Catalysis Today 144 (2009) 112–116

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Abatement of ibuprofen by solar photocatalysis process: Enhancement and scale up

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ARTICLE INFO

Article history:
Available online 23 February 2009

Keywords:
Ibuprofen
Solar photocatalysis
NSAID remediation
PPCP emerging contaminants

ABSTRACT

The aim of this work is to evaluate the degradation of the emerging pharmaceutical contaminant ibuprofen (IBP) in water by heterogeneous photocatalysis in three different solar pilot plants. IBP and TOC removal increase directly proportional to concentration of catalyst (TiO_2). The addition of H_2O_2 increases the removal efficiency. The complete IBP removal and decrease of TOC to sufficient extent was stated in optimal experimental conditions and biodegradability and average oxidation state (AOS) results conducted suggest a post-biological treatment of solution. Surface responses obtained from the experimental results, for different initial IBP and TiO_2 concentrations used, can allow to predict time needed for a sufficient TOC removal to reach sufficient biodegradability.

1. Introduction

New emerging contaminants have attracted special attention: the pharmaceutical compounds [1]. Non-Steroidal Anti-Inflammatory Drugs (NSAIDs), as ibuprofen (IBP), are widely used and prescribed as analgesic and antipyretic medicaments. The rank of IBP prescriptions dispensed in USA was placed 17th in 2005 [2]. Unfortunately the extensive use of IBP has enclosed a secondary effect: IBP has been detected in water and the ecotoxicological impact on the microbiological systems can provoke irreversible harmful effects on bioreceptors. For example Richards and Cole [2] report the toxic response from the FETAX test (Frog Embryo Teratogenesis Assay-Xenopus) as effect of several concentrations of IBP after 96 h of exposition: 30 mg/L showed inhibition on the growth of embryos, >70 mg/L no survival embryos were detected. Concentration of IBP has been reported in the range of 0.01–990 μg/L. The wastewater treatment plants are not able to eliminate IBP completely; however, this drug reaches an important removal by biological oxidation, in some cases more than 70% [3]. Even relatively acceptable removal efficiencies can be assumed, the harmful presence of IBP, as consequence of metabolic, photolytic and/or attenuation processes [4], remains along its occurrence in environment also at low concentrations. Several typical strategies for IBP removal from water have been reported, for example ozonation, chlorination, etc. However, the secondary products after such treatments increase the toxic properties of the processed effluent. On the other hand advanced oxidation processes (AOPs) are non-classical water remediation techniques which promote mineralization of the pollutants and/or biodegradable byproducts through radical-species. Some of them are able to take the advantage to employ solar renewable energy, for instance the heterogeneous photocatalysis with semiconductors like titanium dioxide (TiO_2). Solar energy contains energy capable to generate electron/hole pairs (e^-/h^+), especially the UV energy with wavelength below 387 nm. The e^-/h^+ react with adsorbed water or oxygen on the surface of the catalyst producing the powerful oxidative specie $^{\bullet}OH$, which carries out the photocatalytic degradation of organic compounds. Thus, this process improves the cost-effectiveness through photoactivation with solar irradiation.

There are some reports about the degradation of pharmaceutical compounds like antiepileptic, beta blockers, cholesterol, triglyceride reducers, steroid hormones, ionated X-ray contrast media, etc. by heterogeneous photocatalysis [1], most of them at lab-scale and by using electric sources of irradiation. And only few works are available with solar energy at large-scale [5], however their results are promising.

The aim of this work is to study the degradation of the pharmaceutical pollutant ibuprofen using photocatalysis and solar irradiation in three different pilot plants located in Barcelona University and in Solar Platform of Almeria (PSA), Spain. The effect of TiO_2 loading, initial IBP concentration and extra-oxidant agent on the IBP removal and mineralization has been studied in order to obtain the irradiated-time required to reach a biodegradable dissolution able to be coupled to a biological reactor.

