrated by XRD analysis. The film morphology investigated by AFM exhibited a highly rough surface area with 6 nm agglomerates. Degradation of amoxicillin antibiotic in aqueous solution by TiO_2 thin film photocatalysis under UV (365 nm) irradiation was studied. No significant degradation occurred during 90 min using only UV irradiation. The lower adsorption affinity favors a better mobility of AMX on the TiO_2 surface, and consequently the AMX can reach the photocatalytically active TiO_2 sites more easily. pH had a great effect on antibiotic degradation and the highest degradation was achieved at pH 11. Photocatalytic reactions approximately followed a pseudo-first order kinetics and the rate constants (k) were 7.45×10^{-3} min^{-1} at pH 11.

ACKNOWLEDGEMENT

The authors are grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for supporting this study.

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