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Efficiency of blue-glass-metal oxides immobilized system in the Photodegradation of different pharmaceuticals compounds

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INTRODUCTION

Photo-catalysis using titanium dioxide (TiO_2) is currently being considered for many environmental applications such as water decontamination. This is due to its ability to degrade organic pollutants to CO_2, water and mineral acids [1]. Despite the usage of this semiconductor as catalyst for environmental applications, it has proved very effective, one main problem of using TiO_2 is the separation of the powder in the aqueous media after the photo-catalytic process. To avoid this problem, TiO_2 and other metal oxides used as photo-catalysts have been supported in a variety of materials [2], by this it is possible to keep out an enough active surface, but at the same time the separation of the catalyst becomes an easy procedure. The aim of our research is to compare the effectiveness of blue-glass photo-catalyst to TiO_2 suspension to photo-degrade some pharmaceutical compounds.

RESEARCH ACTIVITY

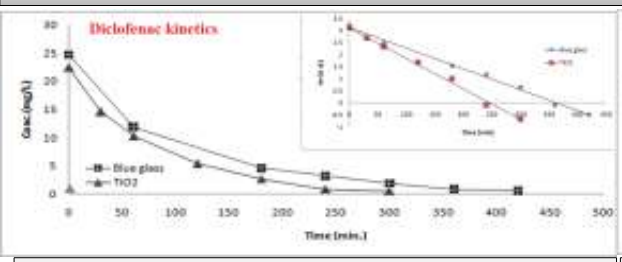
❖ Kinetics of photo-degradation and photo-products identification of different pharmaceutical compounds (Diclofenac and Naproxen) in water phase were determined in laboratory-scale experiments using light irradiation with a solar simulator in presence either of Titanium dioxide (TiO_2) in aqueous suspension or metal oxides immobilized on blue-glass surface (Fig.1).

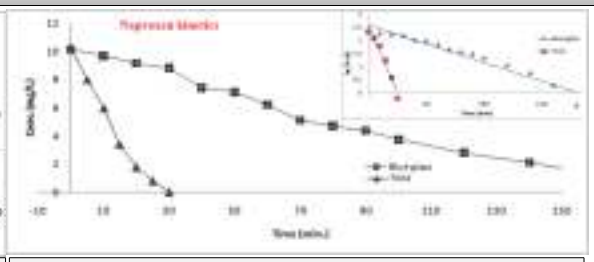
LABORATORY-SCALE EXPERIMENTS

Fig.1 Blue-glass system

Fig.2 Suntest CPS (solar simulator) device

RESULTS AND DISCUSSION





Process	k (min^{-1})	$t_{1/2}$ (min)	R^2
Photo-catalysis / TiO_2	0.012	54.6	0.994
Photo-catalysis / Blue glass	0.0087	79.7	0.994

Process	k (min^{-1})	$t_{1/2}$ (min)	R^2
Photo-catalysis / TiO_2	0.007	9.0	0.94
Photo-catalysis / Blue glass	0.001	69.3	0.994

DICLOFENAC

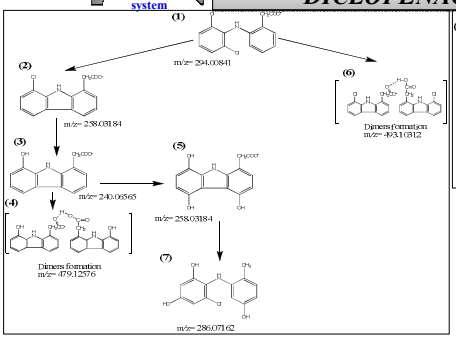


Fig.3: Photocatalytic degradation pathway for diclofenac sodium with blue glass

Table 1: Compounds identified as [M-H]- by LC–ESI-FTICR MS in blue glass experiment.