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doi:10.1016/j.cattod.2009.01.028

2. Materials and methods

IBP sodium from Sigma (pK_a 4.9 and solubility in water at 25 °C of 21 mg/L) and TiO_2 Degussa P-25 (70% Anatase –30% Rutile) was used without further pre-treatment. H_2O_2 (30% w/v, Panreac) and $Na_2S_2O_8$ (PRS Panreac) were employed as oxidant agents. IBP concentrations were monitored, after sample-filtration (0.22 μm), by HPLC. The parameters employed for HPLC analysis are now detailed - (B) indicates the conditions used in Barcelona and (A) these ones used in Almeria. Mobile phase: (B) acetonitrile–0.25 acetic acid (75–25), (A) methanol–0.1 formic acid (70–30); flow-rate (mL/min): (B) 1.75, (A) 0.50; injection volume (μL): (B) and (A) 20; λ detection (nm): (B) 254, (A) 220, 254, 280; temperature (°C): (B) 25, (A) 30; column characteristics: (B) RP Trace Extrasil OD52-5 Micromet 25 cm × 0.46 cm Teknockroma, (A) C-18 LUNA 5 μm, 150 mm × 3 mm from Phenomenex.

TOC was measured in a Shimadzu TOC-V CNS in order to evaluate the mineralization degree during the experiment. Biodegradability of the treated sample at several times was estimated through the BOD_5 and COD determinations according to Standard Methods [6]. Solar irradiation was measured by a global UV radiometer (KIPP&ZONEN, model CUV3) and/or obtained from Universidad Politécnica de Catalunya [7].

Photocatalytic degradation experiments were carried out in three solar pilot plant reactors: PC-1.5, CPC-6 (both located in Barcelona) and CPC-35 (located in Almeria). Operational and technical parameters are described in Table 1. Summarizing, the three devices are very similar in their elements, changing, of course, their dimensions. Thus, they consist in a feeding tank from which the solution to be treated is pumped to the tubular photoreactor or CPCs and reflowed, from there, to the feeding tank. TiO_2 and/or oxidants reagents were added from concentrated suspension. Suspension was homogenized under dark conditions during 30 min. After that, the photoreactors were uncovered being this the initial time of experiment.

3. Results and discussion

The solar UV energy used in each system depends strongly on each particular geometrical setting and operative conditions. Moreover during 1-day experimental period, also the environmental conditions affect the effective energy applied per volume unit. In order to compare systems with different geometrical configurations, operative conditions and location, the conversion of the compound was described versus the solar UV energy per volume used in each case (Q). The amount of solar energy applied per total volume (Q, kJ/L or J/L) was calculated according to the following equation

$$Q = \sum_{i=0}^{n} Q_{t_i} = \sum_{i=0}^{n} \left(\frac{A\,\Delta t\,\bar{I}}{V_T} \right)_{t_i} \qquad (1)$$

where A (m^2) is the mirroŕs area of caption-reflection of solar irradiation; V_T (L) is the volume of the treated solution. $\bar{I}$ is the average of the incident solar UV energy (J/s m^2) for Δt (s) between two sampling times (i). Q (kJ/L or J/L) is the cumulative solar UV energy per volume applied along the experiment, and it is used instead of experimentation time in order to show the evolution of pollutant degradation.

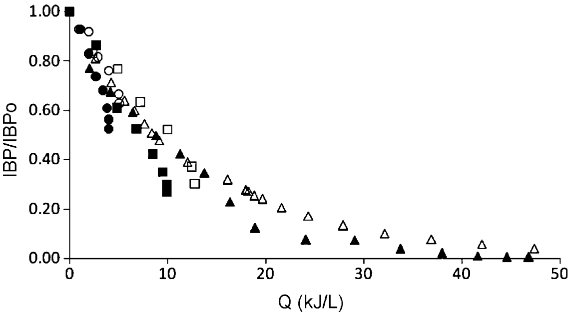

Fig. 1. Influence of catalyst load on IBP conversion. PC-1.5 ((○) 0.1 g/L TiO_2, (●) 1.0 g/L TiO_2), CPC-6 ((□) 0.1 g/L TiO_2, (■) 1.0 g/L TiO_2) and CPC-35 ((△) 0.1 g/L TiO_2, (▲) 1.0 g/L TiO_2). 200 mg/L of initial IBP.

