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Solar light-induced degradation of bisphenol-A with TiO_2 immobilized on Ti

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ABSTRACT

The photocatalytic degradation of bisphenol-A (BPA) was investigated over immobilized TiO_2/Ti-film catalysts irradiated by artificial solar light. Catalysts were prepared either by a sol–gel method (TIP catalyst) or deposition of Degussa P-25 slurry (P-25 catalyst) and characterized by X-ray diffraction. The effect of TiO_2 loading (0.65 and 1.3 mg), initial BPA concentration (150, 300 and 600 ppb) and initial solution pH (3, 6, 8 and 10) on degradation was studied. The latter was assessed following changes in BPA concentration by means of high performance liquid chromatography equipped with a fluorescence detector. It was found that both catalysts, consisting of about 75:25 anatase:rutile, were equally active in degrading BPA (e.g. 85% reduction at 300 ppb BPA concentration, 180 min of reaction, 0.65 mg catalyst loading and inherent pH) and conversion increase with increasing the TiO_2 loading; however, the P-25 catalyst was considerably unstable at high loadings suffering about 50% active phase dissolution. Conversion decreased with increasing BPA concentration and it was favored in the pH range 6–8. BPA degradation can be approached by a pseudo-first order rate expression with the apparent kinetic constant taking values between 6×10^{-3} and 2×10^{-2} s^{-1}.

1. Introduction

Bisphenol-A (BPA) has been widely used as raw material in the manufacturing of numerous chemical products, such as polycarbonate plastics and epoxy resins. Due to its wide usage and its endocrine disrupting effects, BPA has been regarded as a representative compound, among various endocrine disruptors, which are responsible for reproductive damages to aquatic organisms. For the above reasons, there have been intensive efforts towards the development of efficient, environmentally friendly and low-cost technologies for the degradation of persistent organic pollutants, such as BPA. These efforts include sonochemical [1] and biological treatment [2,3], as well as electrochemical [4] or chemical oxidation [5].

Over the past several years, heterogeneous photocatalysis has received enormous attention for the treatment of various classes of organic contaminants found in waters and wastewaters. Of the various semiconductors, TiO_2 has almost exclusively been employed in environmental applications; the process can exploit the near-UV band of the solar spectrum to excite TiO_2 in contact with water and in the presence of oxygen. The fundamentals of the process can be summarized as follows [6]: the electronic structure of TiO_2, consisting of an empty conduction band and a filled valence band, facilitates the formation of an electron/hole pair when the semiconductor absorbs photonic energy greater than its band gap energy. Holes are strong oxidizing agents and electrons are good reductants, therefore both promote redox reactions. Most organic photodegradation reactions utilize the oxidizing power of holes either directly or indirectly, i.e. through the formation of hydroxyl radicals and other reactive oxygen species.

In recent studies, BPA degradation has been investigated by means of visible [7], UV-A [8,9] and natural solar irradiation [10] over TiO_2 suspensions with emphasis given on the effect of various operating conditions on performance. Enhanced catalytic activity was achieved doping TiO_2 with nitrogen [10,12] or zirconia [12]. The aforementioned studies [7–12] refer to slurry systems that are known to suffer a serious drawback, namely the requirement for separation of the fine catalyst particles from the treated solution. This can be overcome immobilizing the catalyst on suitable supports or carriers; Wang et al. [13] studied BPA degradation by UV-C irradiation over TiO_2 fixed to polyurethane foam cubes, while Nakashima et al. [14] immobilized TiO_2 on PTFE mesh sheets to degrade BPA and other endocrine disrupting compounds under UV-A irradiation.

The aim of this work was to investigate BPA degradation using TiO_2/Ti films under solar irradiation, a versatile and sustainable system that has not been studied before. The effect of various operating conditions such as the catalyst preparation method and loading, BPA concentration and solution pH on conversion have been examined.

