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SUCCESSFUL ELIMINATION OF A REFRACTORY EMERGENT ORGANIC COMPOUND FROM AQUEOUS SYSTEM USING DIFFERENT CATALYTIC MATERIALS

Iasmina- Florina BURLACU[1], Lidia FAVIER[2], Ecaterina MATEI[3], Cristian PREDESCU[4], György DEÁK[5]

In this paper, the photocatalytic degradation of the pharmaceutical drug clofibric acid (CA) using different types of catalytic materials based on TiO_2 *and ZnO was investigated under UVA irradiation. The results shown that the both types of* TiO_2 *(named VLP 7500 and PC 500) used in the experiments can be employed as photocatalytic materials for the elimination of clofibric acid from wastewater but under the same experimental conditions, ZnO proved to have a higher catalytic activity. The effects of some parameters such as catalytic material concentration, initial pollutant concentration was studied. In order to evaluate degradation rate of CA, a high-performance liquid chromatography (HPLC) method was used. Morphology and structure of catalytic materials were investigated by using scanning electron microcopy (SEM).*

Keywords: catalytic materials, AOPs, UV, refractory pharmaceutical compound, water treatment

1. Introduction

Clofibric Acid (CA) is the bioactive metabolite of the lipid regulators clofibrate, etofibrate, and etofyllinclofibrate and is also considered as a potential endocrine disruptor, since it interferes with the synthesis of cholesterol [1, 2]. Owing to the complex structure of the CA and their intermediates, biological degradation is insufficient to remove this chemical. So, this drug has a very high persistence in the environment. Up to now, various methods have been tested to remove this molecule from the wastewater as follows: biodegradation [3, 4, 5], photo degradation [6], advanced oxidation processes [7, 8]. As a response to this

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[1] Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, E-mail: iasminaburlacu@yahoo.com

[2] Ecole Nationale Supérieure de Chimie de Rennes, France, E-mail: lidia.favier@ensc-rennes.fr

[3] Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, E-mail: ecaterinamatei@gmail.com

[4] Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, E-mail: predescu@ecomet.pub.ro

[5] National Institute for Research & Development in Environmental Protection- Bucharest, Romania, E-mail: incdpm@incdpm.ro

problem, advanced oxidation processes (AOPs) have appeared as potentially powerful method for transforming pollutants into harmless substances.

Among the AOPs, heterogeneous photocatalysis has been considered as an promising technology for the purification of water against a high number of pollutants (inorganics or organics) [9,10,11]. Semiconductors, in particular ZnO and TiO_2, are different compared to other AOPs for the photo degradation of persistent pollutants from wastewaters [12, 13, 14, 15, 16].

In this context, the photocatalytic degradation of the pharmaceutical drug CA using different type of catalytic materials (ZnO, TiO_2-VLP 7500, TiO_2- PC 500) was investigated in this work in aqueous suspensions under artificial light irradiation. In addition, this study dicusses in detail the influence of two process parameters such as load of catalytic material and initial pollutant concentration on the degradation kinetics of the target molecule. It has been proved that the heterogeneous photocatalysis using a suspension of ZnO could be efficiently used to degraded the target molecule (more than 98 %) and can be a useful technique for the treatment of wastewaters. Thus, the results are satisfactory enough to encourage further researches in this topic.

2. Experimental part

2.1. Materials

The CA (2-(p-chlorophenoxy)-2-methylpropionic acid, MW 214.65 g/mol) was purchased from Sigma- Aldrich. The chemical structure of CA is shown in *Fig. 1* and the main characteristics are presented in *Table 1.*

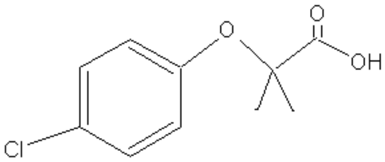

Fig. 1. Molecular structure of CA

Table 1

CA characteristics

Therapeutic class	lipid regulator
Formula	$C_{10}H_{11}ClO_3$
CAS number	882 09 7
Aspect	white powder
Molar mass (g/mol)	214.65
pK_a at 295°K	4.2
Water solubility at 20°C (mg/L)	583
log K_{ow} – Octanol Water Partition (coefficient at pH 7.5)	0.76

