

PHOTOCATALYTIC DEGRADATION OF SOME AQUEOUS SUSPENSIONS OF PROPRANOLOL

Georgeta-Maria Simu^{1*}, Codruta Soica¹, Cristina Trandafirescu¹, Savoiu-Balint
Germaine¹, Cristina Dehelean¹

¹University of Medicine and Pharmacy „Victor Babeş” Timișoara, Faculty of Pharmacy, 2
Eftimie Murgu, 300041, Timișoara, Romania
e-mail: simu.georgeta@umft.ro

Abstract

In this work, the photocatalytic degradation of Propranolol aqueous solutions of different concentrations was investigated in the presence of TiO₂ and TiO₂-MoO₃ catalysts. Among the two photocatalysts used, the best performance can be attributed to the TiO₂-MoO₃ catalyst. Optimal reaction conditions were established: C_{cat.} = 2 g/L; C_{Propranolol.} = 0,25 mM; V = 20 mL, lampe – sample distance = 10 cm, when the UV-A-induced photocatalytic oxidation over the Propranolol suspensions was able to degradate almost completely the studied drug. The speed of decomposition of Propranolol was accelerated when the process was carried out at a temperature of 50°C.

Introduction

One of the major problems that arise at global level since the end of the last century is the scarcity of fresh water. It was stated that global water consumption has increased substantially, 32% of the total taken being attributed to industries [1].

Among the great number of chemicals which can penetrate into the aquatic and terrestrial environment, the pharmaceutical active substances constitute a growing environmental concern [2,3]. These compounds play an important role in the life expectancy of the population over the past centuries, and this matter of fact explains their increasingly growing consumption in human and veterinary medicine. A major issue raised by these compounds is that the drug residues present in the (residual) waste water more often leave the STEP (cleansing stations) almost unchanged.

Studies conducted in several countries noted the presence of more than 80 pharmaceutical products in urban sewage at concentrations ranging from ng L⁻¹ to μg L⁻¹ [3,4]. Time of residence of drugs in the environment varies, being depend by their physicochemical characteristics. On the other hand, the increasing use of drugs, as well as their inadequate disposal constitutes two factors which are responsible for their presence and their "persistence" in the environment. Thus, these substances could be considered to contribute to the phenomenon of the emergence and dissemination of resistant germs, as well as failures of antibiotic therapy [5].

This complex problem, reveal the need for the development of new methods, more effective for the treatment of wastewater. From this point of view, during the last decade, much research have been focused onto the advanced oxidation processes (AOP), which have already shown their potential in the treatment of toxic and biologically refractory organic pollutants [6-11].

Propranolol ((RS)-1-(isopropylamino)-3-(naphthalen-1-yloxy)propan-2-ol) is a beta blocking not selective sympatholytique drug, used in the treatment of hypertension, states of anxiety and panic. This drug is available in the generic form of Propranolol hydrochloride under different trade names. Propranolol has been studied in the treatment of diseases of post-traumatic stress, because this drug inhibits the action of the norepinefrine, a neurotransmitter that contributes to

the consolidation of memory [12-15]. In addition, Propranolol (in combination with etodolac), has been studied as a potential therapeutic agent in the recurrence of colorectal cancer [13]. The aim of this present work, was to carry on an experimental study regarding the purification of residual waters contaminated with pharmaceuticals. In this context, the study focused on the development of an advanced oxidation process, specifically the heterogeneous photocatalysis and its application to the degradation of Propranolol from aqueous solutions.

Experimental

The reagents used in this work were of analytical purity and were used as such. Propranolol, of 99% purity was obtained from Sigma - Aldrich. In this work, we used the following catalysts: TiO_2 and $\text{TiO}_2\text{-MoO}_3$, which were prepared and characterized according to previous work, as well as literature data [16-20]. The photocatalytic activity of these two catalysts has been evaluated by following the kinetics of photodegradation of a series of azo compounds [19].

The heterogeneous photocatalysis process was conducted in a photochemical reactor in Pyrex glass whose dimensions were 3 cm in diameter and 5 cm high. The reactor was initially loaded with 20 ml of Propranolol solution. During the experiment, the mixture was held under continuous stirring (100 rpm) using a magnetic stirrer, placed underneath the photoreacteur. The source of irradiation was a UV Bioblock VL-4LC lamp; 8 W; 230V; 50Hz; 4W-365nm Tube and 4W-254nm Tube. The reactor had also a spring system that enabled us to vary lamp UV-sample distances. The catalyst was added in the reaction medium prior to photodegradation and the irradiation began after 30 minutes, in order to achieve the equilibrium of absorption. A sample was taken every 5 minutes, the catalyst being eliminated by filtration on Whatman filter 0, 45 μm . The degradation process of Propranolol was monitored by means of UV-Vis spectroscopy, au cours de la photodégradation a été suivie qualitativement et quantitativement par spectroscopie UV-visible, using a Perkin-Elmer-Lambda -950 spectrophotometer.

The Propranolol solutions were prepared by dissolution in an aqueous medium (distilled water) at 50°C, at the limit of solubility of the compound. Sulfuric acid has been added directly in the solution of Propranolol in order to adjust the pH to the desired value. Catalyst concentrations ranged from 1 to 6 g/L.

Results and discussion

According to literature data, the TiO_2 catalyst is the most frequently used, while $\text{TiO}_2\text{-MoO}_3$ is a newer compound, used most of the time as a catalyst for the oxidation of propylene in acetone.

