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Optimization of mild solar TiO₂ photocatalysis as a tertiary treatment for municipal wastewater treatment plant effluents

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Abstract

The appropriate catalyst concentration for industrial wastewater treatment is several hundred milligrams per liter in solar photoreactors. Nonetheless, when the purpose of eliminating emerging contaminants in municipal wastewater treatment plant effluents is for reuse of the water, and they are present at extremely low concentrations, a tertiary treatment with a much lower photocatalyst concentration might be possible. TiO₂ concentrations of only tens of mg L⁻¹ were selected to evaluate the influence of catalyst load, initial hydrogen peroxide dose and radiation intensity on the degradation rate of five emerging contaminants (100 µg L⁻¹ of ofloxacin, sulfamethoxazole, flumequine, carbamazepine, and 2-Hydroxy-biphenyl) spiked in a real municipal wastewater treatment plant effluent. Response surface methodology based on a spherical central composite design was used to optimize the parameters to find the maximal degradation rate. The experiments were carried out using an Evonik P-25 titanium dioxide suspension in a Suntest solar simulator. It has been demonstrated that the use of hydrogen peroxide is highly recommendable for working with TiO₂ at low concentrations and high photon flux must be avoided. It has also been demonstrated that too low (less than 40 mg L⁻¹) TiO₂ concentration is not recommendable.

Keywords: emerging contaminants, photocatalysis, solar photoreactors

Introduction

Compounds such as substituted phenols, non-biodegradable chlorinated solvents, pesticides and surfactants have long been recognized as typical relevant substances difficult to remove from water. In this context, pharmaceuticals and personal care products, and especially endocrine-disrupting chemicals have recently been labeled emerging contaminants (ECs), which means they are still unregulated or regulation is in process [1-6]. A multitude of risks, such as bacterial resistance, sterility, and feminization of aquatic organisms derive from the presence of these substances in water. In recent years, ECs have been found in treated wastewater, surface and groundwater, and even drinking water in tens of $\mu\text{g L}^{-1}$ [5, 7-9]. Furthermore, their growing use is directly increasing their concentration in natural and treated water [10-12], as conventional wastewater treatment plants are unable to completely remove them. The continuously rising concentrations of these compounds show that conventional wastewater treatments are not efficient enough and consequently, available, simple advanced technologies are necessary to remove these contaminants from water.

Advanced oxidation processes (AOPs), which drive organic matter oxidation by means of the hydroxyl radicals they generate, have been proposed as a valuable method for degrading persistent organic compounds with high reaction rates and low selectivity. TiO_2 is the most widely used catalyst in heterogeneous photocatalysis, although several other semiconductors exist, because of its photostability, non-toxicity, low cost and stability in water under most environmental conditions [13, 14]. One of the main drawbacks of heterogeneous photocatalysis, however, is its relatively high operating cost due to the use of UV lamps. Nevertheless, the UV lamps in such systems could be replaced by natural solar radiation, which is free and feasible for large-scale aqueous-phase applications [14, 15].

The appropriate catalyst concentration for industrial wastewater treatment is several hundred milligrams per liter in solar photoreactors [16]. Nonetheless, when the purpose of eliminating ECs in municipal wastewater treatment plant (MWTP) effluents is for reuse of the water, and they are present at extremely low concentrations, a tertiary treatment with a much lower catalyst (TiO_2) concentration might be possible. This way, the catalyst would be more easily recovered and reused, and the addition of large

amounts of TiO₂ to water treated in the MWTP and already relatively clean would also be avoided. It is also important to consider that one of the main problems of working with concentrated TiO₂ slurries is membrane separation of the particles from water [17-20], which becomes more expensive the more concentrated the slurry is.

On the other hand, reducing the catalyst load has the drawback of wasting useful photons passing through the reactor without reacting with TiO₂ with its consequences for the EC degradation rate [21, 22]. However, the TiO₂ solar photocatalysis reaction rate can be enhanced by using chemical oxidants, doped or modified TiO₂, or combination with other AOPs for more efficient contaminant removal [23]. Hydrogen peroxide, which was one of the first oxidants tested in this type of application [24], was chosen in this study as the chemical oxidant. It is very commonly used, environmentally friendly and cheap. Moreover, it fulfills the criteria of forming hydroxyl radicals and dissociating into harmless by-products [25, 26].

The positive effect of H₂O₂ dosing is prevention of e⁻/h⁺ pair recombination and production of additional hydroxyl radicals by Reactions 1 and 2 (below). Photolysis of H₂O₂ (Eq. 3) yields hydroxyl radicals when irradiated by photons with wavelengths below 300 nm [27, 28], and therefore, it is not expected to enhance the reaction rate when illuminated by solar irradiation. However, there could be inhibition due to TiO₂ surface modification by peroxide adsorption, scavenging of photo-produced holes (Reaction 4) and reacting with hydroxyl radicals (Reaction 5).



Inhibition of adsorption not only depends on the characteristics of the contaminant, but also on the H₂O₂/contaminant ratio. If contaminant concentration is too low, as it is in this study with effluents from an MWTP, and the H₂O₂ concentration is too high,

contaminant adsorption decreases because of adsorption of H_2O_2 , and therefore, the reaction rate decreases. Consequently, and although the effect of adding H_2O_2 to the photocatalytic reaction has already been studied, it must be optimized to the specific conditions of very low pollutant concentrations ($\mu\text{g L}^{-1}$ range) and low catalyst load.

TiO_2 concentrations of only tens of mg L^{-1} were therefore selected for this study, which evaluated the influence of catalyst load, initial hydrogen peroxide dose and radiation intensity on the initial degradation rate of five ECs (100 $\mu\text{g L}^{-1}$ of ofloxacin, sulfamethoxazole, flumequine, carbamazepine, and 2-Hydroxy-biphenyl, all commonly found in MWTP effluents) spiked in a real MWTP effluent. Furthermore, response surface methodology based on a spherical central composite design (CCD) was used to optimize the catalyst concentration, initial hydrogen peroxide dose and radiation intensity to find the maximal initial EC degradation rate.

Materials and methods

Reagents and Real wastewater

The experiments were carried out using an Evonik P-25 titanium dioxide (surface area 51-55 $\text{m}^2 \text{g}^{-1}$) suspension. Sulfuric acid used to strip $\text{HCO}_3^-/\text{CO}_3^{2-}$ and hydrogen peroxide (30% w/v) were purchased from Panreac. All reagents used for chromatographic analyses, and ultrapure (Milli-Q) water, were HPLC grade. Analytical standards of ofloxacin, sulfamethoxazole, flumequine, carbamazepine, and 2-Hydroxy-biphenyl for chromatography analyses and for experiments were purchased from Sigma-Aldrich. The same real MWTP effluent taken downstream from the secondary biological treatment of the El Ejido MWTP (in the Province of Almería, Spain) was used in all the experiments. Dissolved organic carbon (DOC), total inorganic carbon (TIC) and chemical oxygen demand (COD) were in the 21, 114 and 57 mg L^{-1} ranges, respectively. Other characteristics of the effluent were, in mg L^{-1} : Cl^- 41, SO_4^{2-} 17, NO_3^- 2.6, Na^+ 31, K^+ 3.2, Ca^{+2} 13, Mg^{+2} 9.5, NH_4^+ 2.6.

Analytical Procedures

Dissolved organic carbon and total inorganic carbon were measured immediately by a Shimadzu TOC-VCSN analyzer. The concentration of the five emerging contaminants was monitored by ultra-performance liquid chromatography (flow rate: 1 mL min^{-1})

(Agilent Technologies, series 1200) with a UV-DAD detector and a C-18 analytical column (Agilent XDB-C18, 1.8 μm , 4.6 mm x 50 mm, 600 bar). The mobile phase was 10% UPLC-grade acetonitrile and 90% water with formic acid 25 mM. Detection was done at four different wavelengths depending on the compound: 267 nm (Sulfamethoxazole and Carbamazepine), 248 nm (Flumequine), 243 nm (2-Hydroxybiphenyl) and 295 nm (Ofloxacin). For UPLC analyses 10 mL of sample were passed through a 0.22- μm syringe filter, then 3 mL of UPLC-grade acetonitrile were also passed through the filter to extract any compound adsorbed on the TiO_2 retained in the filter or on the filter itself.

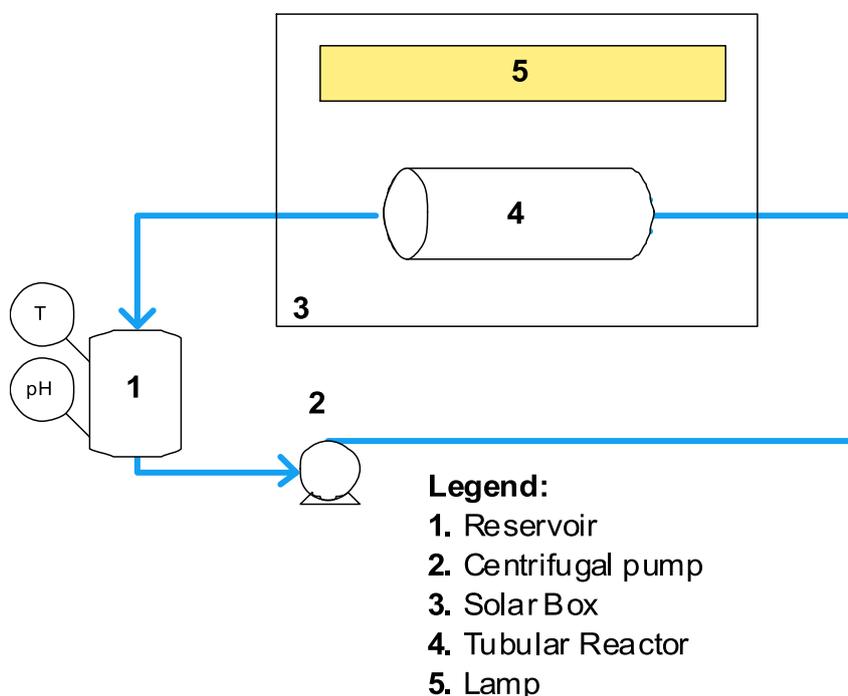


Figure 1. Lab-scale photoreactor

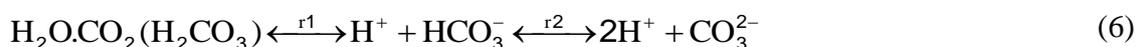
Experimental setup

A battery of experiments was carried out in a Suntest solar simulator (Suntest XLS+ photoreactor from Atlas, <http://atlas-mts.com/>) equipped with a 765-250 W m^{-2} Xe lamp (61-24 W m^{-2} from 300 to 400 nm, electronically controlled) and a cooling system to keep the temperature at 35°C. The lab-scale reactor was made up of a 170-mm-long Pyrex glass tube with a 32 mm O.D. (29.2 mm inner diameter, 1.4-mm-thick glass wall, light transmission $\lambda < 400 \text{ nm}$ 91% and 120 mL illuminated volume, V_i), and a glass container and connecting tubing to complete a total volume V_T of 1.5 L (see Figure 1).

The distance of the lamp axis to the photoreactor longitudinal axis was 250 mm, being illuminated only from one side, very similar to outdoors solar photoreactors. This feature is important to better simulate the effect of different catalyst loads on outdoor solar photoreactors from experiments performed in the solar simulator. A centrifugal pump (Pan World Co, LTD, model NH-30PX) was used to create a turbulent flow (STD point: 11 L min⁻¹, speed 3100 rpm, power consumption 30W) and ensured complete homogenization. Temperature and pH were monitored during the experiments by a Hanna check-temp 1 and a CRISON pH-meter, respectively.