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2. Materials and methods

2.1. Catalyst preparation

Immobilized TiO_2 films on Ti substrates were prepared either by a sol–gel procedure [6] or through a commercial Degussa P-25 catalyst and non-ionic surfactant Triton X-100 [polyoxyethylene-(10) isooctylphenyl ether] slurry. The first type of catalyst (called TIP) was prepared by the following procedure: 4.2 g of the non-ionic surfactant Triton X-100 was mixed with 22.8 mL of ethanol, followed by the addition of 3.9 mL of glacial acetic acid and 2.16 mL of titanium isopropoxide under vigorous stirring. Self organization of the surfactant in this original sol creates organized assemblies which act as templates defining nanoparticle size. The surfactant was burned out during calcination. After stirring for a few minutes, a squared shaped titanium substrate (2.4 cm × 2.4 cm) was dipped in the above solution and was withdrawn at a constant speed. The nanocomposite film [15] formed by dipping was left to dry in air for a few minutes and then it was calcined in an oven at 550 °C for 10 min. When the film was taken out of the oven it was transparent and optically uniform. The above procedure was repeated until the appropriate amount of titania was deposited on the Ti substrate. The second type of catalyst (called P-25) was prepared by applying a thin film of a TiO_2 slurry solution (containing 20 mg of Degussa P-25, 10 mL of ethanol and 1 g of Triton X-100) on both sides of the Ti substrate. The film was left to dry in air for a few minutes and then it was calcined in an oven at 550 °C for 10 min. The above procedure was repeated until the appropriate amount of titania was deposited on the Ti substrate. In both preparation methods the titanium substrate was first sandblasted to ensure good adhesion of the deposit on its surface followed by a chemical treatment (using a 1 M oxalic acid solution at the boiling point for 60 min) in order to obtain a totally clean surface. Using the above two procedures, catalysts with two different loadings were prepared (0.65 and 1.3 mg).

2.2. Experimental procedure

Photocatalytic experiments were performed using a solar simulator (Oriel, model 96000) equipped with a 150 W xenon, ozone free lamp in an open cylindrical pyrex cell at ambient conditions under continuous stirring. In a typical experiment, the immobilized TiO_2/Ti was immersed in the 60 mL BPA solution which was kept in the dark under stirring for 20 min in order to achieve air equilibrium and then it was exposed to solar irradiation. If necessary, the inherent solution pH which was slightly acidic (pH of about 6), was adjusted adding the appropriate volume of NaOH or HNO_3 solutions.

2.3. Analytical techniques

Samples were taken for analysis at several irradiation times. Changes in BPA concentration were followed by means of high performance liquid chromatography (HPLC, Waters 2690) equipped with a Luna 54 (18C2) 100A column and two detectors connected in series, namely a diode array detector (Waters 996) and a fluorescence detector (Waters 474). The mobile phase consisted of 65:35 acetonitrile:water at a flow rate of 1 mL min^{-1} and ambient temperature. BPA was monitored by the fluorescence detector, while the diode array set at 280 nm was used to identify possible reaction by-products.

The catalysts were characterized for their phase composition by means of X-ray diffraction using a Philips, PW1830/40 powder diffractometer. Further details concerning the apparatus and the methods used for catalyst characterization can be found elsewhere [16].

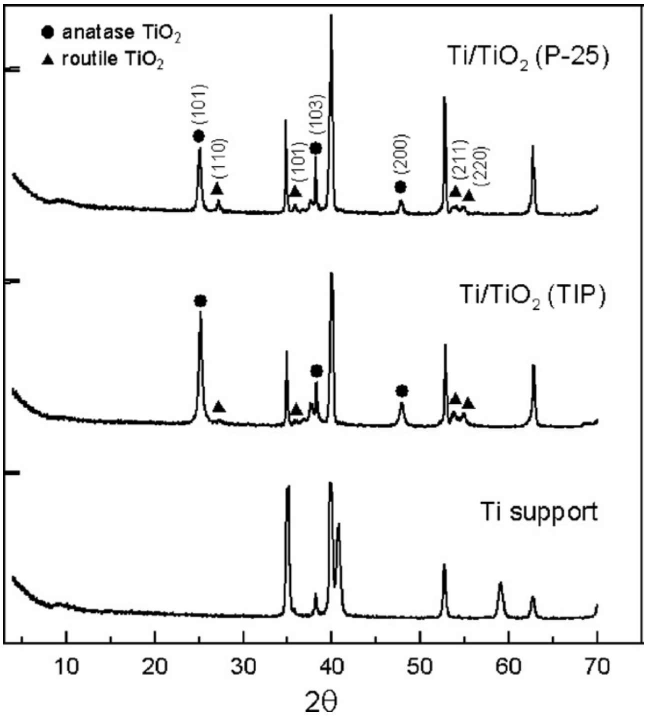

Fig. 1. XRD patterns of P-25 (0.65 mg) and TIP (0.65 mg) films immobilized on Ti support.