Data source: https://pubchem.ncbi.nlm.nih.gov/compound/Clofibric-acid#section=3D-Conformer

PC-500 TiO_2 was purchased from Degussa, and VLP 7500-TiO_2 and ZnO, 98% from Alfa Aesar. The main characteristics of these materials used as catalytic materials are presented in *Table 2.*

Table 2

Characteristics of the catalytic materials

	TiO_2 VLP 7500	**TiO_2 PC-500**	**ZnO**
TiO_2 content (wt%)/ZnO	> 99	99.9	> 98
Crystal form	100% anatase	100% anatase	80% anatase, 20% rutile
Particle size (nm)	15	5-10	21
Surface area (m^2/g)	> 225	350	35-65
Density, 20 °C (g/cm^2)	3.9	-	4.23

All other reagents used in the experiments were analytical grade and purchased from VWR Chemicals. Before use all reagents were filtrated.

2.2. Experimental set-up

Experiments were carried out in a batch reactor *Fig. 2* with 1 L capacity at the lab temperature (between 25 and 27°C).

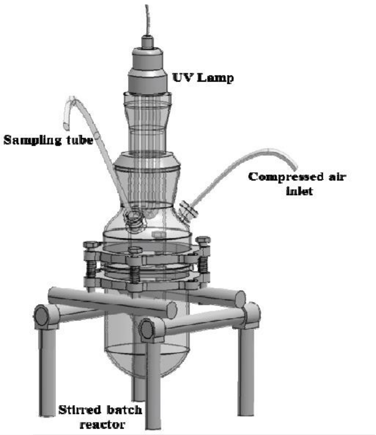

Fig. 2. Schematic representation of the reactor used

Catalytic materials were used as suspensions in solutions and were irradiated in the reactor with one lamp UV (Philips). The UV lamp was placed in a glass tube and immersed in the middle of the solution. The irradiation intensity of the lamp was 17.2 mW/cm^2 and the wavelength was 227 nm. The photo reactor lid was provided with ports for the inlet and outlet of oxygen and sampling. To maintain the homogeneous suspension during the reaction the stirring and aeration were maintained. The reactor walls were covered by aluminum foil to minimize the interference of external radiation.

2.3. Photo degradation experiments

1 L of the solution containing CA was put in contact with each catalytic material and transferred into the reactor. The solution was continuously aerated and circulated for 1 h under darkness in order to establish a clofibric acid adsorption/desorption equilibrum. After this, the lamps were switched on for initiating the photoreaction. Agitation and aeration were maintained during the reaction to keep the suspension homogeneous. 5 mL of each samples were taken at regular time intervals, filtered using membrane syringe filters with pore size of diametre 0.45 μm then centrifuged at 60 rpm for 10 min in order to remove catalytic particles and analyse the residual concentrations of CA.

Concentrations of CA in the aqueous solution were determined by high performance liquid chromatography HPLC (WATERS) equipped with Photodiode Array Detector Waters 996, Autosampler Plus 717 and C18 column (5μm 4,6X 250 mm). The analysis was carried out with 60% Acetonitrile, 40% water and 1% formic acid for mobile phase, flow rate was set at 50 μL, injected volume $1 ml \cdot min^{-1}$. The target compund was detected at 227 nm. Under these conditions, the CA retention time was around 7.6 min. The catalytic materials used in the experiment were characterized using QUANTA 450 FEG scanning electron microscope (SEM) from FEI Company, with minimum imaging resolution at 30 kV of 1 nm in high vacuum operating mode. The energy dispersive spectra device (EDS) was used for identifying the presenec of elements in the analyzed samples.

3. Results and discussion

Photocatalytic experiments were developed under the following operational conditions: C_0 = 10 mg/L CA as initial concentration, 100 mg/L for TiO_2 - VLP 7500, 100 mg/L for PC 500 and 100 mg/L for ZnO respectively, at natural pH, contact time 60 minutes. In *Fig. 3* we can see the plots of $\ln(C/C_0)$ vs. time.