Experimental procedure

When received, the MWTP secondary biological treatment effluent was pretreated with H₂SO₄ under agitation to remove HCO₃⁻/CO₃²⁻, which are known to be hydroxyl radical scavengers [29]. The acid was added until elimination of HCO₃⁻/CO₃²⁻ without attaining any decrease of pH. From pH 6.5 to 8.0 (experimental conditions), the main inorganic carbon species present in solution was bicarbonate HCO₃⁻ (around 95% at pH 7.8) as pK_{r1} = 6.37 and pK_{r2} = 10.25 in Reaction 6. The reactivity of HO with bicarbonate was evaluated at a rate constant equal to 8.5 x 10⁶ M⁻¹ s⁻¹ ~~The reactivity of HO with bicarbonate was evaluated at a constant rate equal to 8.5 x 10⁶ M⁻¹ s⁻¹~~ [30]. This is the main reason for the very negative effect of the presence of bicarbonate ions in aqueous solution on the degradation of organic compounds by any advanced oxidation process. 1.5 L of real MWTP effluent were spiked with 100 µgL⁻¹ of ECs (ofloxacin, sulfamethoxazole, flumequine, carbamazepine, and 2-Hydroxy-biphenyl) for each experiment. After 10 minutes of homogenization, a sample was taken to assure the initial contaminant concentration. Then the catalyst was added and 45 minutes more in the dark were needed to ensure homogenization and permit steady state of adsorption of ECs on TiO₂. After that, the lamp was turned on, the first hydrogen peroxide dose was added, and the experiment began. Samples were taken every 5 minutes for the first hour, and from then on, every 15 minutes until H₂O₂ was totally consumed, at which time the experiment ended. All kinetics calculations considered illumination time, i.e., experimental time x (V_i/V_T). ~~All kinetics calculations considered illumination time, i.e., the V_i to V_T ratio.~~



Experimental Design

This study evaluated the influence of the initial hydrogen peroxide dose, TiO₂ concentration and radiation intensity on the initial rate of EC degradation by heterogeneous photocatalysis. Firstly, the range of UV irradiation (300-400 nm) was within the range of natural solar radiation during the year in a sunny location, 27-55 W m⁻². The initial range of H₂O₂ doses depended on the pollutant and photocatalyst concentration, and finally, a low TiO₂ concentration range of 15 to 50 mg L⁻¹ was selected. The purpose was to find out whether the interaction of different factors allows the EC degradation rate to continuously increase or, on the contrary, whether there is an optimum within the range.

Response surface methodology based on a spherical central composite design (CCD) was employed to evaluate the influence of the three operating parameters, H₂O₂, TiO₂ and radiation intensity, on the response factor. This experimental design puts all the factorial and axial design points on the surface of a sphere with a radius \sqrt{k} , where $k=3$ (number of factors). Seventeen runs were performed following this experimental design, 2^k factorial runs that correspond to the limits of the selected ranges, $2k$ axial, which go outside the selected ranges and 3 center runs to check the variance of the design (see Table 1). Statgraphics statistical software was employed to analyze the CCD and to plot the response surfaces. The response factor is the initial EC degradation rate (r_0) of the four contaminants as a whole (sum of concentration of all of them in each sample) in $\mu\text{g L}^{-1} \text{min}^{-1}$, and the parameters are optimized to obtain the maximum r_0 .

Table 1. CCD experimental matrix: 8 factorial (1-8), 6 axial (12-17) and 3 center (9-11) runs.

Runs	Intensity, W m ⁻²	TiO ₂ , mg L ⁻¹	H ₂ O ₂ , mg L ⁻¹
1	27	15	32
2	55	15	100
3	55	50	100
4	55	50	32
5	55	15	32

6	27	50	100
7	27	15	100
8	27	50	32
9	41	32.5	66
10	41	32.5	66
11	41	32.5	66
12	17.4	32.5	66
13	41	32.5	8.8
14	41	3.1	66
15	64.5	32.5	66
16	41	61.9	66
17	41	32.5	123.2

Results and discussion

The initial heterogeneous photocatalytic reaction rate increases with catalyst load up to a point above which the reaction rate usually remains constant or decreases. This limit depends on irradiation power, reactor design and geometry, i.e., reactor light path length, and on some catalyst characteristics, mainly its point of zero charge, aggregation state, and optical properties. The reaction rate also depends on the initial contaminant concentration. At a certain catalyst mass and radiant flux, lower initial concentrations lead to lower reaction rates [31]. There is a correlation between the optimal catalyst mass and initial contaminant concentration, since the main heterogeneous photocatalysis mechanisms include several steps, like contaminant adsorption on catalyst surface, photogeneration of hydroxyl radicals, oxidative reaction, and desorption of reaction products. Therefore, when contaminant concentrations increase, reaction rate increases. However, due to saturation on the semiconductor surface, the reaction rate becomes constant when the initial concentration is too high [32].

This study aimed to optimize the degradation of emerging contaminants present in MWTP effluents in the micrograms-per-liter range by heterogeneous photocatalysis with TiO₂. A much lower amount of catalyst is required for that than for elimination of higher contaminant concentrations. Figure 2 shows the early stages of degradation of four of these contaminants over normalized time in two experiments performed with 50 mg L⁻¹ of TiO₂, with and without an initial dosage of 100 mg L⁻¹ of H₂O₂. It is quite clear that the experiment with H₂O₂ leads to a higher reaction rate. This is true of all four contaminants, which are quickly degraded during the experiment with H₂O₂. Reaction rates are from 5.6 μg L⁻¹min⁻¹ for sulfamethoxazole to 24.5 μg L⁻¹min⁻¹ for 2-Hydroxy-biphenyl, while they remain almost constant after the same reaction time without peroxide, and r_0 goes from 0.26 μg L⁻¹ min⁻¹ for sulfamethoxazole to 0.9 μg L⁻¹ min⁻¹ for 2-Hydroxy-biphenyl degradation.

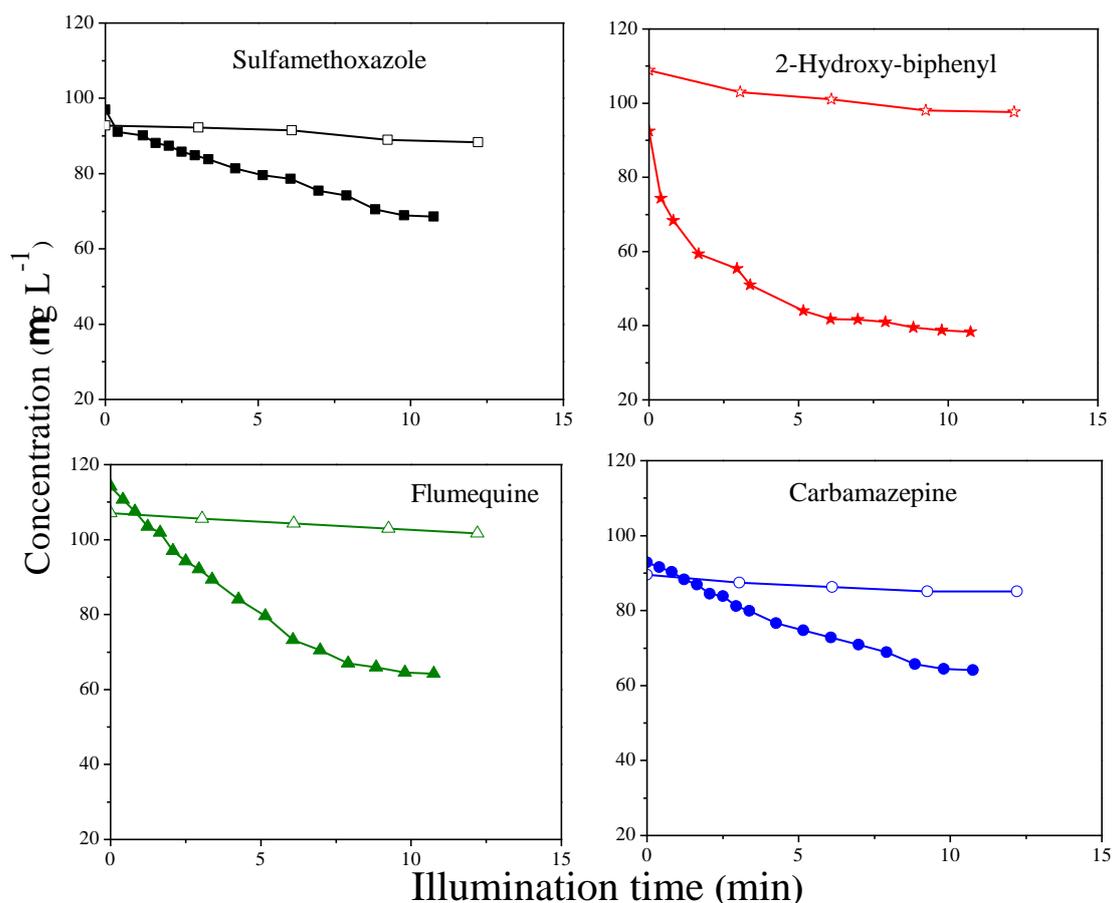


Figure 2. Heterogeneous photocatalytic treatment of sulfamethoxazole, 2-Hydroxy-biphenyl, Carbamazepine and Flumequine using 50 mg L⁻¹ of TiO₂ with (solid dots) and without (open dots) 100 mg L⁻¹ of H₂O₂ as initial dosage.

As demonstrated, at low TiO₂ loads, the addition of another oxidizing reagent may be justified to enhance the organic degradation rate. In order to explore this technique (TiO₂/H₂O₂/solar-UV) as an alternative tertiary water treatment, the optimal concentration of H₂O₂ for different low TiO₂ loads and the particular characteristics of the MWTP effluent containing low contaminant concentrations had to be found.

Figure 3 was calculated by the experimental statistical tool. It shows the effect of each parameter (irradiance, catalyst load and hydrogen peroxide concentration) separately and combined over r_0 . Figure 3a was plotted taking two of the three parameters as constant at their center value and following the third parameter separately. Figure 3b shows r_0 as a function of paired factors. In each figure, one factor varies from lowest to highest, behavior of the second factor is shown by a line,

and the third factor involved in the interaction remains constant at its center value. When these lines (Figure 3b) cross or tend to cross, interaction between the corresponding pair of factors must be considered, as for intensity/TiO₂ and TiO₂/H₂O₂. However, when lines are parallel, as for intensity/H₂O₂, interaction between these factors is insignificant or there is none at all.