3.1. Catalyst loading influence and initial IBP effect

IBP was successfully degraded by photocatalytic oxidation with TiO_2 and solar irradiation. Fig. 1 depicts the IBP removal using 0.1 and 1 g/L of TiO_2 in PC-1.5, CPC-6 and CPC-35 photoreactors versus Q (calculated according to Eq. (1)). For the case of PC-1.5 reactor, 50 and 25% IBP removal is observed by using 1 and 0.1 g/L of catalyst, respectively, with 4 kJ/L of solar energy applied. However, the difference between IBP conversions is closer especially in CPC-35 reactor. For instance at 5 kJ/L, only 30% and 35% of IBP conversion is observed by using 0.1 and 1 g/L of catalyst in CPC-35 reactor. Analogous effect was observed regarding the TOC degradation, and 10% of TOC removal was obtained in PC-1.5, CPC-6 and CPC-35, for 0.1 and 1 g/L TiO_2, with an energy consumption of 5 kJ/L.

From these data, it seems that titania concentration has less remarkable effect above 0.1 g/L of TiO_2. In this way, the optimum

Table 1
Technical and operational parameters for each photoreactor employed.

	Photoreactor ID		
	PC-1.5	CPC-6	CPC-35
Place localization (Coordinates)	Barcelona (latitude 41°28′, longitude 2°06′) at sea level	Barcelona (latitude 41°28′, longitude 2°06′) at sea level	Almeria (latitude 37°05′, longitude 2°21′) 503 m altitude
Collector geometry	One-axis parabolic collector (PC)	Compound parabolic concentrator (CPC)	Compound parabolic concentrator (CPC)
Inclination	41° guided to south	41° guided to south	37° guided to south
Collector material	Al-reflective mirrors	Al-reflective mirrors	Al-reflective mirrors
Irradiated area (m^2)	0.01	0.1	3.08
Photoreactor number	1	1	8
Length (m)	0.26	1	1.5
Diameter (m)	0.02	0.04	0.03
Glass material	Borosilicate Duran	Quartz	Borosilicate Duran
Total volume of photoreactor (L)	0.075	1.98	22
Total volume of suspension (L)	1.5	6	35
Stirring system	Magnetic	Exterior mechanic	None
Volumetric flow (L/s)	0.003	0.025	0.33
V_{irr}–V_{dark} (%–%)	5–95	20–80	62–37
Date of experiments	August 2006	August 2006	October–November 2007

amount of TiO_2 can be estimated using the optical data reported by Li Puma (2003) [8] and the expressions proposed by Li Puma and Brucato (2007) [9]. In these works, the optical thickness (τ) is proposed as a key parameter to estimate the amount of catalyst for an optimal absorption of irradiation. The τ for the three reactors tested, for 0.1 g/L of TiO_2, was $\tau_{PC\text{-}1.5} = 2.6$, $\tau_{CPC\text{-}6} = 5.1$ and $\tau_{CPC\text{-}35} = 3.9$. The optical thickness, to achieve optimum absorption of radiation, is approximately 6 [8,9]. Thus, for a titania concentration of 0.1 g/L, the optical thickness has a value near to the optimum but slightly lower. On the contrary, in the case of 1 g/L of TiO_2, the τ estimations were $\tau_{PC\text{-}1.5} = 26$, $\tau_{CPC\text{-}6} = 51$ and $\tau_{CPC\text{-}35} = 39$, notably higher than the optimal value. From a theoretical point of view, under these conditions, irradiation cannot reach the middle section of the tubular reactor and a proportion of catalyst remain non-reactive. Thus, above ~0.1 g/L of TiO_2 slight improvement of the photocatalytic degradation is observed. This fact explains also that the necessary Q to degrade the compound is quite similar for the three tested systems PC-1.5, CPC-6 or CPC-35 reactors. However, besides the optimal thickness values, several important parameters as type of pollutant, reactor geometry, the used radiation and concrete experimental conditions can also influence on the reaction rate. Among other reasons particles (agglomerates) diameter can change during experimental and these changes can influence also on reaction rate and can mask the role of catalyst concentration. In this way, Abellán and cols (2007) [10], in the photocatalytic treatment of sulfamethoxazole, observed that TOC removal and sulfamethoxazole degradation increase when titania concentration does it in the range of catalyst concentrations between 0.1 and 1–2 g/L. For all these reasons, titania concentrations between 0.1 and 1 g/L have been tested in this work.