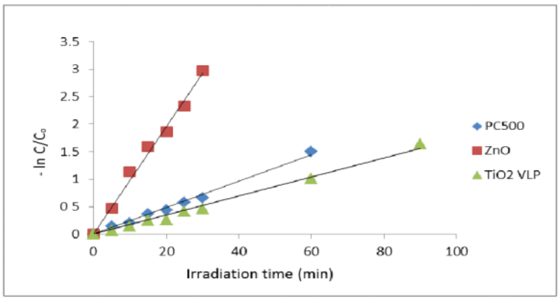

Fig. 3. Kinetics anlaysis for the pseudo first order reaction of CA for the investigated catalytic materials. Experimental conditions: C_0= 10 mg/L, Catalytic material = 100 mg/L, pH natural, maximum light flux

As it can be seen from these plots, the photocatalytic degradation of CA by TiO_2 and ZnO follow pseudo-first-order kinetics according to:

$$-ln\ (C/C_0) = k_{app}t \tag{1}$$

where C_0 is the initial concentration of pollutant in aqueous solution and C is the residual concentration of pollutant at time t. The pseudo-first-order rate constant k is determined by fitting the experimental data with this model.

The rate constants k_{app} and correlation coefficient R^2 is presented in *Table 3*. The obtained values for k_{app} are between 0.0174 for TiO_2 VLP 7500 and 0.0977 for ZnO. Thus, ZnO was selected as catalytic material for further researches, because in the case of this material was obtained the highest value for k_{app}.

Table 3

The values of k and R^2 for the photocatalytic degradation of CA, C_0= 10 mg/L

Semiconductor, Ccatalytic material (mg/L)	**K_{app} (min^{-1})**	**R^2**
a) ZnO = 100	0.0977	0.9906
b) TiO_2 PC 500 = 100	0.024	0.9918
c) TiO_2 VLP 7500 = 100	0.0174	0.9911

The SEM analysis was used to identify morphology homogeneity and size of ZnO as catalytic material. The SEM image *(Fig. 4)* indicates an agglomeration of nano and micro-sized particles with the most particles size between 100 nm and 500 nm. Some of these particles became stuck together into loosely formed agglomerates. The zinc oxide particles keep the same shapes of solids rods as it is indicated in the literature [17, 18].

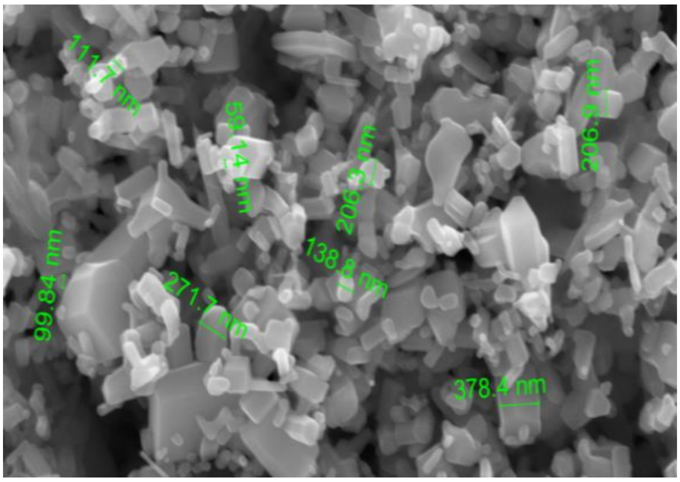

Fig. 4. Image SEM for ZnO used as catalytic material

The elemental analysis was carried out by EDS *(Fig. 5)*, to confirm the presence of the synthesized elements and purity of the products. The spectrum EDS of ZnO show only two peaks that confirm the presence for Zn and O, this proves the purity of the catalytic.