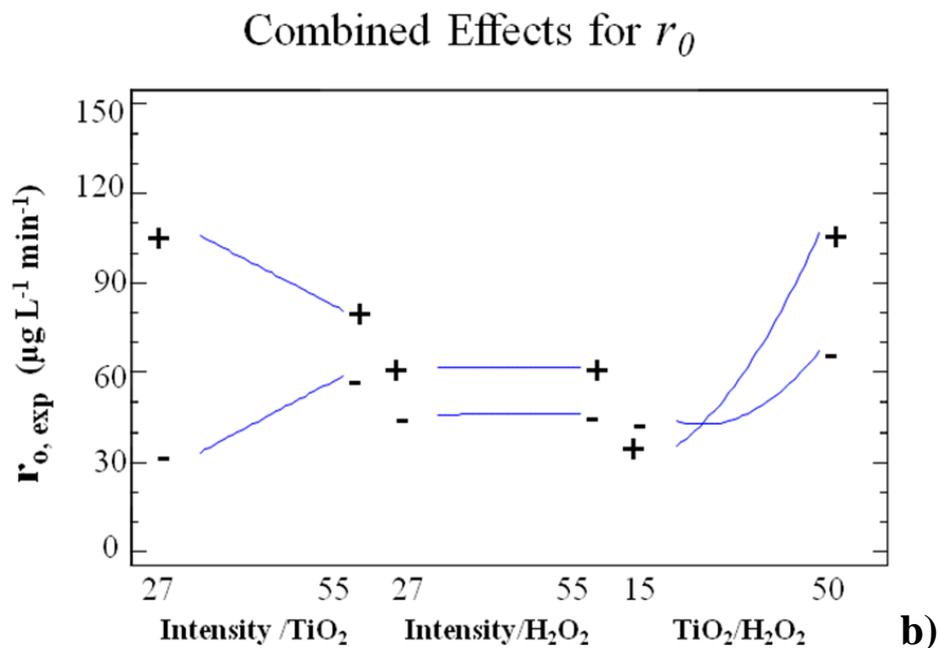
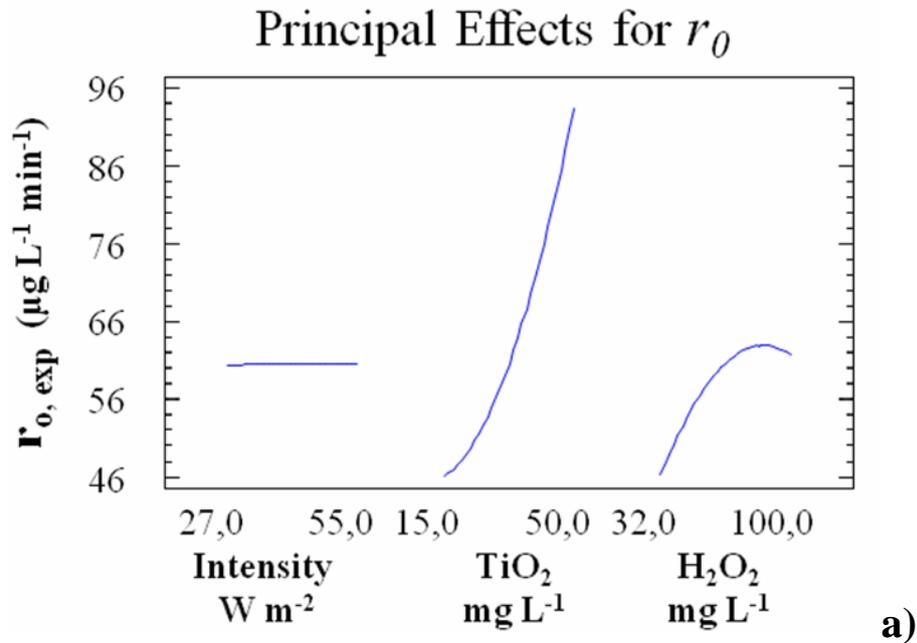


Figure 3.- a) Principal effect of each parameter over r_0 ; b) Combined effect of parameters over r_0 .

In general, under these experimental conditions, the radiant flux intensity within the selected range did not exert any influence on the initial degradation rate. On the contrary, in Figure 3b the intensity/TiO₂ interaction is observed to have had no effect on r_0 at low radiation intensities, while at higher radiation intensities (even higher than the maximum in this experimental design) the trend changed and interaction between the two factors affected r_0 . A clear interaction between TiO₂/H₂O₂ concentrations is observed. The effect of factor interaction on r_0 was analyzed by studying the corresponding response surfaces.

Effect of Radiation Intensity

It is widely known that the reaction rate in heterogeneous photocatalysis is proportional to the photon flux (Φ) up to a certain point over which the reaction rate becomes proportional to $\Phi^{0.5}$, mainly due to the recombination of e^-/h^+ pairs [14, 31], and finally to Φ^0 when the catalyst becomes saturated, there are problems of mass transfer on the surface with photons and the reaction rate no longer increases. Thus, when the photocatalyst concentration is low, photonscatalyst saturation should appear at a lower Φ than at the optimum photocatalyst concentration. It is also well known that addition of H₂O₂ to a photocatalytic process could help raise the limit of Φ at which the rate is directly proportional to it, because H₂O₂ partly impedes the recombination of e^-/h^+ pairs. According to Figure 3, the intensity of light did not affect the reaction rate, perhaps due to the low photocatalyst concentration. However, the overall effect of the three parameters together showed slight differences between the effects of radiant flux with different amounts of catalyst (Figure 4) in the presence of different H₂O₂ concentrations. While r_0 increased slightly with intensity at the lowest concentration of TiO₂ (10 mg L⁻¹), it decreased with higher radiation intensity when the catalyst concentration was 50 mg L⁻¹. This effect is caused by the catalyst concentration along with H₂O₂, i.e., when the catalyst load is very low (10 mg L⁻¹), increased intensity leads to a higher photon density and more e^-/h^+ pairs and higher rate. H₂O₂ concentration did not affect it, because a low concentration is enough to capture the small amount of e^- generated. Nevertheless, when the catalyst concentration was higher (50 mg L⁻¹), the photocatalytic system produced more e^-/h^+ pairs, and the rate was higher than with 10 mg L⁻¹. In this case, the effect of increasing the H₂O₂ concentration was beneficial, because more e^-/h^+ pairs were available. The decrease in reaction rate as a function of intensity at 50 mg L⁻¹ could

be related to Reaction 4, as excess holes generated could scavenge part of the H_2O_2 . It can therefore be concluded from these experiments that H_2O_2 dosing is a good option for working below optimal TiO_2 loads, but not at 10 mg L^{-1} or at too high radiation intensity.

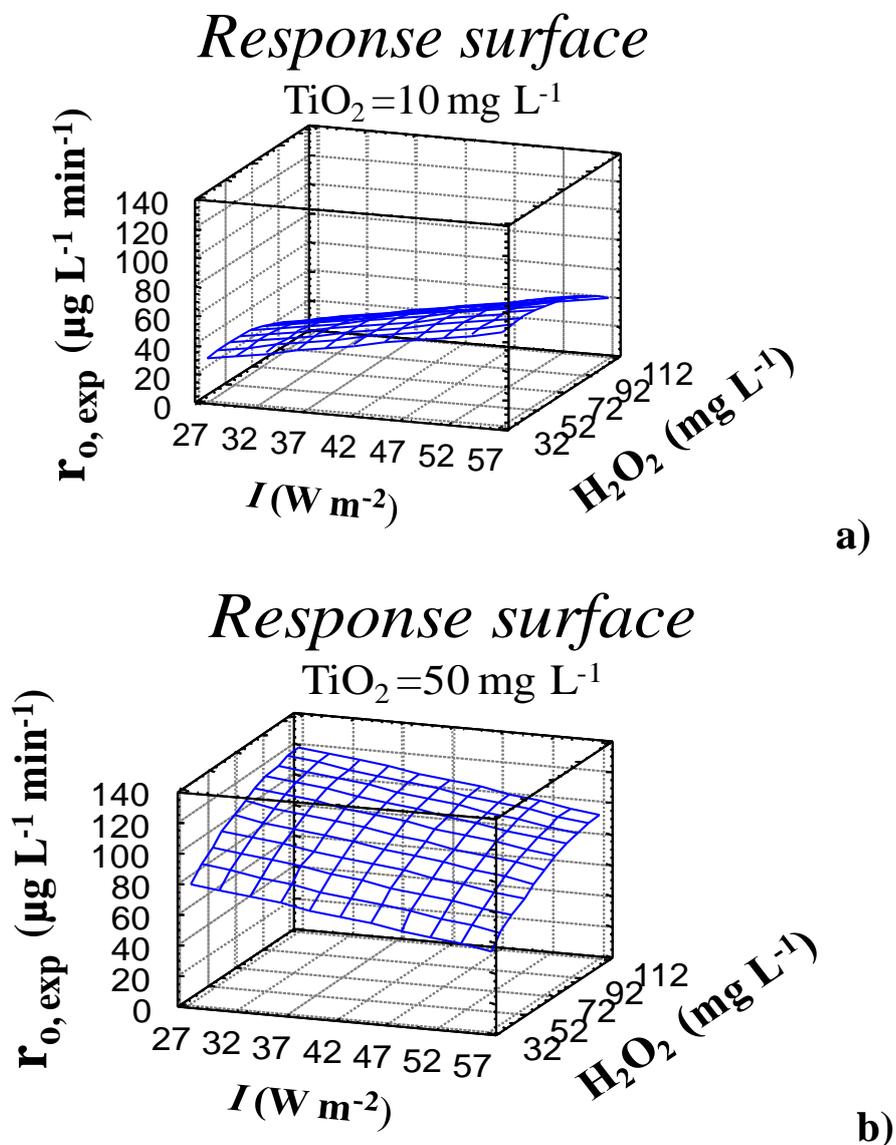


Figure 4. Response surfaces for r_0 over radiation intensity and hydrogen peroxide concentration at 10 (a) and 50 (b) mg L^{-1} of TiO_2 .

Effect of TiO_2 concentration

As mentioned above, the heterogeneous photocatalysis degradation rate usually increases with catalyst concentration toward a limit at high TiO_2 concentrations. However, this study is based on the use of low catalyst concentrations, where this

limit is still very far away, which means that r_0 increases with TiO_2 concentration within the selected range as observed in Figure 3a.

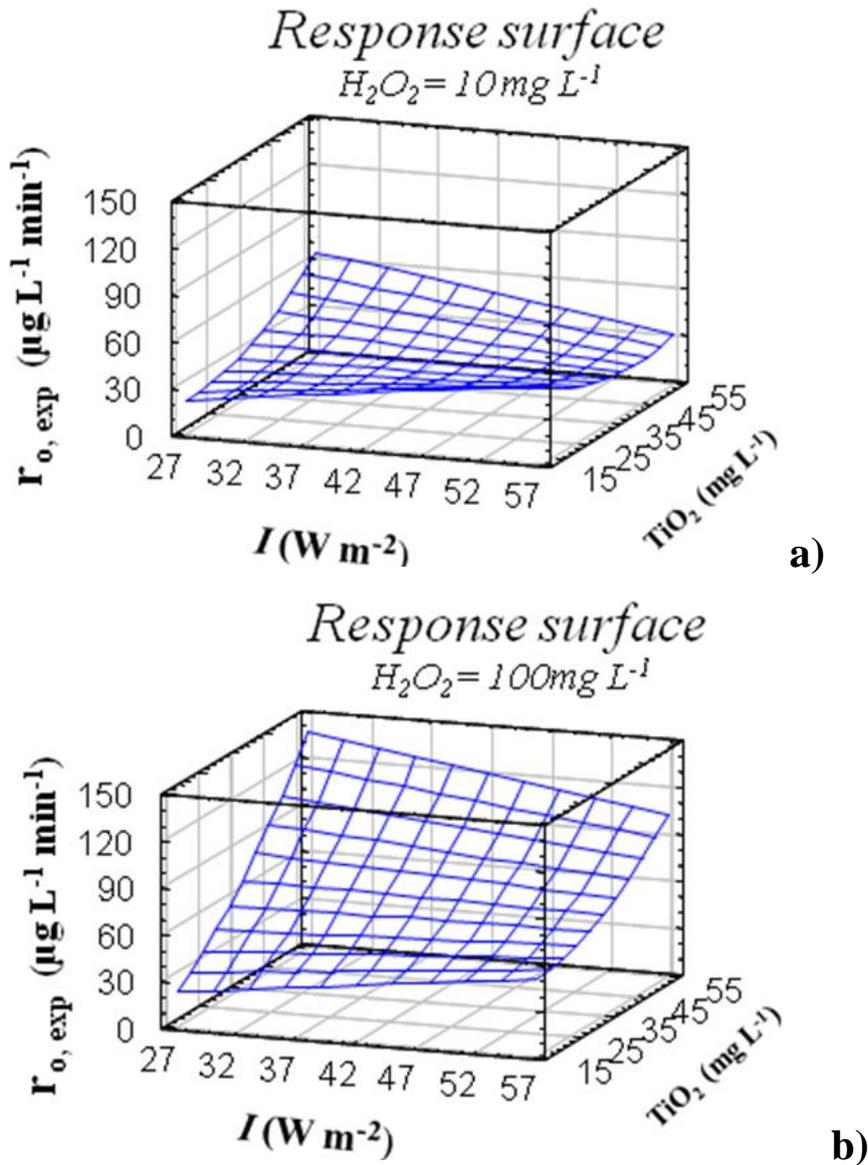


Figure 5. Response surfaces for r_0 over irradiance and TiO_2 concentration at 10 mg L^{-1} (a) and 100 mg L^{-1} (b) of H_2O_2 .