On the other hand several photocatalytic experiments varying the initial concentration of IBP and using 0.1 g/L of TiO_2 were undertaken in the CPC-35 reactor. Fig. 2 shows the IBP degradation and initial degradation rate of IBP (in caste) versus Q. As expected, as lower initial concentration of IBP, lower energy supplied is necessary to remove it. Thus to achieve complete degradation of IBP, 66, 30, 10 and 4 kJ/L for 200, 100, 50 and 20 mg/L IBP_o, respectively are necessary. Initial degradation rates increase reaching a maximum for 100 mg/L of initial IBP concentration. From this point, when IBP initial concentration increases, the initial reaction rates decrease (see Fig. 2). The TOC removal showed an almost lineal decay.

3.2. Additional oxidant as promoter of IBP degradation

Additional oxidant effect was tested, in CPC-35 device, by addition of concentrated solutions of hydrogen peroxide and sodium persulfate in a solution of 200 mg/L of IBP with 0.1 g/L TiO_2 and without catalyst. In the first case, 1028 mg/L of H_2O_2 were added distributed in periodical 30 min proportional volumes (120 mL, 30% w/v), and in the second case 7150 mg/L of persulfate were also added proportionally and hourly distributed three times. Fig. 3 depicts the conversion of IBP and TOC for experiments with H_2O_2, with TiO_2 and with addition of both reagents. When TiO_2 is present, the addition of H_2O_2 accelerates the degradation of IBP likewise TOC removal. In presence of 0.1 g/L of TiO_2, when 1028 mg/L of H_2O_2 were added, 50% of IBP elimination was reached in 30 min of irradiation, corresponding to 4.75 kJ/L. When only TiO_2 was used, without hydrogen peroxide, 120 min of irradiation were necessary to achieve the 50% of IBP removal, corresponding to 9.2 kJ/L of solar energy arriving to the system. In this way, the addition of oxidizing species increases the efficiency of the photocatalytic process due to H_2O_2 is an electron acceptor and reacts with the electrons of the photo-activated surface of the catalyst

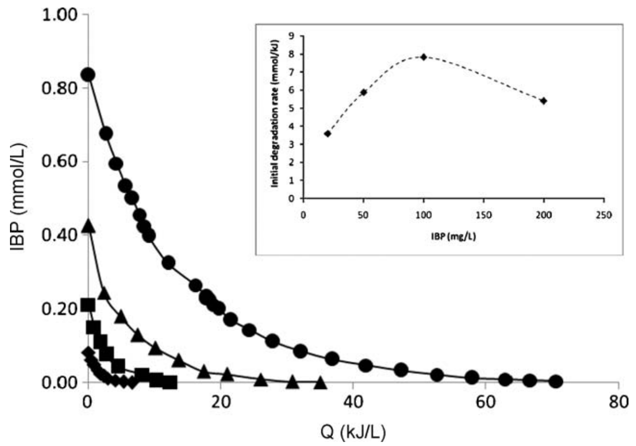

Fig. 2. Effect of initial IBP concentration on IBP degradation and initial degradation rate. Experiments carried out in CPC-35 reactor using 0.1 g TiO_2 and IBP_o (●) 200 mg/L, (▲) 100 mg/L, (■) 50 mg/L and (◆) 20 mg/L.

$$H_2O_2 + e^- \rightarrow {}^\bullet OH + OH^- \quad (2)$$

Thus, the addition of peroxide constitutes an extra source of hydroxyl radicals and increases the photoreactivity of TiO_2 during the photocatalytic degradation. On the other hand, the degradation of IBP only with H_2O_2 under solar irradiated condition was not expected. It is normally accepted that the most common irradiation source for H_2O_2 photolysis applications is reached with 254 nm irradiation-sources (germicides lamps). However, sources of light like UV_A, high-intensity, medium-pressure Hg, broadband or Xe flash-lamps, etc. have also been tested in environmental and industrial application in the photolysis of H_2O_2, for instance for degradation of dyes [11,12]. Under our experimental technical conditions (solar energy and Pyrex glass photoreactor) there is an overlap between the emitted light and the irradiation yet available to be absorbed for H_2O_2 approximately from 290 up to 350 nm. Thus also the degradation of IBP can be attributed to the photochemical cleavage of hydrogen peroxide to yield hydroxyl radicals and/or other radical species by solar light absorption

$$H_2O_2 \xrightarrow{\text{solar } h\nu} 2{}^\bullet OH \quad (3)$$

$$H_2O_2 \xrightarrow{\text{solar } h\nu} HOO^\bullet + {}^\bullet H \quad (4)$$

In addition, the evolution of H_2O_2 during experiments was followed. The amount of the peroxide consumed is higher in the presence of TiO_2. The difference between the amount of H_2O_2 consumed in experiments with and without catalyst is 207.4 mg/L. If catalyst is not present, the main probable pathway of degradation is the hydroxylation of IBP. The last is in correspondence with the TOC behaviour, which decreases slightly when only