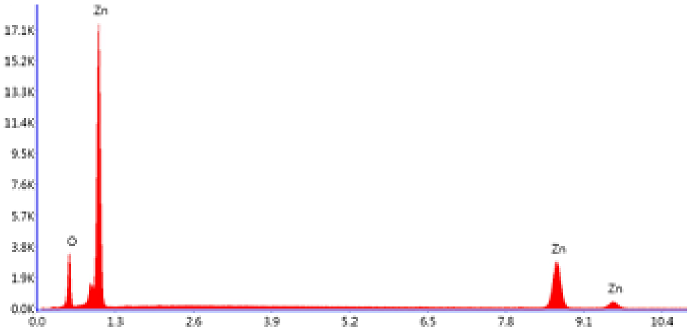

Fig. 5. Elemental analysis using EDS equipment

3.1. Efficiency of photocatalytic oxidation on CA degradation

To investigate the adsorption of CA on the catalytic surface, some adsorption experiments have been carried out ([concentration of CA] = 10 mg/L, [catalytic material] = 50 mg/L and natural pH, corresponding to the solution of CA in water, 5.9) in the dark. The photolysis experiments [catalytic material] = 0) has been developed under the same experimental conditions and the effect of the UV light on CA was investigated. The CA degradation efficiency versus time in 3 different hypothesis: photocatalytic oxidation (UV/ZnO), adsorption (only ZnO) and photolysis (only UV), is presented in *Fig. 6.*

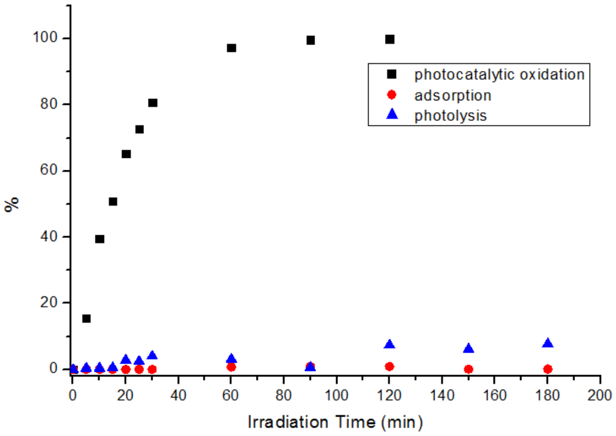

Fig. 6. Graphical representation of the CA degradation percentage versus time, on the following situations: photocatalytic oxidation (UV/ZnO), adsorption (only ZnO) and photolysis (only UV), experimental conditions C0= 10 mg/L, ZnO= 50 mg/L, pH natural of the solution

The results showed that the CA has a low rate of adsorption. Photo degradation of CA was approximately in the range of 5- 10% in the direct photolysis but degradation of CA using photo catalysis and UV irradiation (UV/ZnO) in the same conditions was more than 95%. The results indicated that the observed high decomposition in the UV/photocatalytic process is exclusively attributed to the photocatalytic reaction of the semiconductor particles. On the other hand, these experiments demonstrated that both UV and ZnO as photocatalytic material were needed for the degradation of CA. It has been established that the photocatalytic degradation of CA is initiated by photoexcitation of the semiconductor to electron- hole pair on the catalytic material surface.

3.2. Effect of catalytic material load

The effect of the amount of ZnO catalytic material on the degradation of the CA is shown in *Fig. 7*. Experiments performed with different concentrations of ZnO showed that the photo degradation efficiency increases with an increase in ZnO concentration up to 1000 mg/L. This observation can be explained in terms of availability of active sites on the catalytic material surface and the penetration of UV light into the suspension. The total active surface area increases with increasing catalytic material dosage.

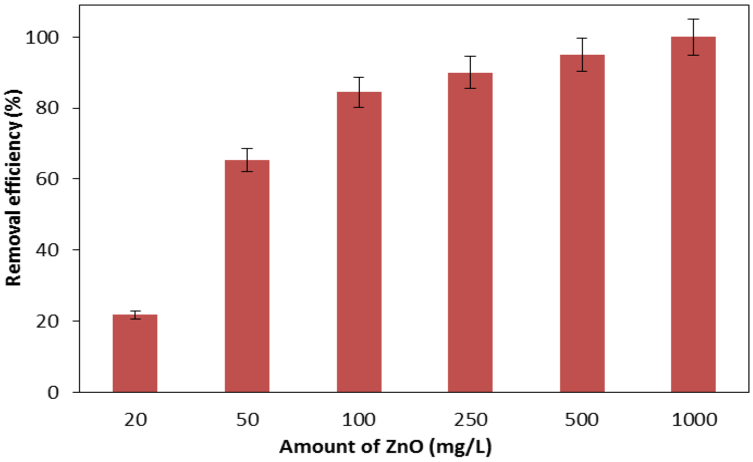

Fig. 7. Effect of ZnO amount on degradation of CA at 20 minutes irradiation time. Initial polutant concentration 10 mg/L, natural pH, maximal irradiation