Figure 5 shows response surfaces found for r_0 plotted over radiation intensity and TiO_2 concentration at two different initial concentrations of hydrogen peroxide, 10 and 100 mg L^{-1} . The positive effect of increasing catalyst load on the initial degradation rate is clearly confirmed. Furthermore, this effect is also favored by high concentrations of H_2O_2 . r_0 remains almost constant when TiO_2 concentration is varied at the highest radiation intensity (57 W m^{-2}) and the lowest concentration of H_2O_2 (10 mg L^{-1}) (Figure 5a). The very high electron-hole formation rate at 57 W m^{-2} favored recombination, and

10 mg L⁻¹ of H₂O₂ was not enough to avoid it. On the other hand, when 100 mg L⁻¹ of H₂O₂ were added, it was observed a very strong effect of the TiO₂ load, which is more relevant at lower than at higher radiation intensities. As explained above, Reaction 4 could reduce the reaction rate at high intensities with high TiO₂ loads.

Effect of initial H₂O₂ dose

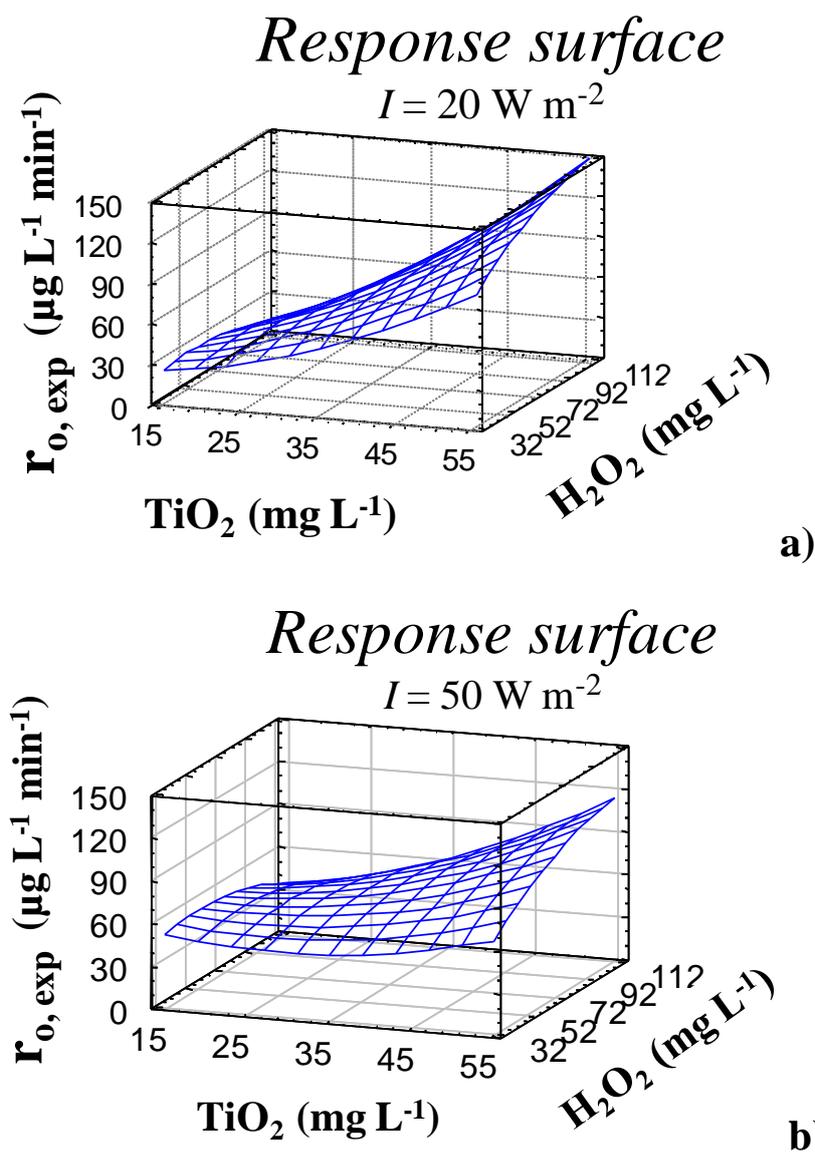


Figure 6. Response surfaces for r_0 versus H₂O₂ and TiO₂ concentration at 20 W m⁻² (a) and 50 W m⁻² (b) radiation intensity.

Figure 6a gives an idea of the general effect of H₂O₂ dosage on the initial degradation rate, and clearly shows an optimal H₂O₂ range. At higher concentrations, the improvement in the degradation rate starts to lessen. The response surfaces in Figure 5

at two different hydrogen peroxide concentrations illustrate the beneficial effect of this reagent by avoiding e^-/h^+ pair recombination and producing additional hydroxyl radicals as explained by Reactions 1-2). At an H_2O_2 concentration of 100 mg L^{-1} , the initial degradation rate reached $140 \text{ } \mu\text{g L}^{-1} \text{ min}^{-1}$, while the maximum r_0 with 10 mg L^{-1} was only $40 \text{ } \mu\text{g L}^{-1} \text{ min}^{-1}$. Nevertheless, inhibition also takes place through Reactions 4 and 5 or due to adsorption of H_2O_2 , and becomes more relevant with lower TiO_2 concentrations, as observed in Figure 6a. Figure 6a shows the response surfaces at the highest and the lowest radiation intensities. The shape of the surface is the same in both cases, but higher r_0 are reached at lower radiation intensities, which is consistent with the above discussion recommending that very high intensities be avoided.

Parameter optimization for maximizing the initial EC degradation rate

From the results of the experimental plan in Table 1, a polynomial response to r_0 was found for the variables selected (Intensity, TiO_2 , H_2O_2 , Eq 7). The polynomial equation (Eq. 7) considers the relative importance of each factor as well as their interaction, where r_0 is the initial EC degradation rate in micrograms per liter per minute, I is the irradiance in W m^{-2} , and, C and P are the catalyst and H_2O_2 concentrations, respectively, in milligrams per liter. The initial degradation rates found experimentally, and calculated by Eq. 7 above are plotted in Figure 7. The experimental results match the polynomial equation within a 95% confidence interval. This equation can therefore predict the effect of these variables on the initial EC degradation rate outside of the evaluated ranges.

$$r_0 = 108.8 - 1.6188 * I - 1.8714 * C - 0.5193 * P + 0.0219 * I^2 - 0.0166 * I * C + 0.008 * I * P + 0.0436 * C^2 + 0.0146 * C * P - 0.0011 * P^2 \quad (7)$$

The degradation rate of ECs in MWTP effluents in the $\mu\text{g L}^{-1}$ range, r_0 , could be optimized at not very high TiO_2 loads, but not below 50 mg L^{-1} , considering that H_2O_2 should be dosed in the 100 mg L^{-1} range. It should be also emphasized that high irradiation power could be detrimental to use of H_2O_2 , and therefore, the solar photoreactor design should be non-concentrating. As a matter of fact, for the best conditions tested in these experiments (41 W m^{-2} and $TiO_2 \text{ } 61.9 \text{ mg L}^{-1}$), complete degradation of the four contaminants was attained after 20 minutes of illumination time.

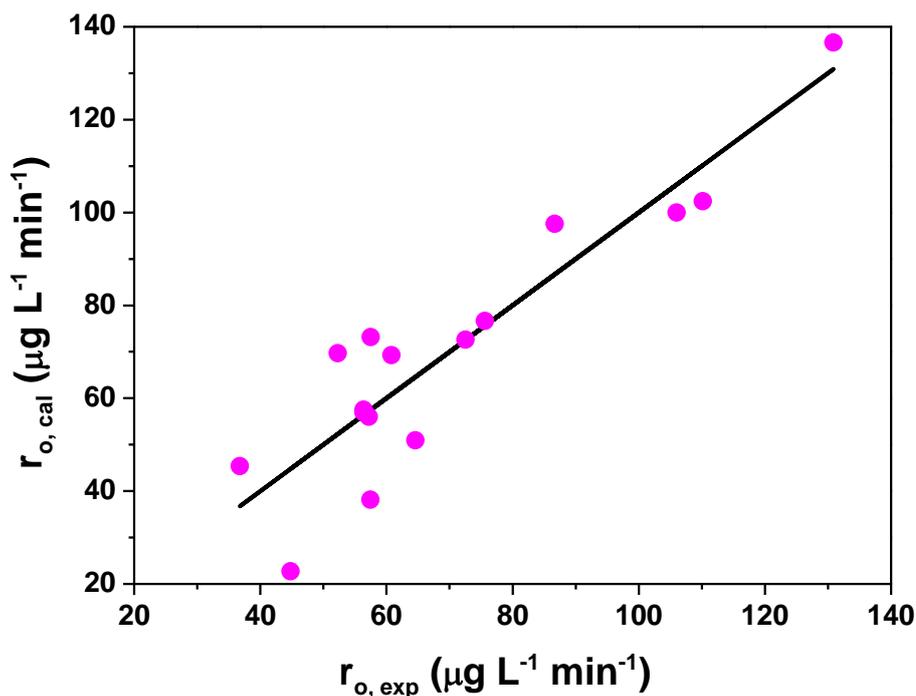


Figure 7. Parity plot for initial experimental degradation rate (dots) and calculated with Eq. 7.

Conclusions

Response surface methodology based on a spherical central composite design (CCD) was used successfully to optimize the catalyst concentration, initial hydrogen peroxide dose and radiation intensity for the maximal initial EC degradation rate using TiO_2 heterogeneous photocatalysis. As a result, a polynomial equation including the relative influence of each factor and their interaction on the degradation rate has been found enabling r_0 in the outer limits of each parameter range to be predicted.

It has been demonstrated that the use of hydrogen peroxide is highly recommendable for working with TiO_2 at low concentrations. However, the concentration of peroxide must be carefully selected and high photon flux avoided. It has also been demonstrated that too low (less than 40 mg L^{-1}) TiO_2 concentration is not recommendable, as then it is not possible for the degradation rate to be enhanced using hydrogen peroxide. Experimentation with a solar simulator led to the design of (photon flux) and decisive operating strategies (TiO_2 and H_2O_2 loading) for solar photocatalytic plants with absorber tubes with a similar design and light path length as tubes installed in solar collectors. Real application of solar $\text{TiO}_2/\text{H}_2\text{O}_2$ in tertiary

treatment needs deeper studies to obtain different operational variables (as treatment time) and costs, but the present study has laid the basis for further research that should avoid $< 50 \text{ mg L}^{-1}$ of TiO_2 , use H_2O_2 in the range of 100 mg L^{-1} and avoid concentration of solar light.

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Optimization of mild solar TiO₂ photocatalysis as a tertiary treatment for municipal wastewater treatment plant effluents

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Abstract

The appropriate catalyst concentration for industrial wastewater treatment is several hundred milligrams per liter in solar photoreactors. Nonetheless, when the purpose of eliminating emerging contaminants in municipal wastewater treatment plant effluents is for reuse of the water, and they are present at extremely low concentrations, a tertiary treatment with a much lower photocatalyst concentration might be possible. TiO₂ concentrations of only tens of mg L⁻¹ were selected to evaluate the influence of catalyst load, initial hydrogen peroxide dose and radiation intensity on the degradation rate of five emerging contaminants (100 µg L⁻¹ of ofloxacin, sulfamethoxazole, flumequine, carbamazepine, and 2-Hydroxy-biphenyl) spiked in a real municipal wastewater treatment plant effluent. Response surface methodology based on a spherical central composite design was used to optimize the parameters to find the maximal degradation rate. The experiments were carried out using an Evonik P-25 titanium dioxide suspension in a Suntest solar simulator. It has been demonstrated that the use of hydrogen peroxide is highly recommendable for working with TiO₂ at low concentrations and high photon flux must be avoided. It has also been demonstrated that too low (less than 40 mg L⁻¹) TiO₂ concentration is not recommendable.