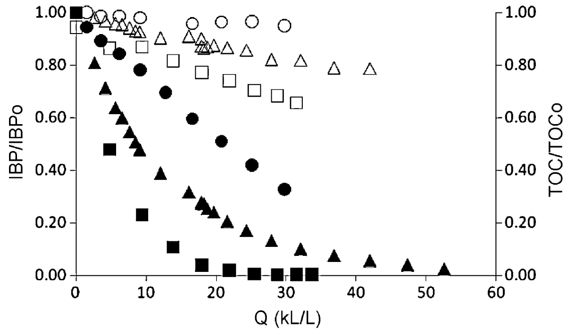

Fig. 3. Influence of H_2O_2 on IBP degradation. Initial 200 mg/L IBP with (●) 900 mg/L of H_2O_2, (▲) 0.1 g/L TiO_2 and (■)TiO_2 + H_2O_2 (0.1 g/L and 900 mg/L, respectively) and their concomitant TOC removal in empty points.

H_2O_2 is present (see Fig. 3). In the case of photocatalytic enhanced process (titania plus hydrogen peroxide in the medium), two times higher TOC removals can be reached with 32 kJ/L due to higher $^{\bullet}OH$ attack. In regard to the pH evolution it is possible to observe the evident decrease of pH in the system TiO_2–H_2O_2. Faster degradation promotes early formation of byproducts possibly addressed to aliphatic acid compounds. In the case of photocatalysis without peroxide, pH evolution does not suffer any change whereas in the case of solar-peroxide degradation the decrease of pH is only after 120 min. The last is well corresponded to the improvement of the photocatalytic activity with the presence of peroxide.

On the other hand in the case of $Na_2S_2O_8$ an enhancement of the degradation did not happen. The pK_a value of IBP is 4.9. Above this value ionic IBP is the predominant specie – the carboxylic group of IBP reaches the ionized state and its hydrophilicity and solubility increase. On the other hand, at a pH value lower than its pK_a, IBP is principally found in its molecular form and has a superior hydrophobic character. An abrupt pH decrease in the solution (7 to 4.5 in the first 15 min) is induced by presence of $Na_2S_2O_8$. Below the pK_a value of IBP and over its solubility limit (21 mg/L), the IBP-molecular form present precipitates by addition of $Na_2S_2O_8$ and a post-redissolution after 30 min was also observed. The TOC evolution increases due to continuous and simultaneous effect of degradation–saturation of IBP in solution. Physical change of phase is the most attributable decrease in the concentration of IBP but neither by direct oxidation nor mineralization.

3.3. *AOS enhancement biodegradable time irradiation*

From a practical point of view, the use of solar photocatalytic device, as unique step of treatment, has shown to be a high operative-cost system, due to the long solar exposition time necessary to reach complete mineralization of recalcitrant pollutants. However, the use of solar photocatalysis as decontamination technique can be made more attractive by coupling it with different oxidative steps, for instance biological processes [13]. The AOPs-biological combination has shown to be a good strategy against recalcitrant contaminants. Thus, high final mineralization is not necessary, in the solar photocatalytic treatment, if products and subproducts coming from are enough biodegradable in a post-biological reactor. Thus the minimum necessary time to pre-treat the contaminated water can be optimized in order to stop the photochemical oxidation and to combine it with a biological operation.