3. Results and discussion

3.1. Catalyst characterization

X-ray diffraction (XRD) patterns were collected in the range of 2θ between 20° and 70° with a scanning rate of $0.05^\circ\ s^{-1}$ (Fig. 1). XRD measurements show that TiO_2 films can be successfully developed on Ti substrate using either the slurry or the sol–gel method. TIP as well as P-25 catalysts contain TiO_2 peaks which can be attributed to both the anatase and rutile phases. The phase composition of both TiO_2/Ti types was estimated by the integral intensities of the anatase (1 0 1) and rutile (1 1 0) reflections [17,18] and it was found to be about 75% and 25%, respectively. Based on the data presented in Fig. 1 and applying Scherrer equation it was found that in both cases the size of the crystallites is about $25 \pm 3\ \mu m$.

3.2. Effect of loading and type of TiO_2/Ti

Fig. 2 shows the effect of catalyst loading on BPA degradation for both P-25 and TIP catalysts. It is worthnoting that negligible BPA removal occurs either without catalyst or in the dark regardless the catalyst employed. On the other hand when the system is illuminated, BPA concentration decreases exponentially with time with either catalyst (P-25 or TIP). The low loading (0.65 mg) catalysts appear to be nearly equally active yielding about 85% BPA degradation after 180 min of reaction. However when the loading is doubled, P-25 results in complete BPA degradation after 60 min, while the same conversion can be achieved only after 180 min with TIP. To assess catalyst stability, TiO_2 loading was measured before and after the 180 min-long experiment and the results are shown in Fig. 3. As clearly seen, the films are remarkably stable with the loss of active phase never exceeding 5% of the initial mass. The exception seems to be the high loading P-25 catalyst; in this case, about 50% of the active phase has been dissolved in the reaction mixture at the end of the experiment and this could explain the increased activity observed in Fig. 2 due to the contribution of the leached TiO_2 in

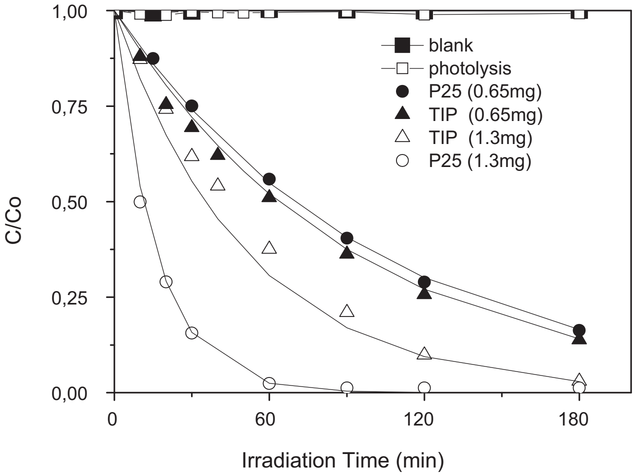

Fig. 2. Variation of normalized BPA concentration in the dark (■) and under solar irradiation with 0.65 mg P-25 (●), 1.3 mg P-25 (○), 0.65 mg TIP (▲), 1.3 mg TIP (△) and without catalyst (□). Other conditions: initial concentration of BPA = 300 ppb; $T = 25^\circ$C; pH: inherent.

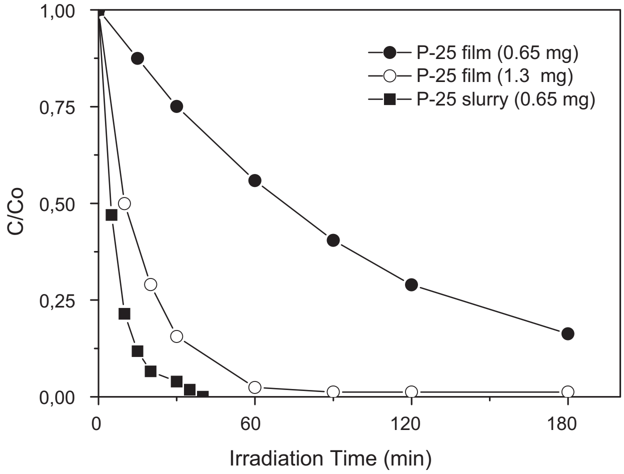

Fig. 4. Variation of normalized BPA concentration under solar irradiation with 0.65 mg P-25 film (●), 1.3 mg P-25 film (○) and 0.65 mg P-25 slurry (■). Other conditions: initial concentration of BPA = 300 ppb; $T = 25^\circ$C; pH: inherent.