Keywords: emerging contaminants, photocatalysis, solar photoreactors

Introduction

Compounds such as substituted phenols, non-biodegradable chlorinated solvents, pesticides and surfactants have long been recognized as typical relevant substances difficult to remove from water. In this context, pharmaceuticals and personal care products, and especially endocrine-disrupting chemicals have recently been labeled emerging contaminants (ECs), which means they are still unregulated or regulation is in process [1-6]. A multitude of risks, such as bacterial resistance, sterility, and feminization of aquatic organisms derive from the presence of these substances in water. In recent years, ECs have been found in treated wastewater, surface and groundwater, and even drinking water in tens of $\mu\text{g L}^{-1}$ [5, 7-9]. Furthermore, their growing use is directly increasing their concentration in natural and treated water [10-12], as conventional wastewater treatment plants are unable to completely remove them. The continuously rising concentrations of these compounds show that conventional wastewater treatments are not efficient enough and consequently, available, simple advanced technologies are necessary to remove these contaminants from water.

Advanced oxidation processes (AOPs), which drive organic matter oxidation by means of the hydroxyl radicals they generate, have been proposed as a valuable method for degrading persistent organic compounds with high reaction rates and low selectivity. TiO_2 is the most widely used catalyst in heterogeneous photocatalysis, although several other semiconductors exist, because of its photostability, non-toxicity, low cost and stability in water under most environmental conditions [13, 14]. One of the main drawbacks of heterogeneous photocatalysis, however, is its relatively high operating cost due to the use of UV lamps. Nevertheless, the UV lamps in such systems could be replaced by natural solar radiation, which is free and feasible for large-scale aqueous-phase applications [14, 15].

The appropriate catalyst concentration for industrial wastewater treatment is several hundred milligrams per liter in solar photoreactors [16]. Nonetheless, when the purpose of eliminating ECs in municipal wastewater treatment plant (MWTP) effluents is for reuse of the water, and they are present at extremely low concentrations, a tertiary treatment with a much lower catalyst (TiO_2) concentration might be possible. This way, the catalyst would be more easily recovered and reused, and the addition of large

amounts of TiO₂ to water treated in the MWTP and already relatively clean would also be avoided. It is also important to consider that one of the main problems of working with concentrated TiO₂ slurries is membrane separation of the particles from water [17-20], which becomes more expensive the more concentrated the slurry is.

On the other hand, reducing the catalyst load has the drawback of wasting useful photons passing through the reactor without reacting with TiO₂ with its consequences for the EC degradation rate [21, 22]. However, the TiO₂ solar photocatalysis reaction rate can be enhanced by using chemical oxidants, doped or modified TiO₂, or combination with other AOPs for more efficient contaminant removal [23]. Hydrogen peroxide, which was one of the first oxidants tested in this type of application [24], was chosen in this study as the chemical oxidant. It is very commonly used, environmentally friendly and cheap. Moreover, it fulfills the criteria of forming hydroxyl radicals and dissociating into harmless by-products [25, 26].

The positive effect of H₂O₂ dosing is prevention of e^-/h^+ pair recombination and production of additional hydroxyl radicals by Reactions 1 and 2 (below). Photolysis of H₂O₂ (Eq. 3) yields hydroxyl radicals when irradiated by photons with wavelengths below 300 nm [27, 28], and therefore, it is not expected to enhance the reaction rate when illuminated by solar irradiation. However, there could be inhibition due to TiO₂ surface modification by peroxide adsorption, scavenging of photo-produced holes (Reaction 4) and reacting with hydroxyl radicals (Reaction 5).



Inhibition of adsorption not only depends on the characteristics of the contaminant, but also on the H₂O₂/contaminant ratio. If contaminant concentration is too low, as it is in this study with effluents from an MWTP, and the H₂O₂ concentration is too high,

contaminant adsorption decreases because of adsorption of H_2O_2 , and therefore, the reaction rate decreases. Consequently, and although the effect of adding H_2O_2 to the photocatalytic reaction has already been studied, it must be optimized to the specific conditions of very low pollutant concentrations ($\mu\text{g L}^{-1}$ range) and low catalyst load.

TiO_2 concentrations of only tens of mg L^{-1} were therefore selected for this study, which evaluated the influence of catalyst load, initial hydrogen peroxide dose and radiation intensity on the initial degradation rate of five ECs (100 $\mu\text{g L}^{-1}$ of ofloxacin, sulfamethoxazole, flumequine, carbamazepine, and 2-Hydroxy-biphenyl, all commonly found in MWTP effluents) spiked in a real MWTP effluent. Furthermore, response surface methodology based on a spherical central composite design (CCD) was used to optimize the catalyst concentration, initial hydrogen peroxide dose and radiation intensity to find the maximal initial EC degradation rate.

Materials and methods

Reagents and Real wastewater

The experiments were carried out using an Evonik P-25 titanium dioxide (surface area 51-55 $\text{m}^2 \text{g}^{-1}$) suspension. Sulfuric acid used to strip $\text{HCO}_3^-/\text{CO}_3^{2-}$ and hydrogen peroxide (30% w/v) were purchased from Panreac. All reagents used for chromatographic analyses, and ultrapure (Milli-Q) water, were HPLC grade. Analytical standards of ofloxacin, sulfamethoxazole, flumequine, carbamazepine, and 2-Hydroxy-biphenyl for chromatography analyses and for experiments were purchased from Sigma-Aldrich. The same real MWTP effluent taken downstream from the secondary biological treatment of the El Ejido MWTP (in the Province of Almería, Spain) was used in all the experiments. Dissolved organic carbon (DOC), total inorganic carbon (TIC) and chemical oxygen demand (COD) were in the 21, 114 and 57 mg L^{-1} ranges, respectively. Other characteristics of the effluent were, in mg L^{-1} : Cl^- 41, SO_4^{2-} 17, NO_3^- 2.6, Na^+ 31, K^+ 3.2, Ca^{+2} 13, Mg^{+2} 9.5, NH_4^+ 2.6.

Analytical Procedures

Dissolved organic carbon and total inorganic carbon were measured immediately by a Shimadzu TOC-VCSN analyzer. The concentration of the five emerging contaminants was monitored by ultra-performance liquid chromatography (flow rate: 1 mL min^{-1})

(Agilent Technologies, series 1200) with a UV-DAD detector and a C-18 analytical column (Agilent XDB-C18, 1.8 μm , 4.6 mm x 50 mm, 600 bar). The mobile phase was 10% UPLC-grade acetonitrile and 90% water with formic acid 25 mM. Detection was done at four different wavelengths depending on the compound: 267 nm (Sulfamethoxazole and Carbamazepine), 248 nm (Flumequine), 243 nm (2-Hydroxybiphenyl) and 295 nm (Ofloxacin). For UPLC analyses 10 mL of sample were passed through a 0.22- μm syringe filter, then 3 mL of UPLC-grade acetonitrile were also passed through the filter to extract any compound adsorbed on the TiO_2 retained in the filter or on the filter itself.

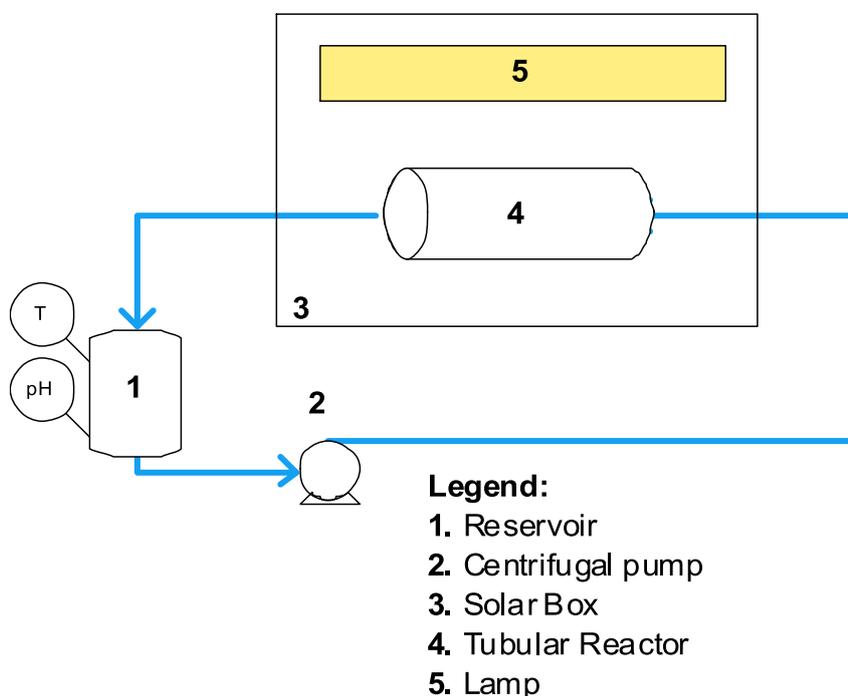


Figure 1. Lab-scale photoreactor

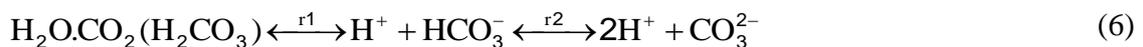
Experimental setup

A battery of experiments was carried out in a Suntest solar simulator (Suntest XLS+ photoreactor from Atlas, <http://atlas-mts.com/>) equipped with a 765-250 W m^{-2} Xe lamp (61-24 W m^{-2} from 300 to 400 nm, electronically controlled) and a cooling system to keep the temperature at 35°C. The lab-scale reactor was made up of a 170-mm-long Pyrex glass tube with a 32 mm O.D. (29.2 mm inner diameter, 1.4-mm-thick glass wall, light transmission $\lambda < 400 \text{ nm}$ 91% and 120 mL illuminated volume, V_i), and a glass container and connecting tubing to complete a total volume V_T of 1.5 L (see Figure 1).

The distance of the lamp axis to the photoreactor longitudinal axis was 250 mm, being illuminated only from one side, very similar to outdoors solar photoreactors. This feature is important to better simulate the effect of different catalyst loads on outdoor solar photoreactors from experiments performed in the solar simulator. A centrifugal pump (Pan World Co, LTD, model NH-30PX) was used to create a turbulent flow (STD point: 11 L min⁻¹, speed 3100 rpm, power consumption 30W) and ensured complete homogenization. Temperature and pH were monitored during the experiments by a Hanna check-temp 1 and a CRISON pH-meter, respectively.

Experimental procedure

When received, the MWTP secondary biological treatment effluent was pretreated with H₂SO₄ under agitation to remove HCO₃⁻/CO₃²⁻, which are known to be hydroxyl radical scavengers [29]. The acid was added until elimination of HCO₃⁻/CO₃²⁻ without attaining any decrease of pH. From pH 6.5 to 8.0 (experimental conditions), the main inorganic carbon species present in solution was bicarbonate HCO₃⁻ (around 95% at pH 7.8) as pK_{r1} = 6.37 and pK_{r2} = 10.25 in Reaction 6. The reactivity of HO• with bicarbonate was evaluated at a rate constant equal to 8.5 × 10⁶ M⁻¹ s⁻¹ [30]. This is the main reason for the very negative effect of the presence of bicarbonate ions in aqueous solution on the degradation of organic compounds by any advanced oxidation process. 1.5 L of real MWTP effluent were spiked with 100 µgL⁻¹ of ECs (ofloxacin, sulfamethoxazole, flumequine, carbamazepine, and 2-Hydroxy-biphenyl) for each experiment. After 10 minutes of homogenization, a sample was taken to assure the initial contaminant concentration. Then the catalyst was added and 45 minutes more in the dark were needed to ensure homogenization and permit steady state of adsorption of ECs on TiO₂. After that, the lamp was turned on, the first hydrogen peroxide dose was added, and the experiment began. Samples were taken every 5 minutes for the first hour, and from then on, every 15 minutes until H₂O₂ was totally consumed, at which time the experiment ended. All kinetics calculations considered illumination time, i.e., experimental time x (V_i/V_T).