In order to evaluate the biodegradability of the solution during the solar photocatalytic degradation, 200 mg/L of IBP and 0.1 g/L of catalyst were solar exposed and the AOS (average oxidation state) parameter and BOD_5/COD ratio were periodically measured. The AOS is a practical factor which indicates the oxidation degree of complex solutions and gives indirect information on their probability of biodegradation [14]. AOS is expressed as follows:

$$\mathrm{AOS} = \frac{4(\mathrm{TOC} - \mathrm{COD})}{\mathrm{TOC}} \tag{5}$$

TOC and COD are expressed in moles of carbon and oxygen per litre of solution, respectively. AOS takes values between −4, for CH_4, and +4, for CO_2, and BOD_5/COD between 0 and 1, being 1 the ideal condition where total oxygen present is biologically up taken.

Fig. 4 shows the IBP conversion, BOD_5/COD and the AOS parameter versus TOC conversion, *Q* and experimental time. 200 mg/L IBP solution is toxic, non-biodegradable and with an AOS value of −2.33. However, byproducts from photocatalysis have shown to increase the biodegradability of the final effluent between 15% and 25%. As possible to observe in Fig. 4, total elimination of IBP is reached when approximately 80% of TOC still remain in solution. At this moment (60 kJ/L and approximately 1.5 day of experiment) the AOS has increased almost 2 units and the BOD_5/COD of the solution has increased 20%. The last analysis drives to suggest that IBP disappearance is a key-point for biodegradability improvement. After this moment and following with the photocatalytic mineralization, it is possible to observe a continuous AOS and BOD_5/COD enhance, for instance when the solution contains 50% of TOC the AOS is approximately +0.5 and BOD_5/COD 40%. As possible to observe, it can be assumed that a solution is biodegradable when IBP was fully removed and when at least 50% BOD_5/COD has increased, *i.e.* approximately in our case after 50% of TOC. Thus an initial solution of IBP containing 200 mg/L and treated by means of photocatalysis could be pre-treated during 2 days or approximately 75 kJ/L of accumulated solar UV energy (considering 6 h/day of experiment, from 9:00 to 15:00, in PSA installations). After this moment the solution presents biodegradable conditions to be coupled to a biological oxidation step.

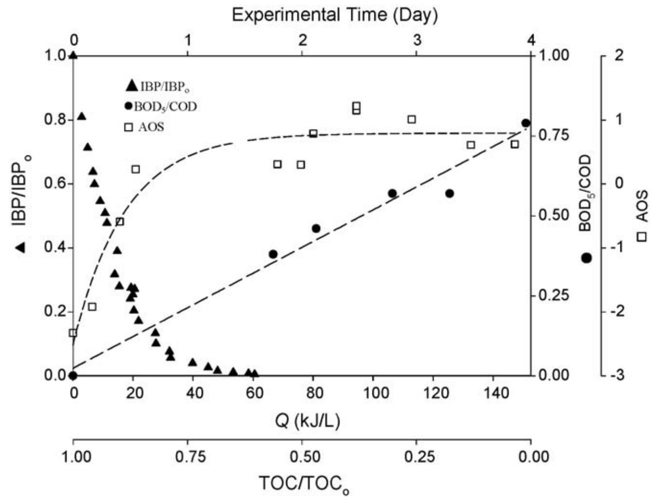

Fig. 4. Evolution of IBP/IBP_o, BOD_5/COD and AOS vs. experimental time (day) and *Q* (kJ/L) and TOC/TOC_o.

In order to predict the necessary time for biological reactor coupling, for different IBP and TiO_2 concentrations, a first condition is the complete degradation of IBP. Thus, the TOC removal at this moment (IBP just exhausted) can be considered as a key parameter by taking into account its relationship with BOD_5/COD, as shown in Fig. 4. In this way, Figs. 5 and 6 show the response surface for TOC and necessary time of irradiation respectively in the range of $20\ \mathrm{mg/L} < IBP_o < 200\ \mathrm{mg/L}$ and $0.1 < TiO_2 < 1.0\ \mathrm{g/L}$. The TOC removal was for all cases above 40%, meaning that treated solution has enough increased its biodegradability, and its treatment can be completed in a biological reactor. As an example (see Figs. 5 and 6), for a solution with an IBP initial concentration of 20–50 mg/L,

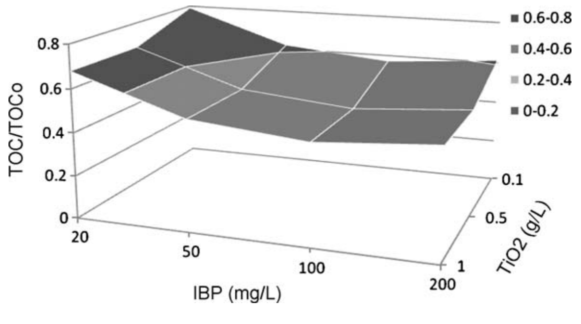

Fig. 5. Response surface for TOC/TOC_o of interpolated results in the range of $20\ \mathrm{mg/L} < IBP_o < 200\ \mathrm{mg/L}$ and $0.1\ \mathrm{g/L} < TiO_2 < 1.0\ \mathrm{g/L}$.

