

Photodegradation study of amlodipine by the synthetic $\text{TiO}_2\text{-SiO}_2$

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Abstract

In this work, we aim to develop a catalyst TiO_2 doped with SiO_2 , varying their mass percentages, synthesized thermally in the presence of Na_2CO_3 used as cooking fondant. The doping was carried out at sintering temperatures of 800 °C, 900 °C and 1000 °C. The synthesized catalysts were characterized by different spectroscopic techniques and were then applied for the photodegradation of amlodipine by exposure to Ultra Violet rays (250 nm-265 nm). The mass of the catalyst, the time of photodegradation and the concentration of amlodipine were optimized. The photodegradation kinetics of amlodipine was monitored by UV-visible spectroscopy. The best photodegradation was obtained at a concentration of 70 mg/L of amlodipine and for a time of 15 min of UV exposure. Structural analyzes by FTIR, TGA/TDA, and morphological by SEM have revealed new phases (anatase, brookite) in the materials.

Key words: $\text{TiO}_2\text{-SiO}_2$, Pharmaceutical rejects, amlodipine, photodegradation, environment.

I. Introduction

In recent years, the release of pharmaceutical compounds into the environment has been recognized as one of the new challenges in environmental chemistry [1-3]. Many methods of treatment have been proposed such as adsorption, membrane separation, nanofiltration[4; 5], but their efficiencies are limited and insufficient [6; 7]. The application of physical-chemical processes, such as photodegradation, nowadays provides satisfactory solutions [7-9].

Photodegradation is often used for the removal of pharmaceutical compounds from wastewater. Among the latter, amlodipine is one of the most frequently encountered pharmaceutical substances in water discharged by the pharmaceutical industries.

Its presence in the environment constitutes a permanent danger for the fauna and flora [10] as well as increasing toxicity in the nature.

More recently, worldwide researches shows that the photodegradation of certain active ingredients (AI), assisted by a catalyst gives even better results [7,11,12]. Apart from the fact that TiO_2 has interesting characteristics and advantages, such as non-toxicity and excellent photo stability, its small surface limits the number of adsorbent sites of the target polluting molecule. To improve photocatalytic performance, researchers [13-16] concentrated on

the creation of a mixed oxide-based material that provides a large number of adsorbent sites by dispersing TiO_2 in a porous support with a high specific surface area, Such as SiO_2 . Thus, the

formation of Ti-O-Si bonds promotes activation of the organic pollutant [17].

The aim of this work is to eliminate the amlodipine by photodegradation assisted by the synthetic catalyst TiO₂-SiO₂ at different mass compositions and sintering temperatures. Subsequently, some parameters influencing photodegradation were studied and optimized.

II. Experimental

II.1. Chemicals

The pharmaceutical compound pollutant used in this study is amlodipine (Fig.1), which is a cardiovascular drug recommended for the treatment of high blood pressure and the preventive treatment of seizures of angina pectoris. Its physical and physical-chemical properties are summarized in Table 1.

Table 1: Physical and physical-chemical properties of amlodipine.

IUPAC Denomination : Benzene sulfonate de (4RS)-2-[(2-aminoethoxy)methyl]-4-(2-Chlorophenyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate of 3-ethyle and 5-methyle.	Physical properties	
	Physical state	solid
	Appearance	White Powder
	Fusion point	203°C
	Solubility	Slightly soluble in water, Easily soluble in Methanol, Fairly soluble in ethanol, Little soluble in 2-propanol.
	Chemical properties	
	Chemical formula	C ₂₆ H ₃₁ ClN ₂ O ₈ S
Molecular weight	567.1 g/mol	

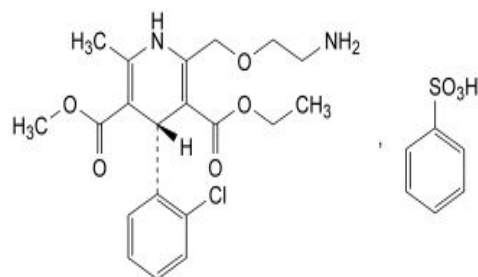


Figure 1: Chemical structure of amlodipine besylate[18].

The catalyst used in these experiments TiO₂ - SiO₂(70%-30%) is a product of thermal synthesis. The characterization of this material is carried out by scanning electron microscopy (SEM), TGA/TDA and FTIR. Its physical-Chemical properties are summarized in Table 2.