Experimental Design

This study evaluated the influence of the initial hydrogen peroxide dose, TiO₂ concentration and radiation intensity on the initial rate of EC degradation by heterogeneous photocatalysis. Firstly, the range of UV irradiation (300-400 nm) was within the range of natural solar radiation during the year in a sunny location, 27-55 W m⁻². The initial range of H₂O₂ doses depended on the pollutant and photocatalyst concentration, and finally, a low TiO₂ concentration range of 15 to 50 mg L⁻¹ was selected. The purpose was to find out whether the interaction of different factors allows the EC degradation rate to continuously increase or, on the contrary, whether there is an optimum within the range.

Response surface methodology based on a spherical central composite design (CCD) was employed to evaluate the influence of the three operating parameters, H₂O₂, TiO₂ and radiation intensity, on the response factor. This experimental design puts all the factorial and axial design points on the surface of a sphere with a radius \sqrt{k} , where $k=3$ (number of factors). Seventeen runs were performed following this experimental design, 2^k factorial runs that correspond to the limits of the selected ranges, $2k$ axial, which go outside the selected ranges and 3 center runs to check the variance of the design (see Table 1). Statgraphics statistical software was employed to analyze the CCD and to plot the response surfaces. The response factor is the initial EC degradation rate (r_0) of the four contaminants as a whole (sum of concentration of all of them in each sample) in $\mu\text{g L}^{-1} \text{min}^{-1}$, and the parameters are optimized to obtain the maximum r_0 .

Table 1. CCD experimental matrix: 8 factorial (1-8), 6 axial (12-17) and 3 center (9-11) runs.

Runs	Intensity, W m ⁻²	TiO ₂ , mg L ⁻¹	H ₂ O ₂ , mg L ⁻¹
1	27	15	32
2	55	15	100
3	55	50	100
4	55	50	32
5	55	15	32
6	27	50	100
7	27	15	100

8	27	50	32
9	41	32.5	66
10	41	32.5	66
11	41	32.5	66
12	17.4	32.5	66
13	41	32.5	8.8
14	41	3.1	66
15	64.5	32.5	66
16	41	61.9	66
17	41	32.5	123.2

Results and discussion

The initial heterogeneous photocatalytic reaction rate increases with catalyst load up to a point above which the reaction rate usually remains constant or decreases. This limit depends on irradiation power, reactor design and geometry, i.e., reactor light path length, and on some catalyst characteristics, mainly its point of zero charge, aggregation state, and optical properties. The reaction rate also depends on the initial contaminant concentration. At a certain catalyst mass and radiant flux, lower initial concentrations lead to lower reaction rates [31]. There is a correlation between the optimal catalyst mass and initial contaminant concentration, since the main heterogeneous photocatalysis mechanisms include several steps, like contaminant adsorption on catalyst surface, photogeneration of hydroxyl radicals, oxidative reaction, and desorption of reaction products. Therefore, when contaminant concentrations increase, reaction rate increases. However, due to saturation on the semiconductor surface, the reaction rate becomes constant when the initial concentration is too high [32].

This study aimed to optimize the degradation of emerging contaminants present in MWTP effluents in the micrograms-per-liter range by heterogeneous photocatalysis with TiO₂. A much lower amount of catalyst is required for that than for elimination of higher contaminant concentrations. Figure 2 shows the early stages of degradation of four of these contaminants over normalized time in two experiments performed with 50 mg L⁻¹ of TiO₂, with and without an initial dosage of 100 mg L⁻¹ of H₂O₂. It is quite clear that the experiment with H₂O₂ leads to a higher reaction rate. This is true of all four contaminants, which are quickly degraded during the experiment with H₂O₂. Reaction rates are from 5.6 μg L⁻¹min⁻¹ for sulfamethoxazole to 24.5 μg L⁻¹min⁻¹ for 2-Hydroxy-biphenyl, while they remain almost constant after the same reaction time without peroxide, and r_0 goes from 0.26 μg L⁻¹ min⁻¹ for sulfamethoxazole to 0.9 μg L⁻¹ min⁻¹ for 2-Hydroxy-biphenyl degradation.

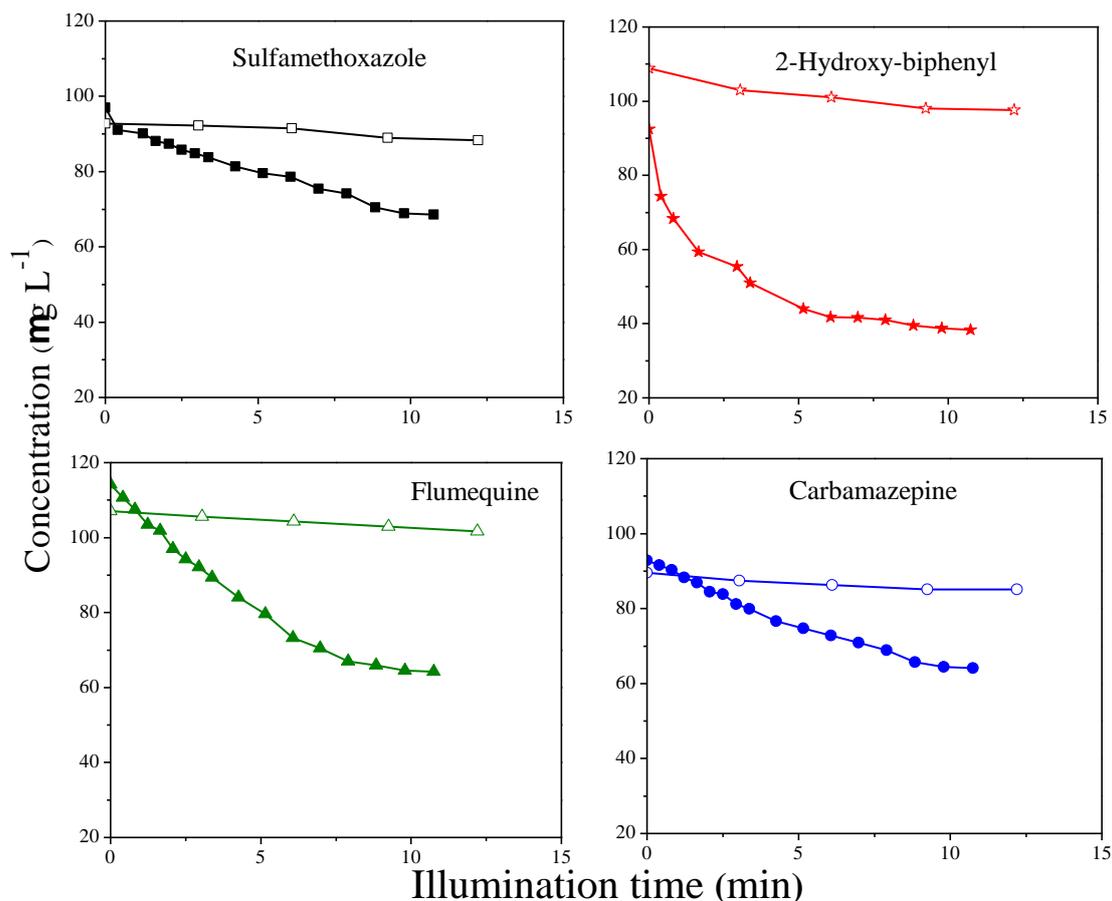


Figure 2. Heterogeneous photocatalytic treatment of sulfamethoxazole, 2-Hydroxy-biphenyl, Carbamazepine and Flumequine using 50 mg L⁻¹ of TiO₂ with (solid dots) and without (open dots) 100 mg L⁻¹ of H₂O₂ as initial dosage.

As demonstrated, at low TiO₂ loads, the addition of another oxidizing reagent may be justified to enhance the organic degradation rate. In order to explore this technique (TiO₂/H₂O₂/solar-UV) as an alternative tertiary water treatment, the optimal concentration of H₂O₂ for different low TiO₂ loads and the particular characteristics of the MWTP effluent containing low contaminant concentrations had to be found.

Figure 3 was calculated by the experimental statistical tool. It shows the effect of each parameter (irradiance, catalyst load and hydrogen peroxide concentration) separately and combined over r_0 . Figure 3a was plotted taking two of the three parameters as constant at their center value and following the third parameter separately. Figure 3b shows r_0 as a function of paired factors. In each figure, one factor varies from lowest to highest, behavior of the second factor is shown by a line,

and the third factor involved in the interaction remains constant at its center value. When these lines (Figure 3b) cross or tend to cross, interaction between the corresponding pair of factors must be considered, as for intensity/TiO₂ and TiO₂/H₂O₂. However, when lines are parallel, as for intensity/H₂O₂, interaction between these factors is insignificant or there is none at all.

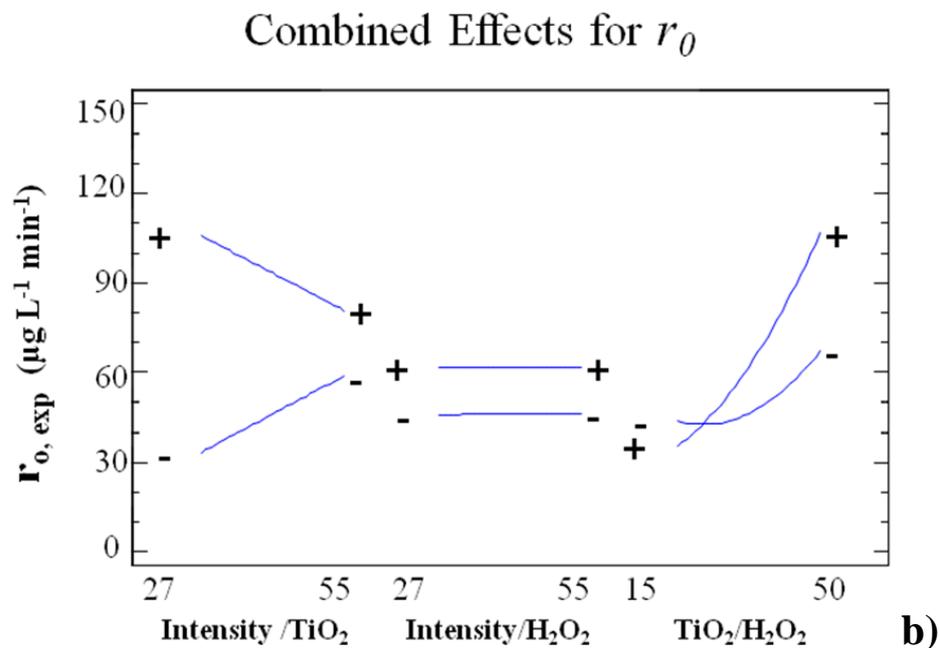
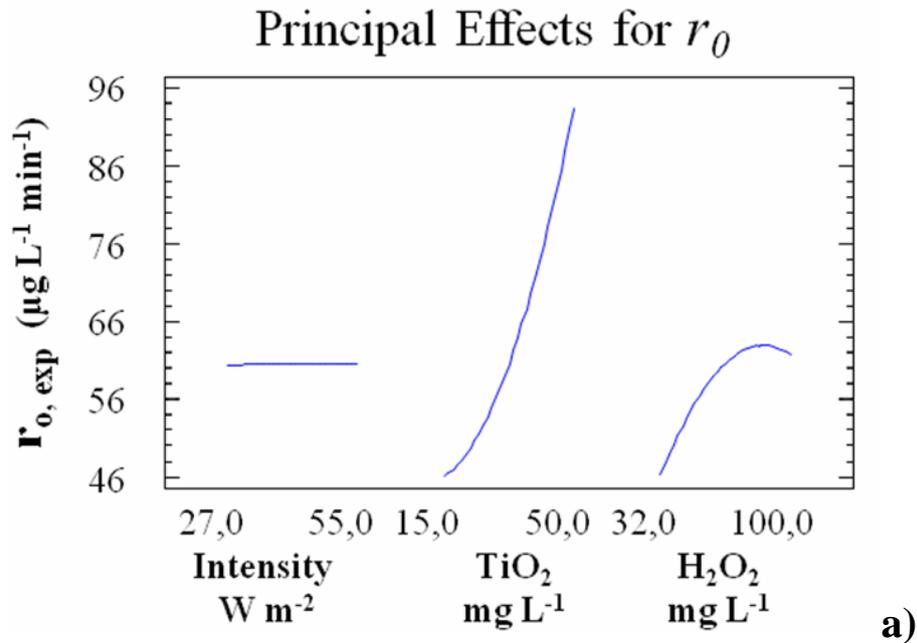


Figure 3.- a) Principal effect of each parameter over r_0 ; b) Combined effect of parameters over r_0 .