Compound	Molecular formula [M-H] –	Accurate m/z [M-H+]	RT min.	Error (ppm)
(1)	$C_{14}H_{11}NO_2Cl_2$	294.00841	17.51	-0.93810
(2)	$C_{14}H_9NO_3Cl$	258.03184	16.96	1.59091
(3)	$C_{14}H_{10}NO_3$	240.06565	14.18	-2.09650
(4)	Dimers formation	479.12576	15.17	-2.08530
(5)	$C_{14}H_9NO_3Cl$	258.03184	16.96	1.59091
(6)	Dimers formation	493.10312	10.05	1.79240
(7)	$C_{13}H_{12}NO_3Cl$	286.07162	5.04	-----

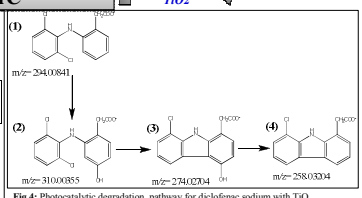


Fig.4: Photocatalytic degradation pathway for diclofenac sodium with TiO_2

Table 2: Compounds identified as [M-H]-by LC–ESI-FTICR MS in TiO_2 experiment.

Compound	Molecular formula [M-H] -	Accurate m/z [M-H] -	RT min.	Error (ppm)
(1)	$C_{14}H_{11}NO_2Cl_2$-	294.00841	25.31	-0.93
(2)	$C_{14}H_{10}NO_2Cl_2$-	310.00355	9.06	1.04
(3)	$C_{14}H_9NO_3Cl$-	274.02704	5.56	1.79
(4)	$C_{14}H_9NO_2Cl$-	258.03204	15.71	1.59

Photoproducts of irradiated samples in all experiments were detected by LC/FTRCR-ESI-MS. Electrospray (ESI)-MS, all Diclofenac and Naproxen photoproducts were identified as shown in the figures 3, 4 and 5. Metabolites were detected as listed in Tables 1, 2 and 3.

NAPROXEN

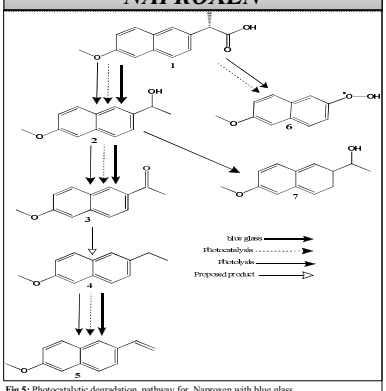


Fig.5: Photocatalytic degradation pathway for Naproxen with blue glass

Table 3: Compounds identified as [M+H]+ by LC–ESI-FTICR MS.

Compound	Chemical formula	m/z	Photolysis	TiO2	Blue glass
2	$C_{13}H_{14}O_2$	203.10566	×	×	×
3	$C_{13}H_{12}O_2$	201.09102	×	×	×
5	$C_{13}H_{13}O$	185.09609	×	×	×
6	$C_{13}H_{10}O_3$	191.06927	×	×	
7	$C_{14}H_{14}O_2$	205.08511	×		

In presence either of titanium dioxide (TiO_2) in aqueous suspension or metal oxides immobilized on blue-glass the decline in concentration for both drugs with irradiation time followed first order kinetics, which are confirmed by the linear behaviour of ln C_t as a function of irradiation time, all kinetic parameters are listed in tables under figures, the performance of blue glass in diclofenac experiments was approximately similar to that with conventional TiO2. While the photo-degradation reaction of Naproxen tested compound using blue-glass-TiO_2 was slow by comparison to TiO_2 powder, this may be due to chemical structure which affect the chemical stability of the tested compound. Our final results showed that the photo-catalysts tested in the experiments are able to degrade the pharmaceuticals used as model molecules and may find application in the remediation of water contaminated with recalcitrant residues due to poor efficiency of treatment plants normally adopted for the purification of wastewater.

…..IN CONCLUSION

All photoproducts have been successfully identified using LC/FTICR-ESI-MS. Photocatalysis by aqueous suspension has shown better results than immobilized on blue-glass. in fact, original compounds and all metabolites identified were completely mineralized after 7 hours for Diclofenac and 30 min. for Naproxen. During immobilized on blue-glass the metabolites appeared, also complete mineralized after 8 & 3 hours for both Diclofenac and Naproxen, respectively. It could be useful to design a suitable pilot reactor to be tested in outdoor experiments using solar irradiation.

[1] A.Y.C. Tong, R. Braund, D.S. Warren, B.M. Peake. TiO2-assisted photodegradation of pharmaceuticals — a review, Cent Eur J Chem, 10 (2012), pp. 989–1027
[2] F.J. Rivas, F.J. Beltrán, A. Encinas, Removal of emergent contaminants: integration of ozone and photocatalysis, J Environ Manage, 100 (2012), pp. 10–15

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