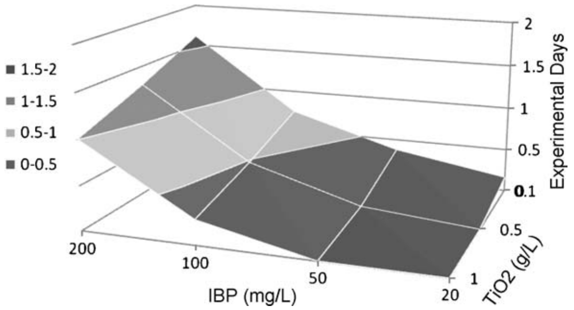

Fig. 6. Response surface for necessary time of irradiation of interpolated results in the range of 20 mg/L < IBP_o < 200 mg/L and 0.1 g/L < TiO_2 < 1.0 g/L.

using from 0.1 to 1.0 g/L of TiO_2, less than 1 day would be necessary to obtain a solution with enough biodegradability to be disposed in a biological reactor. This simple analysis for post-biological coupling fills as tool for the prediction of IBP degradation by photocatalysis in CPC-35 reactor, in other experimental conditions.

3.4. Degradation rates and efficiencies in all devices

The design of solar detoxification reactors is a multi-step task which involves several technical, chemical, local, etc. considerations. An exhaustive list and well-systematized description of design of an engineering scale project is well boarded by Blanco Gálvez and Malato Rodriguez [15]. Sometimes previous lab-scale experiments can be helpfulness to evaluate geometrical parameters and/or operative conditions for large-scale purpose. In our case, in order to evaluate the correspondence between the three experimental solar reactors, the initial degradation rate was calculated for experiments carried out at initial 200 mg/L of IBP and varying TiO_2 concentration from 0.1 to 1 g/L. Fig. 7 depicts the initial degradation rate for the experiments above described. The energy needed has been calculated according to Eq. (1) for the time period considered for the evaluation of the initial degradation rate. As it can be seen, the ratio between degradation rate and energy needed is slightly different in the three tested devices. Considering that the experimental errors involved in the operation of pilot plant reactors are in an approximately 15%, the results in Fig. 7 show that there is no remarkable difference between the initial rate with catalyst concentration. For CPC-35, it seems that the catalyst concentration (between 0.1 and 0.5) does not practically affect the efficiency of the process and the ratio degradation rate-energy used remains practically constant around 0.65 mmol/kJ. Similar behaviour is shown for the case of PC-1.5 and CPC-6. The efficiency does not increase when the TiO_2 concentration increases (from 0.1 to 0.5 g/L) due to the non-illuminated amount of TiO_2 as explained in Section 3.1. However, at higher catalyst load (1 g/L) important differences for PC-1.5 and CPC-6 are observed. The devices depending on the solar energy are complicated system with several besides operational and geometry considerations: illuminated surface and volume, total volume of the system and recirculation rate, catalyst amount, etc. Optimization of these conditions with well-approximated a priori estimations can change drastically the photocatalytic treatment performance.

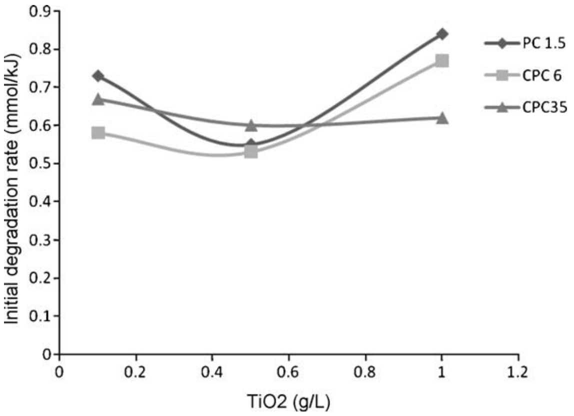

Fig. 7. Initial degradation rates of IBP in each solar reactor. 200 mg/L initial IBP and 0.1–1 g/L of TiO_2 in PC-1.5 (◆), CPC-6 (■), and CPC-35 (▲).