In *Fig. 8* is presented CA degradation kinetics, at constant pollutant concentration (10 mg/L), and different quantities of ZnO (20mg/L, 50 mg/L, 100 mg/L, 250 mg/L, 500 mg/L, 1000 mg/L), after 3 h of UV irradiation. From *Fig. 8*, where C_t is the concentration of CA at the end of the process and C_0 is the initial concentration, it is observed that for the amount of 1000 mg/L more than 98 % of the CA degradation is obtained after 15 minutes. Thus, it can be observed that the increasing of the quantity of catalytic material conducts to a high degradation rate.

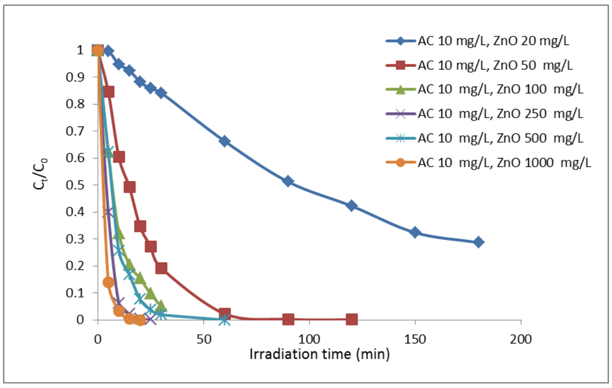

Fig. 8. Effect of catalytic material concentration

3.3. Effect of the pollutant

The influence of initial concentration of pollutant solution on the photocatalytic degradation is an important aspect to be studied because this parameter could influence the photo degradation efficiency. Initial concentrations of CA were varied in the range of 5- 300 mg/L and kept the quantity of ZnO (1000 mg/L) constant, under UV irradiation at maximal flux and natural pH of the solution.

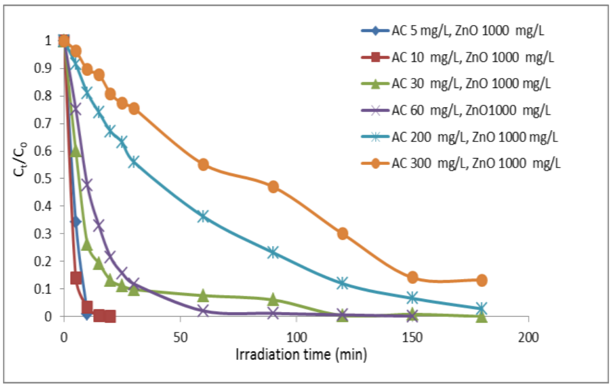

Fig. 9. Effect of the pollutant concentration

From *Fig. 9*, it can be seen that for a CA concentration of 5mg/L after 15 minutes, degradation of the pollutant was completed, and for 300 mg/L of pollutant concentration about 3hours were necessary for a complete degradation. This, indicates that the initial degradation rate increases with CA concentrations.

4. Conclusions

The obtained results indicate that UV/ZnO system could be efficiently used for degradation of the CA as bioactive metabolite present in wastewaters. ZnO and UV light expose a low efficiency when are used separately. The combination between ZnO and UV light lead to important rate of degradation for CA, indicating that the degree of CA degradation is obviously affected by irradiation time and catalytic material amount. The photocatalytic oxidation process of CA generates some intermediates, but the analysis of these will be further treated. The most relevant data were obtained at 1000 mg/L as optimal amount of catalytic material for 10 mg/L CA, under natural pH of the CA solution.

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