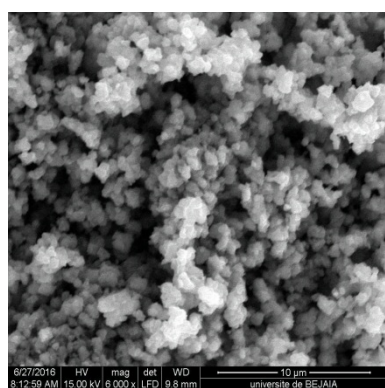
Table 2: Physical-chemical properties of the catalyst TiO₂-SiO₂[15].

Appearance	White Powder
Chemical formula	TiO ₂ -SiO ₂
Molecular weight	139,948 g/mol
Particle diameter	1µm

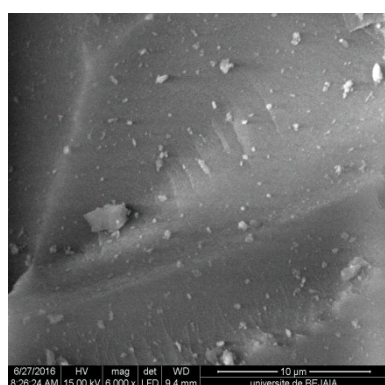
II.2. Physical-chemical characterization of the TiO₂-SiO₂ catalyst

II.2.1. Scanning Electron Microscopy (SEM)

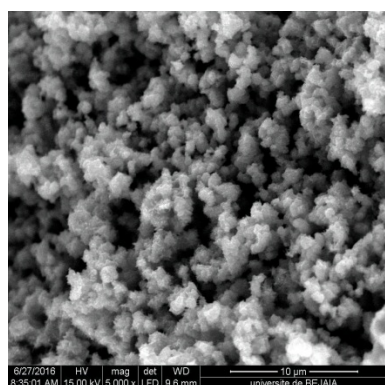
The images of TiO₂ grains (Fig 2-a), SiO₂(Fig. 2-b) and mixed TiO₂ -SiO₂(Fig. 2-c) after curing at 800°C, in a more spherical shape (image c) of average size of about 1 µm in diameter for the TiO₂ -SiO₂ catalyst, compared with the TiO₂ grains alone (image a) of less spherical shape and of relatively higher grain size. On the other hand, the image of silica (b) shows that at 800°C., the material underwent almost complete melting.



-a-



-b-

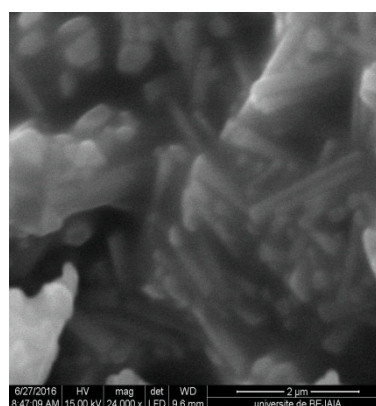


-c-

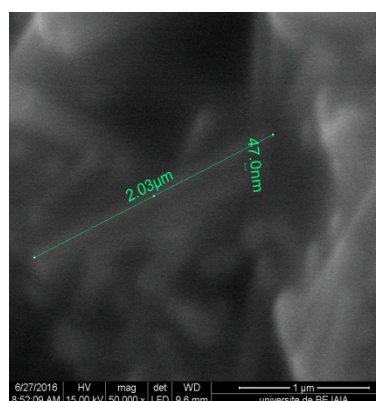
Figure 2: SEM images with a magnification of grains x5000 at T = 800 °C of, a) TiO₂; B) SiO₂ and C) TiO₂-SiO₂(70% - SiO₂).

Scanning Electron Microscopy (SEM)(Figure 2)allowed us to observe the external morphology of the TiO₂-SiO₂ catalyst at the surface.

The TiO₂ sample at 70% and SiO₂ at 30% cured at 900°C (Figure 2) gives images very distinct from the first, with appearance of tubular particles of about 2.03 µm in length attributed to the onset of the rutile phase of TiO₂, by thermal transformation of the anatase phase [19].



-I-



-II-

Figure 3: SEM images at different magnifications, I) x 24000; II) x50000, of TiO₂-SiO₂ catalyst grains (70% -30%) at T = 900 °C.

II.2.3. FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) enabled us to identify the chemical functional groups present in the catalyst by detecting the vibrations characteristic of the chemical bonds in the spectra (Fig.4). The identification of the different vibration compared to the data reported in the literature [17; 20-22] relative to SiO₂, TiO₂ and TiO₂-SiO₂ showed after the spectra examination the appearance of the adsorption bands, presented as following:

-the spectrum (3) of mesoporous TiO₂ nanoparticles is shown in Fig.4. It was observed that the strong band in the range of 900–500 cm⁻¹ is associated with the characteristic vibrational modes of TiO₂, 1380 cm⁻¹ show stretching vibrations of Ti-O-Ti.