4. Conclusions

The photocatalysis with solar light and TiO_2 can be useful in the removal of IBP in water. The degradation of IBP and TOC removal increase when TiO_2 loading does it independently on the solar device employed. TOC decay is almost linear in regard to the solar energy applied. The photocatalytic treatment increases the biodegradability of IBP solutions. Similar initial degradation rates were observed in all solar devices.

The IBP and TOC removal show an important improvement when hydrogen peroxide, as extra oxidative agent, is present but the last did not happen with persulphate ion.

Total IBP removal and enough TOC removal can enhance the biodegradability and AOS enough to suggest a post-biological treatment of solution. Thus, from the experimental results obtained, by considering the initial IBP and TiO_2 concentrations used, the time needed for a sufficient TOC removal can be predicted. For usual concentrations (IBP from 50 to 100 mg/L, TiO_2 from 0.1 to 1.0 g/L), between 0.5 and 1.5 day is necessary to reach biodegradable properties of the treated solution.

The solar photocatalytic degradation enhances the cost-efficiency of the treatment of micropollutants at large-scale and looking on a possible coupling with biological treatment.

Acknowledgements

The authors appreciate Barcelona University, Spanish Ministry of Education and Science (CICYT Projects CTQ2004-02311/PPQ, CTQ2005-00446), Consolider-Ingenio 2010 program (project NOVEDAR, ref. CE-CSD2007-00055), the “Programa de Acceso y Mejora de Grandes Instalaciones Científicas Españolas” (Plataforma Solar de Almería, GIC-05-17) for the financial support and facilities granted to develop this research and Agustin Carrion, Holger Weisshaupt and Carsten Riemeier for assistance during experiments execution.

References

[1] M. Klavarioti, D. Mantzavinos, D. Kassinos, Environment International (2008), doi:10.1016/j.envint.2008.07.009.
[2] S.M. Richards, S.E. Cole, Ecotoxicology 15 (2006) 647.
[3] M. Gómez, M. Martinez, S. Lacorte, A. Fernandez-Alba, A. Aguera, Chemosphere 66 (2007) 993.
[4] M.J. Focazio, D.W. Kolpin, K.K. Barnes, E.T. Furlong, M.T. Meyer, S.D. Zaugg, L.B. Barber, M.E. Thurman, Science of the Total Environment 402 (2008) 201.
[5] L.A. Perez-Estrada, M.I. Maldonado, W. Gernjak, A. Aguera, A.R. Fernandez-Alba, M.M. Ballesteros, S. Malato, Catalysis Today 101 (2005) 219.
[6] Standard Methods for the Examination of Water and Wastewater, APHA, Washington, 1998, ISSN: 8755-1979.
[7] Universidad Politécnica de Catalunya, Atlas de radiació solar a Cataluña 1971-2005, Document tècnic: versió preliminar, UPC, Barcelona, 2006.
[8] G. Li Puma, Environmental Science and Technology 37 (2003) 5783–5791.
[9] G. Li Puma, A. Brucato, Catalysis Today 122 (2007) 78–90.
[10] M.N. Abellán, B. Bayarri, J. Giménez, J. Costa, Applied Catalysis B: Environmental 74 (2007) 233–241.
[11] D.E. Kritikos, N.P. Xekoukoulotakis, E. Psillakis, D. Mantzavinos, Water Research 41 (2007) 2236.
[12] T. Tuhkanen, in: S. Parsons (Ed.), Advanced Oxidation Processes for Water and Wastewater Treatment, IWA, London, UK, 2004, p. 86.
[13] M. Carballa, F. Omil, A.C. Alder, J.M. Lema, Water Science and Technology 53 (2006) 109.
[14] R. Torres, V. Sarria, W. Torres, P. Peringer, C. Pulgarin, Water Research 37 (2003) 7.
[15] J. Blanco Gálvez, S. Malato Rodriguez, Solar Detoxification, UNESCO, France, 2003.