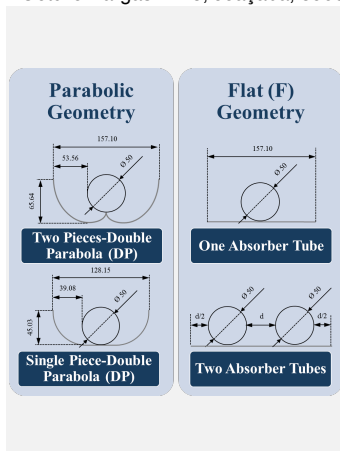


P. Peri^{1,2}, T. Silva¹, L. Paulista¹, R. Martins³, P. Soares⁴, R. Boaventura¹, V. Vilar¹. (1) LSRE-LCM, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, vilar@fe.up.pt. (2) Foundation for Research and Innovation Support of the State of Santa Catarina (FAPESC), Parque Tecnológico Alfa - Rod. José Carlos Daux - João Paulo, Florianópolis, 88030-902, Brazil. (3) Department of Chemical and Biological Technology, School of Technology and Management, Polytechnic Institute of Bragança, Campus de Santa Apolónia, 5301-857 Bragança, Portugal. (4) University of the West of Santa Catarina (UNOESC), R. Getúlio Vargas 2125, Joaçaba, 89600-000, Brazil.



Solar hardware design for photocatalytic processes includes aspects of optics, geometry and reactor materials. Compound parabolic collectors (CPCs) have widely been used to promote heterogeneous and homogeneous photocatalytic reactions. In this work, different reflective surface (RS) materials (anodized aluminum with [MS] and without [R85] protective coating, soiled aluminum [R85s] and stainless steel [SS]) and geometries (flat [F], single piece-double parabola [SP] and two pieces-double parabola [DP]) were tested aiming the degradation of a recalcitrant organic compound, gatifloxacin (GAT), by using a heterogeneous TiO₂ photocatalytic system. Firstly, the photonic flux entering the system was measured by 2-nitrobenzaldehyde actinometry, considering the different RSs. After that, the catalyst (TiO₂-P25) was immobilized in the surface of a static mixer and axially inserted in the tubular borosilicate photoreactor. Finally, the efficiency of the heterogeneous photocatalytic system was evaluated for GAT removal from aqueous solution using the best photoreactor configuration.

Introduction

Advanced Oxidation Processes (AOPs), which include heterogeneous and homogeneous photocatalytic reactions, are considered as a promising method for the removal of toxic and bio-recalcitrant pollutants from wastewaters [1-3]. Amongst AOPs, the TiO₂-assisted heterogeneous photocatalytic process has shown high efficiency and applicability on the persistent organic pollutants elimination. Typically, TiO₂ can be used dispersed in aqueous solution, or immobilized on an inert support, which even being the less efficient option, it does not present issues related to the particles separation and light scattering/absorption effect [4]. Therefore, the scientific community has been focusing on the deposition of catalysts on inert surfaces. A large number of support surfaces have been tested. However, mass and photon transfer limitations remain one of the main challenges for the heterogeneous photocatalysis [5]. Kenics® static mixer (Fig. 1) is a motionless device that utilize the energy of the flow stream to produce consistent and reliable mixing. This device, assembled in a tubular photoreactor, improves mass transfer, even using a laminar regime, and illumination efficiency, since the entire catalytic surface area is irradiated by using sunlight combined with parabolic reflectors.

Regardless the efficiency of AOPs, they can be quite expensive, essentially due to the high energy and chemicals consumption [3, 6, 7], being the reflective surface (RS) responsible for 15-25% of the solar collector cost. Compound Parabolic

Collectors (CPCs) have been used to ably capture the solar photons [8]. However, a serious drawback of the anodized aluminum, used on CPCs manufacturing, is the poor long-term stability accompanied by a large decrease of reflectance properties [9], thus implying additional maintenance costs for the substitution of the soiled surface. Furthermore, the double truncated parabola geometry presents a clear disadvantage since it requires two separate pieces to constitute a single reflector mirror. Therefore, considering that the reflector element represents a considerable fraction of the collector cost, there seems to be an opportunity to study different RS design solutions.

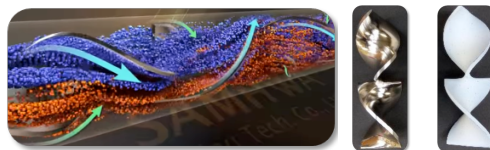


Figure 1. Kenics® static mixer device: flow pattern, clean surface, and surface coated with TiO₂.