- The spectrum (2) of mesoporous SiO₂ nanoparticles is shown in Fig. 4. The two strong bands 1092 cm⁻¹ and 802 cm⁻¹ observed are

associated with asymmetric and symmetric Si–O–Si stretching vibrations respectively. The absorption bands at 1382 cm^{-1} in the spectra, is attributed to the stretching vibration of Si–OH. The absorption bands at 3475 cm^{-1} and 1645 cm^{-1} were due to the presence of O–H stretching and bending vibrations respectively.

- The spectrum (1) of as-synthesized mesoporous $\text{TiO}_2/\text{SiO}_2$ nanocomposite is shown in Fig.4. The band observed at 937 cm^{-1} is associated with Si–O–Ti vibration. The strong bands in the range $900\text{--}500\text{ cm}^{-1}$ are associated with vibrational modes of TiO_2 . The band observed at 440 cm^{-1} corresponds to the Si–O–Si bending mode. The peak in the range of $1380\text{--}1400\text{ cm}^{-1}$ is commonly attributed to Ti–O–Ti vibrations. However, these bands also overlap with vibration involving Si–O–Si bonds.

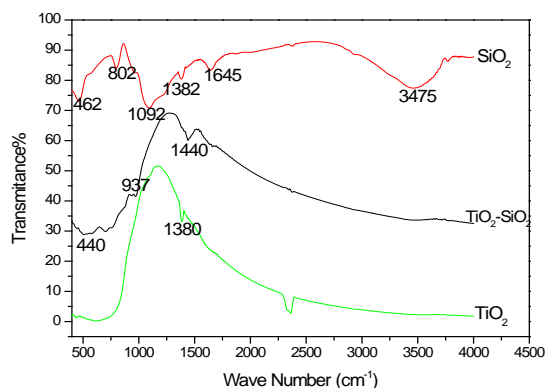


Figure 4: Infrared spectra of : 1) $\text{TiO}_2\text{-SiO}_2$ (70%-30%); 2) SiO_2 ; 3) TiO_2 , heated at 800°C .

II.2.4. Thermogravimetric analysis

Figure 5 shows the mass losses as a function of temperature for the catalyst TiO_2 and the catalyst $\text{TiO}_2\text{-SiO}_2$ (70% -30%) baked at 800°C . According to the results obtained, the TA curve of TiO_2 shows the appearance of three levels corresponding respectively to three mass losses in succession, the first level from 20°C to 200°C is attributed to dehydration (evaporation of surface water).

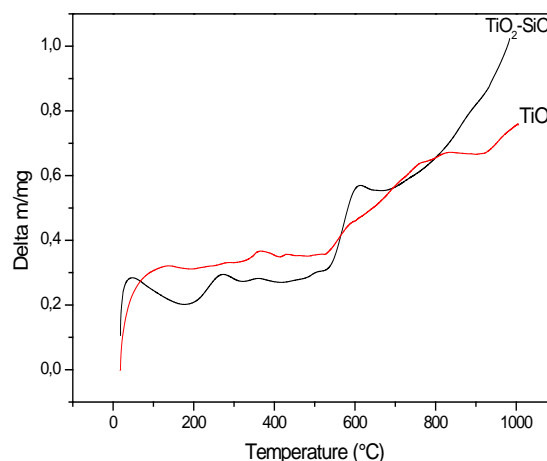


Figure 5: Thermogravimetric analysis curves : 1) TiO_2 ; 2) $\text{TiO}_2\text{-SiO}_2$ (70%-30%), at 800°C .

The second level from 400°C to 600°C is attributed to the loss of the structural water by dehydroxylation of the OH. The last level between 800°C and 900°C is due to the transformation of anatase into rutile [23]. For the mass loss curve of the synthesized catalyst $\text{TiO}_2\text{-SiO}_2$, the increase in bearing heights and their shift to lower temperatures due to the presence of silanol groups of SiO_2 (between 400 and 600°C) can be observed. We also noticed the disappearance of the 4th level of TiO_2 between 800°C and 900°C . This suggests the formation of Si–O–Ti bond in the catalyst, which stabilizes much more the anatase phase [24].

II.3. Kinetics photodegradation of the amlodipine/ $\text{TiO}_2\text{-SiO}_2$

We introduced 100 ml of amlodipine (70 mg/L) into the photoreactor, in the presence of the synthetic catalyst $\text{TiO}_2\text{-SiO}_2$. The suspension is first stirred for a few minutes (30 minutes) in the dark to reach the equilibrium of the adsorption of amlodipine on the catalyst. Subsequently, the suspension is subjected to irradiation with UV rays (250–365 nm) with a UV lamp placed above the solution.