In general, under these experimental conditions, the radiant flux intensity within the selected range did not exert any influence on the initial degradation rate. On the contrary, in Figure 3b the intensity/TiO₂ interaction is observed to have had no effect on r_0 at low radiation intensities, while at higher radiation intensities (even higher than the maximum in this experimental design) the trend changed and interaction between the two factors affected r_0 . A clear interaction between TiO₂/H₂O₂ concentrations is observed. The effect of factor interaction on r_0 was analyzed by studying the corresponding response surfaces.

Effect of Radiation Intensity

It is widely known that the reaction rate in heterogeneous photocatalysis is proportional to the photon flux (Φ) up to a certain point over which the reaction rate becomes proportional to $\Phi^{0.5}$, mainly due to the recombination of e^-/h^+ pairs [14, 31], and finally to Φ^0 when the catalyst becomes saturated, there are problems of mass transfer on the surface and the reaction rate no longer increases. Thus, when the photocatalyst concentration is low, catalyst saturation should appear at a lower Φ than at the optimum photocatalyst concentration. It is also well known that addition of H₂O₂ to a photocatalytic process could help raise the limit of Φ at which the rate is directly proportional to it, because H₂O₂ partly impedes the recombination of e^-/h^+ pairs. According to Figure 3, the intensity of light did not affect the reaction rate, perhaps due to the low photocatalyst concentration. However, the overall effect of the three parameters together showed slight differences between the effects of radiant flux with different amounts of catalyst (Figure 4) in the presence of different H₂O₂ concentrations. While r_0 increased slightly with intensity at the lowest concentration of TiO₂ (10 mg L⁻¹), it decreased with higher radiation intensity when the catalyst concentration was 50 mg L⁻¹. This effect is caused by the catalyst concentration along with H₂O₂, i.e., when the catalyst load is very low (10 mg L⁻¹), increased intensity leads to a higher photon density and more e^-/h^+ pairs and higher rate. H₂O₂ concentration did not affect it, because a low concentration is enough to capture the small amount of e^- generated. Nevertheless, when the catalyst concentration was higher (50 mg L⁻¹), the photocatalytic system produced more e^-/h^+ pairs, and the rate was higher than with 10 mg L⁻¹. In this case, the effect of increasing the H₂O₂ concentration was beneficial, because more e^-/h^+ pairs were available. The decrease in reaction rate as a function of intensity at 50 mg L⁻¹ could be related to Reaction 4,

as excess holes generated could scavenge part of the H_2O_2 . It can therefore be concluded from these experiments that H_2O_2 dosing is a good option for working below optimal TiO_2 loads, but not at 10 mg L^{-1} or at too high radiation intensity.

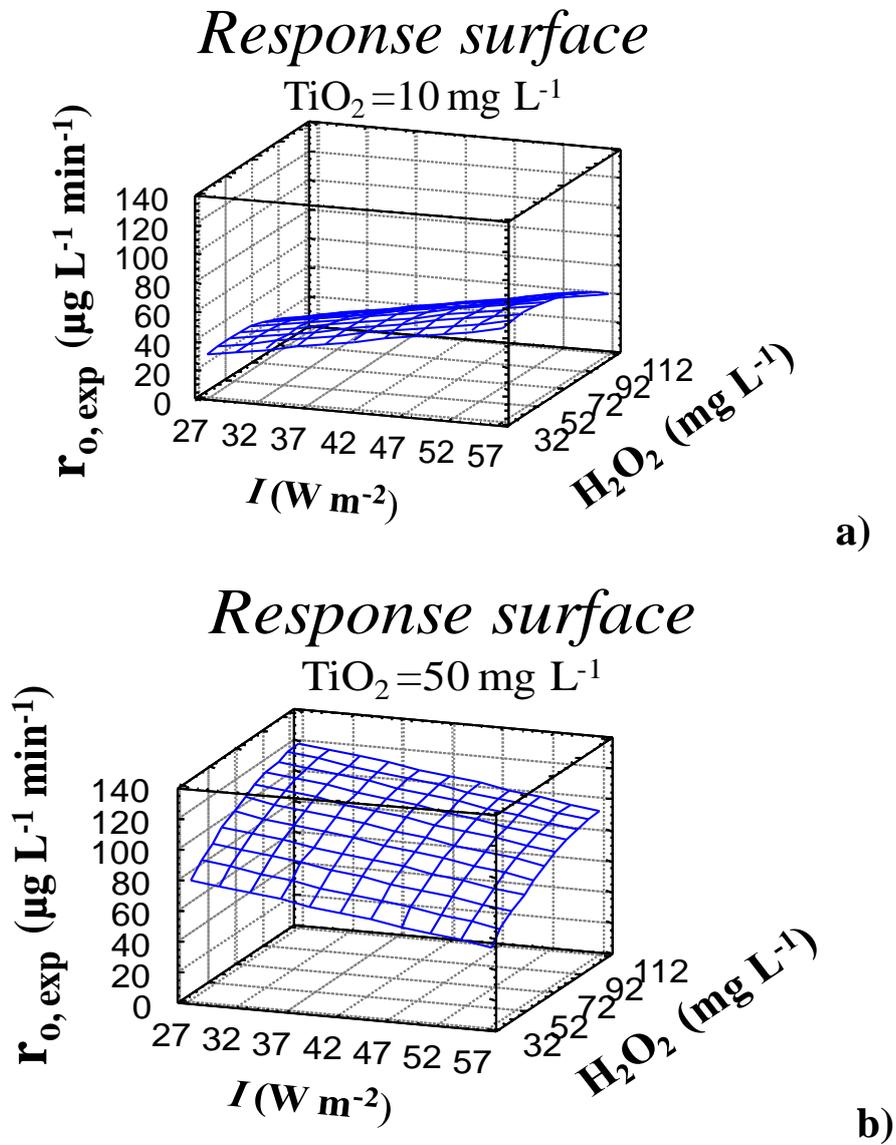


Figure 4. Response surfaces for r_0 over radiation intensity and hydrogen peroxide concentration at 10 (a) and 50 (b) mg L^{-1} of TiO_2 .

Effect of TiO_2 concentration

As mentioned above, the heterogeneous photocatalysis degradation rate usually increases with catalyst concentration toward a limit at high TiO_2 concentrations. However, this study is based on the use of low catalyst concentrations, where this limit is still very far away, which means that r_0 increases with TiO_2 concentration within the selected range as observed in Figure 3a.

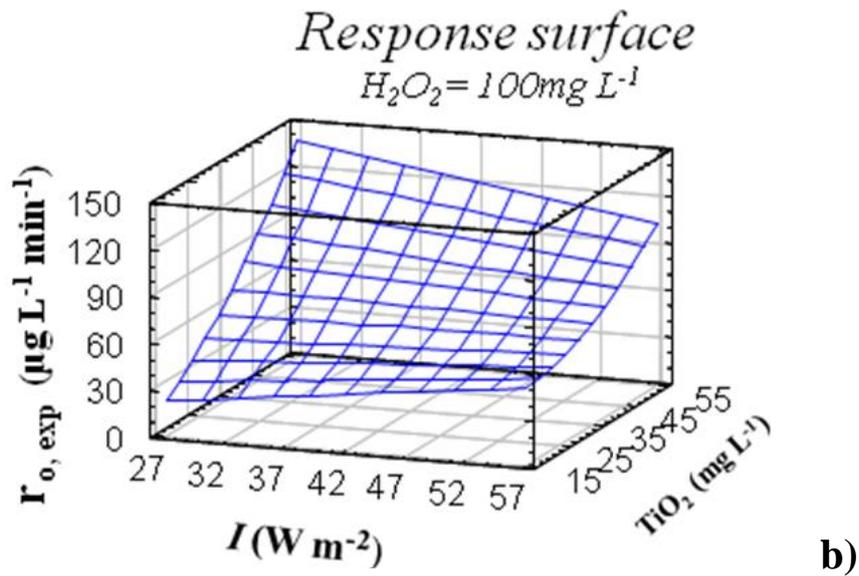
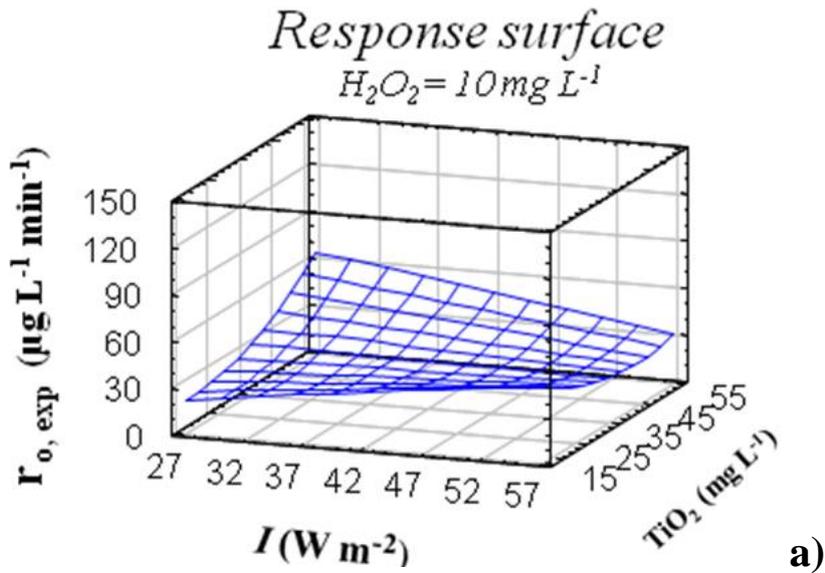


Figure 5. Response surfaces for r_0 over irradiance and TiO_2 concentration at 10 mg L^{-1} (a) and 100 mg L^{-1} (b) of H_2O_2 .

Figure 5 shows response surfaces found for r_0 plotted over radiation intensity and TiO_2 concentration at two different initial concentrations of hydrogen peroxide, 10 and 100 mg L^{-1} . The positive effect of increasing catalyst load on the initial degradation rate is clearly confirmed. Furthermore, this effect is also favored by high concentrations of H_2O_2 . r_0 remains almost constant when TiO_2 concentration is varied at the highest radiation intensity (57 W m^{-2}) and the lowest concentration of H_2O_2 (10 mg L^{-1}) (Figure 5a). The very high electron-hole formation rate at 57 W m^{-2} favored recombination, and 10 mg L^{-1} of H_2O_2 was not enough to avoid it. On the other hand, when 100 mg L^{-1} of H_2O_2 were added, it was observed a very strong effect of the TiO_2 load, which is more

relevant at lower than at higher radiation intensities. As explained above, Reaction 4 could reduce the reaction rate at high intensities with high TiO₂ loads.