In order to study the influence of experimental parameters on the photodegradation process, we conducted a series of measures on Propranolol solutions, in order to establish the optimal conditions of degradation by heterogeneous photocatalysis. This study focused on the following experimental parameters: distance of irradiation, type of catalyst, concentration of the solution of Propranolol, the initial concentration of the catalyst, the pH and the temperature of the reaction medium.

Propranolol (initial concentration of 0.25 mM) has been degraded in acidic medium (pH = 3) in the presence of different amounts of catalysts (TiO_2 and $\text{TiO}_2\text{-MoO}_3$) in order to determine the optimal lamp-sample distance necessary for the most suitable degradation of Propranolol. It was found that the speed of degradation of Propranolol at 30 cm lamp-sample distance is less important than that of solutions situated at 25 cm, 20 cm, 15 cm and 10 cm. In fact, more the lamp-sample distance is lower, most the degradation occurs faster. After 8 min of treatment, we managed to degrade with a rate of 45, 95, 97 and 99% the solutions situated at 15 cm, 10 cm and 30 cm distance from the lamp.

In another series of experiments, it was noticed that the nature of the catalyst (TiO_2 and $\text{TiO}_2\text{-MoO}_3$) influence in a great extent the kinetics of degradation of Propranolol, e.g. the photodegradation of Propranolol was faster when the $\text{TiO}_2\text{-MoO}_3$ catalyst was used.

In order to study the influence of the initial concentration of Propranolol, four aqueous solutions of Propranolol with concentrations ranging from 0.25×10^{-3} to 1×10^{-2} M were submitted to degradation process. The obtained results revealed that the heterogeneous photocatalysis remains applicable in a wide range of concentrations; the speed of degradation of a $1 \cdot 10^{-2}$ M Propranolol solution was less important than in the case of the solutions whose concentrations ranged from $0,75 \cdot 10^{-2}$ M to $0,25 \cdot 10^{-2}$ M. After 10 min of treatment, we managed to degrade with a rate of 45, 95, 97 and 99% the solutions of $1 \cdot 10^{-2}$ M, $0,75 \cdot 10^{-2}$ M, $0,50 \cdot 10^{-2}$ M and $0,25 \cdot 10^{-2}$ M concentrations.

Further, equal volumes of Propranolol solutions (100 mL) were degraded in acidic medium ($\text{pH} = 3$) in the presence of different $\text{TiO}_2\text{-MoO}_3$ concentrations (ranging from 1 to 6 g/L), in order to establish the optimal catalyst concentration for the complete degradation of Propranolol. It was noticed that the degradation was more effective for a 2 g/L $\text{TiO}_2\text{-MoO}_3$ concentration than at 6 g/L, but in all cases the Propranolol was completely degraded in 30 min for an initial concentration of 0.25 mM.

Under our experimental conditions thus determined ($C_{\text{cat.}} = 40$ mg; $C_{\text{Propranolol}} = 0,25$ mM; $V = 20$ mL, lampe – sample distance = 10 cm), the evolution of the solution of Propranolol during the heterogeneous photocatalytic degradation process was qualitatively and quantitatively monitored by UV-visible spectroscopy, as it can be seen in Figure 1.

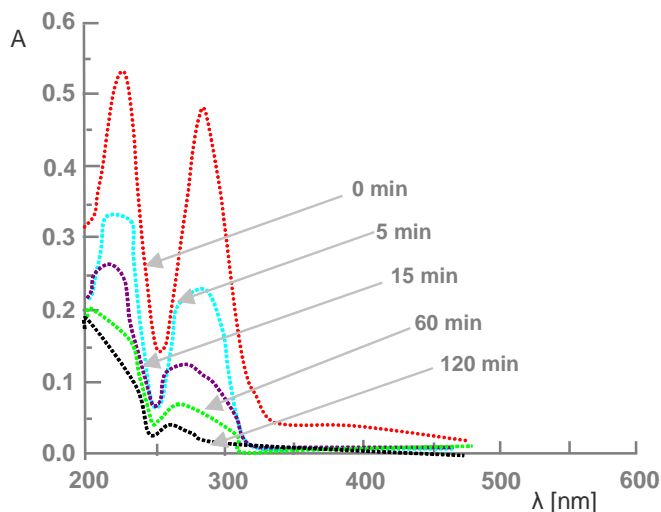


Figure 1. UV-Vis spectra of Propranolol during the heterogeneous photocatalytic treatment. $[\text{Propranolol}] = 0,25$ mM, $V = 20$ ml $[\text{TiO}_2\text{-MoO}_3] = 40$ mg, $\text{pH} = 3$

This figure shows that the disappearance of Propranolol during the heterogeneous photocatalysis process occurs fast. The absorbance peak located at $\lambda = 225$ nm decreases gradually and then completely disappears after 15 min. The peak located at $\lambda = 288$ shows a similar evolution.

Conclusion

The obtained results revealed that among the two photocatalysts used, the best performance can be attributed to the $\text{TiO}_2\text{-MoO}_3$ catalyst.

The optimal concentration of this photocatalyst was of 2 g/L TiO₂-MoO₃. This concentration increases the efficiency of the method to treat aqueous solutions of Propranolol.

The speed of decomposition of Propranolol is accelerated if the process is carried out at a temperature of 50°C.

From ecological point of view, as well as economic, heterogeneous photocatalysis process presents a significant advantage as compared to conventional methods of wastewater treatment.

This method proved effective for the clean-up of contaminated water by Propranolol, with rates of mineralization above 95% in the adopted working conditions.

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