Accordingly, this work aims to compare RSs with different geometries (flat [F], single piece double parabola [SP] and two pieces double parabola [DP]) and materials (anodized aluminum with and without protective coating [MS and R85, respectively], soiled aluminium [R85s] and stainless steel [SS]), on the efficiency of heterogeneous TiO₂ photocatalytic system for the degradation of a recalcitrant organic compound. The efficiency

assessment of the different RSs was performed by means of 2-nitrobenzaldehyde (2-NB) actinometry, to determine the radiant power incident (RP_i) on the photo-reactor tube and the radiant power (RP) that reaches the reaction medium. Heterogeneous photocatalytic efficiency was evaluated for the degradation of GAT, using the best photoreactor configuration and with a Kenics® static mixer device as catalyst (TiO_2 -P25) support.

Material and Methods

To test the different RS configurations, a lab-scale photo-reactor placed into a sunlight simulator (ATLAS, model SUNTEST XLS+) was used. The sunlight simulator was equipped with a 1700 W air-cooled xenon arc lamp, with a daylight and quartz filters with infra-red coating, as artificial solar radiation source. The artificial light source was focused on a borosilicate cylindrical photo-reactor (Schott-Duran type 3.3, Germany, cut-off at 280 nm, internal diameter 46.4 mm, length 160 mm and thickness 1.8 mm).

The radiant power (Eq. (1)) incident on the different photocatalytic systems was determined by 2-NB actinometry, according to the following experimental procedure: a recirculation cooling-jacketed glass vessel of the lab-scale prototype was filled with 1 L of 2-NB solution (1.25, 2.5, 5 and 7.5 mM), which was pumped, by means of a peristaltic pump (Ismatec, model Ecoline VC-380 II, at a flow rates of 50, 75 and 100 L/h), to the photo-reactor unit (without reflector (NoRS) and with R85-DP, MS-DP, SS-DP, SS-SP, R85s-DP, R85-F, SS-F reflectors), homogenized by a magnetic stirrer and recirculated in the closed system in the darkness. In the meantime, the temperature set-point of the refrigerated thermostatic bath was controlled to keep the solution at 25°C and the solar simulator was turned on at a radiation intensity (I) of 500 W/m^2 (equivalent to 44 W_{UV}/m^2). After temperature and irradiance stabilization, a sample was taken and the solar collector was uncovered, starting the reaction. After that, samples were taken every 5 min during 1 hour of irradiation. For the flat geometries (R85-F and SS-F), actinometric measurements were also performed using two absorber tubes at different distances (25, 50 and 70 mm), thus increasing the reflective surface areas. Actinometric measurements were also performed according to the same procedure, but using natural sunlight and a borosilicate tube with 425 mm of length, for MS-DP reflector with and without the static mixer.

$$\frac{dn_{Ac}}{dt} = RP_i \sum_{\lambda} \left[\frac{S_{e,\lambda} T_{D,\lambda} \Phi_{\lambda}}{E_{ph,\lambda}} (1 - 10^{-A_{\lambda}}) \right] \quad (1)$$

Where: dn_{Ac}/dt is the number of actinometer ions formed during the irradiation time, under polychromatic irradiation; $S_{e,\lambda}$ is the relative spectral

distribution of the incident radiation (calculated from the integration of the radiation source spectral irradiance); $T_{D,\lambda}$ is the transmission spectrum of Duran glass; A_{λ} is the average absorption spectra of the actinometric solution; Φ_{λ} is the quantum yield of the 2-NB; and $E_{ph,\lambda}$ is the energy of a photon at wavelength λ .

Finally, for MS-DP configuration and with the static mixer coated with approximately 1.7 g of TiO_2 (spray coating method), two heterogeneous photocatalytic experiments were also executed, in order to evaluate the degradation of 2 mg/L GAT, with and without the addition of H_2O_2 (100 mg/L).

Results and Discussion

Initially, using the R85-DP reflector, the photonic flux was determined as a function of 2-NB concentration and recirculation flow rate. The maximum photonic flux was obtained using 5 mM of 2-NB at 75 L/h (Table 1). Table 1 shows that the lower RP_i value was obtained for the photo-reactor with no reflector (No-RS), whereas the highest value was obtained with R85-DP reflector (2.2 times higher), corresponding to 93% of the emitted irradiance by the xenon lamp ($CRO = 0.93 \pm 0.09$). However, after 10-years of outdoor exposure (R85s-DP), the RP_i decrease 34%, thus making the MS-DP reflector the most suitable for solar collectors to promote heterogeneous TiO_2 photocatalysis. Finally, tests with flat reflector and with two absorber tubes at different distances were performed. The highest CR_O values were obtained for a distance of 50 mm. This apparent trend may be explained due to the occurrence of two different phenomena: for distances < 50 mm a shadow effect may occur between the tubes; and for distances > 50 mm, the fix position of the lamp inside the Suntest® chamber may influence the measurements, according to the inverse square law, related to the distance to the light source, and the cosine law related to the incident angle. The overall efficiency of light reflection by the reflective surfaces tested was from the lowest to the highest: SS-F < R85-F < R85s-DP < SS-SP < SS-DP < MS-DP < R85-DP. This is in good agreement with the ray trace analysis and the materials specular reflectance values.