Effect of initial H₂O₂ dose

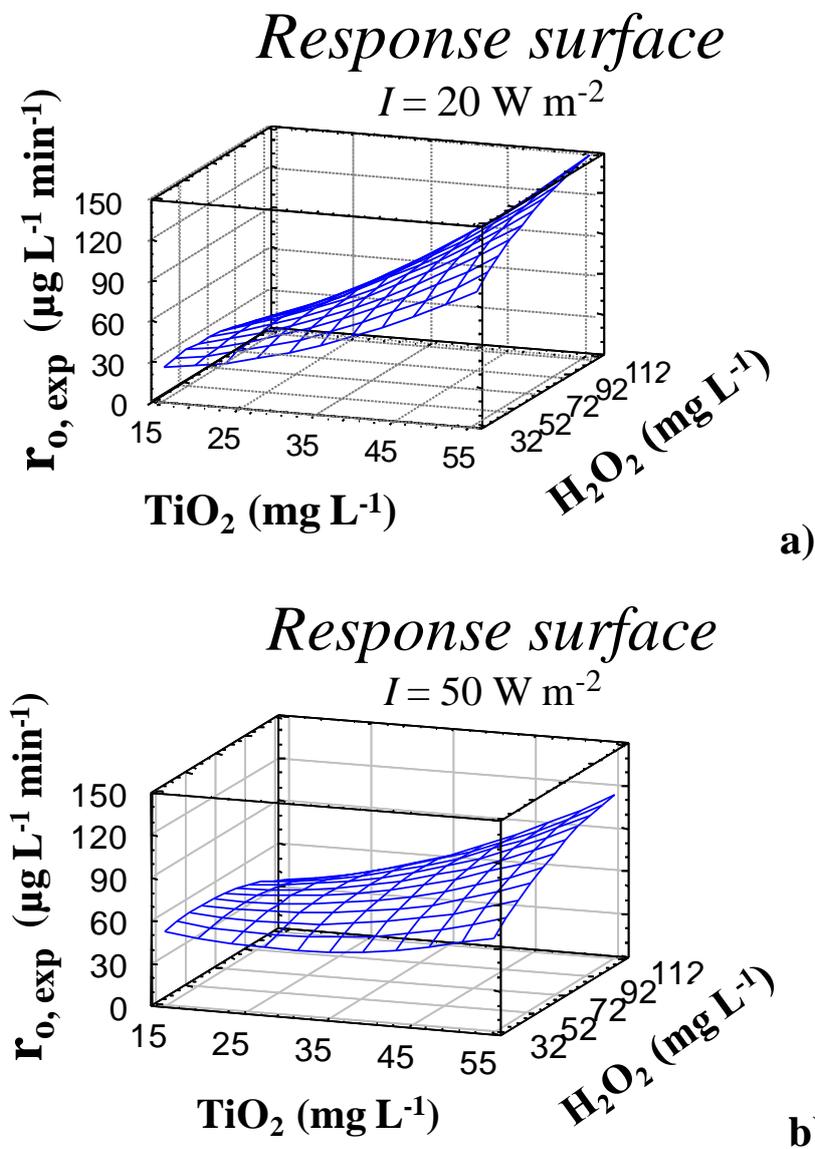


Figure 6. Response surfaces for r_0 versus H₂O₂ and TiO₂ concentration at 20 W m⁻² (a) and 50 W m⁻² (b) radiation intensity.

Figure 6a gives an idea of the general effect of H₂O₂ dosage on the initial degradation rate, and clearly shows an optimal H₂O₂ range. At higher concentrations, the improvement in the degradation rate starts to lessen. The response surfaces in Figure 5 at two different hydrogen peroxide concentrations illustrate the beneficial effect of this reagent by avoiding e^-/h^+ pair recombination and producing additional hydroxyl radicals

as explained by Reactions 1-2). At an H₂O₂ concentration of 100 mg L⁻¹, the initial degradation rate reached 140 µg L⁻¹ min⁻¹, while the maximum r_0 with 10 mg L⁻¹ was only 40 µg L⁻¹ min⁻¹. Nevertheless, inhibition also takes place through Reactions 4 and 5 or due to adsorption of H₂O₂, and becomes more relevant with lower TiO₂ concentrations, as observed in Figure 6a. Figure 6a shows the response surfaces at the highest and the lowest radiation intensities. The shape of the surface is the same in both cases, but higher r_0 are reached at lower radiation intensities, which is consistent with the above discussion recommending that very high intensities be avoided.

Parameter optimization for maximizing the initial EC degradation rate

From the results of the experimental plan in Table 1, a polynomial response to r_0 was found for the variables selected (Intensity, TiO₂, H₂O₂, Eq 7). The polynomial equation (Eq. 7) considers the relative importance of each factor as well as their interaction, where r_0 is the initial EC degradation rate in micrograms per liter per minute, I is the irradiance in W m⁻², and, C and P are the catalyst and H₂O₂ concentrations, respectively, in milligrams per liter. The initial degradation rates found experimentally, and calculated by Eq. 7 above are plotted in Figure 7. The experimental results match the polynomial equation within a 95% confidence interval. This equation can therefore predict the effect of these variables on the initial EC degradation rate outside of the evaluated ranges.

$$r_0 = 108.8 - 1.6188 * I - 1.8714 * C - 0.5193 * P + 0.0219 * I^2 - 0.0166 * I * C + 0.008 * I * P + 0.0436 * C^2 + 0.0146 * C * P - 0.0011 * P^2 \quad (7)$$

The degradation rate of ECs in MWTP effluents in the µg L⁻¹ range, r_0 , could be optimized at not very high TiO₂ loads, but not below 50 mg L⁻¹, considering that H₂O₂ should be dosed in the 100 mg L⁻¹ range. It should be also emphasized that high irradiation power could be detrimental to use of H₂O₂, and therefore, the solar photoreactor design should be non-concentrating. As a matter of fact, for the best conditions tested in these experiments (41 W m⁻² and TiO₂ 61.9 mg L⁻¹), complete degradation of the four contaminants was attained after 20 minutes of illumination time.

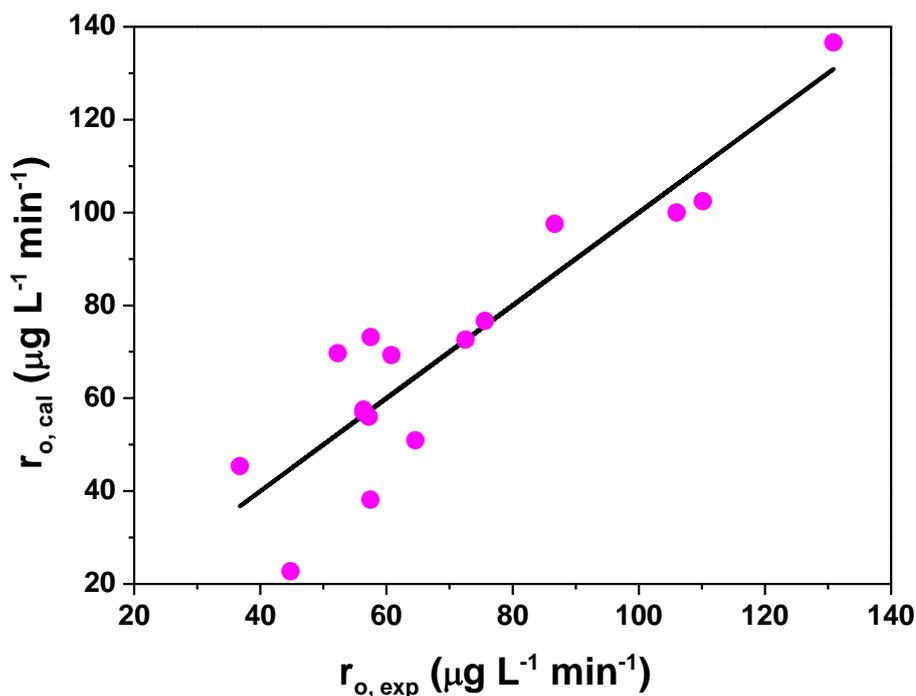


Figure 7. Parity plot for initial experimental degradation rate (dots) and calculated with Eq. 7.

Conclusions

Response surface methodology based on a spherical central composite design (CCD) was used successfully to optimize the catalyst concentration, initial hydrogen peroxide dose and radiation intensity for the maximal initial EC degradation rate using TiO_2 heterogeneous photocatalysis. As a result, a polynomial equation including the relative influence of each factor and their interaction on the degradation rate has been found enabling r_0 in the outer limits of each parameter range to be predicted.

It has been demonstrated that the use of hydrogen peroxide is highly recommendable for working with TiO_2 at low concentrations. However, the concentration of peroxide must be carefully selected and high photon flux avoided. It has also been demonstrated that too low (less than 40 mg L^{-1}) TiO_2 concentration is not recommendable, as then it is not possible for the degradation rate to be enhanced using hydrogen peroxide. Experimentation with a solar simulator led to the design of (photon flux) and decisive operating strategies (TiO_2 and H_2O_2 loading) for solar photocatalytic plants with absorber tubes with a similar design and light path length as tubes installed in solar collectors. Real application of solar $\text{TiO}_2/\text{H}_2\text{O}_2$ in tertiary

treatment needs deeper studies to obtain different operational variables (as treatment time) and costs, but the present study has laid the basis for further research that should avoid $< 50 \text{ mg L}^{-1}$ of TiO_2 , use H_2O_2 in the range of 100 mg L^{-1} and avoid concentration of solar light.

Acknowledgements

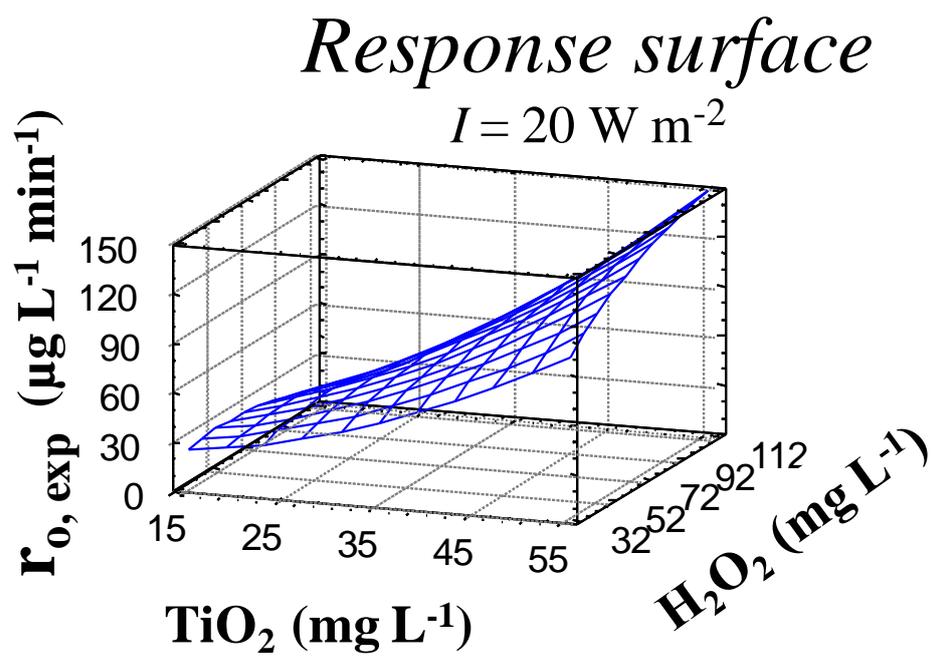
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Effect of H_2O_2 dosing in photocatalytic reaction rate at low solar radiation intensity and working with low TiO_2 photocatalyst concentration.

Highlights

- Solar Photocatalytic treatment for eliminating emerging contaminants
- We studied it in municipal wastewater treatment plant effluents.
- Hydrogen peroxide is highly recommendable with TiO₂ at low concentrations
- High photon flux must be avoided.
- Too low (less than 40 mg L⁻¹) TiO₂ concentration is not recommendable.