II.3.1. Influence of exposure time to the UV rays

It can be seen (Fig.6) that the photodegradation of amlodipine in the solution prepared in the presence of 20 mg of the synthetic catalyst $\text{TiO}_2\text{-SiO}_2$ (70%-30%, 800°C) increases during the first 15 minutes by decreasing the intensities of the amlodipine

absorption bands (230-238 nm).

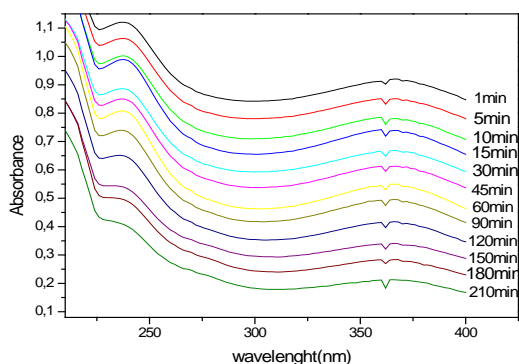


Figure 6: UV spectra of amlodipine photodegradation (70 mg/L) assisted with TiO₂-SiO₂ catalyst (20 mg) in function of the time.

The intensities tend to increase between 15 minutes and 180 minutes, which shows a phenomenon of electronic relaxation between the photodegraded radical species, which promote their recombination. Subsequently, the process decreases, along with the intensities of the bands, which tend towards equilibrium at 180 min and at 210 min (end of photodegradation).

These results indicate that the photodegradation of amlodipine on the catalyst is proportional to the time and reaches a maximum threshold of photodegradation at only 15 min.

II.3.2. Influence of catalyst mass on amlodipine photodegradation

According to figure 7, it is noticed that 20 mg of the catalyst TiO₂-SiO₂ is more efficient for the photodegradation of 70 mg/L of amlodipine, corresponding to the minimum intensity of the absorption bands characteristic of this substance.

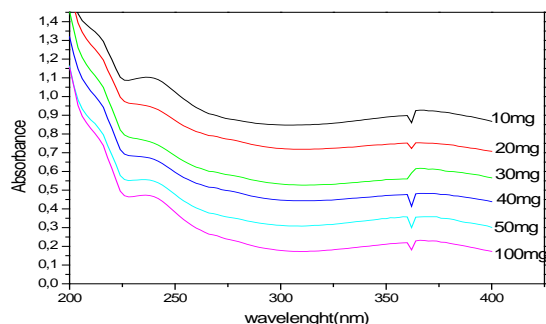


Figure 7: UV spectra of amlodipine photodegradation (70 mg/L) assisted with TiO₂-SiO₂ catalyst (70%-30%, 800°C) in function of the catalyst masse at maximal time of photodegradation.

II.3.3. Influence of amlodipine concentration on the photodegradation

The obtained results (Fig. 8) by varying the concentration of the amlodipine solution while maintaining the other parameters showed. The obtained results indicate that the degradation of amlodipine under the UV rays in the presence of 20 mg of catalyst is more important for the concentrations less than 30 mg/L. Effectively, at 10 mg/L of amlodipine, we noticed the disappearance of the total bands characteristic to amlodipine.

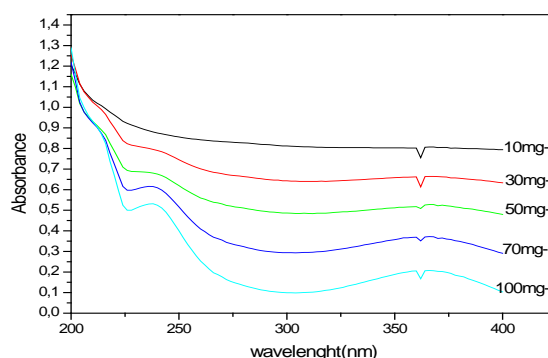


Figure 8: UV spectra of amlodipine photodegradation assisted with TiO₂-SiO₂ catalyst (20 mg-70%-30%, at 800°C) in function of the concentration.

III. Conclusion

The spectroscopic analyzes showed that the structures and the morphology of the elaborated catalyst TiO₂-SiO₂ are significantly influenced by the chemical composition and the cooking temperature. Better photodegradation results are obtained with a mass of 20 mg of catalyst, and these are proportional to the time of exposure to UV rays. The study of the photodegradation of amlodipine on the catalyst TiO₂-SiO₂, has produced very interesting results, that can be exploited in the elimination of toxic substances in pharmaceutical rejects.

Acknowledgment

We thank all who contributed to the realization of this humble work.

List of symbols

TDA: Differential Thermal Analysis
TGA: Thermogravimetric Analysis

FTIR: Fourier transform infrared spectroscopy
SEM: Scanning Electron Microscopy

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