Heterogeneous photocatalytic efficiency (Fig. 2), under natural sunlight (49-50 W/m^2), using the borosilicate tube assembled with six static mixing elements and coated with TiO_2 , and with the MS-DP collector configuration was evaluated for GAT removal.

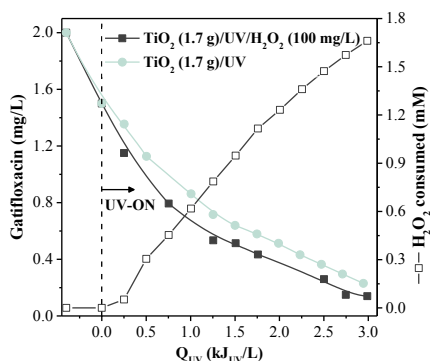


Table 1. Illumination efficiency parameters obtained from O-nitrobenzaldehyde (2-NB) actinometric measurements.

Sunlight	Reflective Surface	I_0^b (W/m ²)	A_r^c (m ²)	Q (L/h)	[2-NB] (mM)	d^d (mm)	RP ^e (W)	RP _i (W)	CR _o ^f	
Simulated	R85-DP	44	0.025	75	1.25	n.a.	0.63±0.07	0.76±0.08	0.69±0.08	
							0.7±0.1	0.9±0.2	0.8±0.2	
							0.87±0.08	1.0±0.1	0.93±0.09	
							0.78±0.08	0.9±0.1	0.83±0.08	
	R85-DP	44	0.025	75	50	5	n.a.	0.78±0.08	0.9±0.1	0.84±0.09
					75			0.87±0.08	1.0±0.1	0.93±0.09
					100			0.8±0.1	0.9±0.1	0.9±0.1
	R85-DP	44	0.025	75	5	n.a.	0.87±0.08	1.0±0.1	0.93±0.09	
	MS-DP						0.71±0.08	0.85±0.09	0.77±0.08	
	SS-DP						0.61±0.03	0.73±0.04	0.66±0.03	
	SS-SP						0.58±0.08	0.68±0.09	0.62±0.09	
	R85s-DP						0.56±0.05	0.66±0.05	0.60±0.05	
	R85-F						0.46±0.04	0.54±0.05	0.49±0.05	
	SS-F						0.44±0.04	0.52±0.05	0.47±0.04	
	NoRS						0.42±0.04	0.50±0.05	0.45±0.05	
	R85-F						44	0.050	75	5
		50	0.9±0.1	1.1±0.1	0.48±0.07					
		75	0.85±0.06	1.00±0.07	0.45±0.03					
	SS-F	44	0.050	75	5	n.a.	25	0.8±0.1	0.9±0.2	0.42±0.08
							50	0.86±0.07	1.02±0.08	0.46±0.04
75							0.82±0.08	0.97±0.09	0.44±0.04	
Natural	MS-DP	50	0.067	75	5	n.a.	2.1±0.4	2.5±0.4	0.74±0.09	
	MS-DP-SM ^g	52					1.7±0.3	2.0±0.3	0.60±0.07	

^a Test performed with the static mixer inserted into the absorber tube (425 mm of useful length); ^b Irradiance incident on the collector aperture; ^c area of the receiver; ^d distance between the absorber tubes; ^e RP is determined in the same way than the RP_i, excluding the term related to the Duran glass transmission from Eq. (1); ^f Optical Concentration Ratio (=RP_i/(A_r×I₀)).

Almost complete GAT removal was achieved in less than 3 kJ_{UV}/L and the addition of 100 mg/L of H₂O₂ to the UV/TiO₂ system improved the reaction rate in about 14%, consuming 0.64 mmol H₂O₂/kJ. More tests are on-going to evaluate the photocatalytic efficiency for different RS configurations.

Conclusions

CR_o (average flux over the receiver divided by the flux over the aperture) values obtained for the reflectors surfaces tested, follows the sequence: SS-F (CR_o = 0.47) < R85-F (CR_o = 0.49) < R85s-DP (CR_o = 0.60) < SS-SP (CR_o = 0.62) < SS-DP (CR_o = 0.66) < MS-DP (CR_o = 0.77) < R85-DP (CR_o = 0.93). Kenics® static mixer can be used as catalyst support to promote heterogeneous photocatalysis, enhancing mass transfer (even using a laminar regime) and illumination efficiency (the entire catalytic surface area is irradiated with front side illumination mechanism by using sunlight combined with CPCs).

Acknowledgments

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