the reaction rate. To confirm this hypothesis, an additional run was performed with 0.65 mg P-25 in slurry since this corresponds to the quantity of dissolved P-25 after 180 min. The results are shown in Fig. 4, alongside data of the respective runs with the immobilized P-25 catalyst. It is obvious that the immobilized catalyst leads to far lower conversions than the respective slurry system (e.g. 25% and 97%, respectively after 30 min of reaction at 0.65 mg loading) and, in this respect, the contribution of the dissolved catalyst is expected to be important to the overall rate of reaction. This contribution cannot be precisely quantified though from the data shown in Fig. 4 since leaching is likely to occur progressively throughout the course of the reaction, while in the slurry system the catalyst was added from the beginning in the reaction mixture. Overall, an increase in TiO_2 loading may result in higher photocatalytic activity (as evidenced in the case of TIP) but also in decreased stability (as evidenced in the case of P-25). Due to the greater mechanic stability of low loading catalysts, all subsequent runs were carried out at 0.65 mg TiO_2 loading.

In a fixed catalyst system, the reactant diffuses from the bulk solution through a boundary layer to reach the liquid–catalyst interface. Subsequently, the reactant molecules diffuse through the catalyst layers to locate active sites where they get adsorbed and react. For immobilized photocatalysts, the optimum film thickness depends on the light penetration depth and the width of the space charge layer. An increase of the catalyst loading increases the degradation rate due to more catalyst surface sites being available for reaction. At the same time, there are two likely loss mechanisms within the catalyst films due to the increase of the catalyst layer thickness that will restrict the presence of charge carriers at the interface. One is the attenuation of light due to absorption by the catalyst, and the other is the increased probability of charge carrier recombination presumably due to the increased diffusion lengths through the grain boundaries and constrictions within the microporous film. Within the bulk of the catalyst film, the extinction of light follows the exponential decay [19,20]. As the film thickness increases, at some point the penetration depth of light will be such that most of the electrons and holes are generated relatively close to the solid–liquid interface. The photocatalytic reaction rate will be about maximum at this point. With further increase in the film thickness, the charge carriers are generated relatively far from the liquid–catalyst interface, and consequently, are more susceptible to recombination loss. A further increase of film thickness will lower the photocatalytic reaction rate.

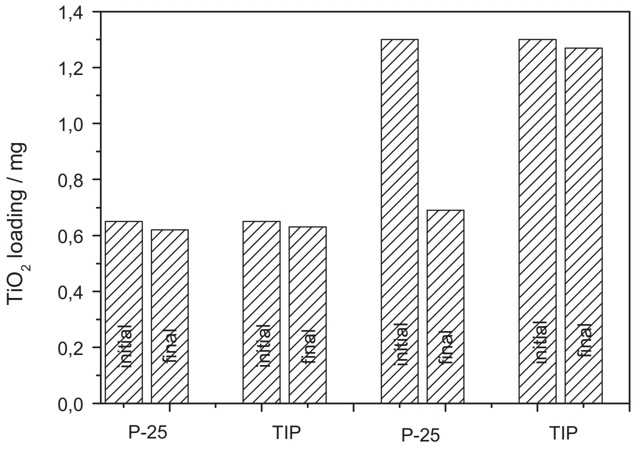

Fig. 3. Stability of P-25 and TIP catalysts. TiO_2 loading before and after 180 min of reaction. Other conditions as in Fig. 2.

3.3. *Effect of BPA concentration*

The effect of initial BPA concentration on degradation was also investigated for the low loading catalysts and the results are shown in Fig. 5. Increasing BPA concentration from 150 to 300 ppb has practically no effect on conversion for either catalyst, while a further increase from 300 to 600 ppb results in decreased conversions; for example, the 180 min conversion at 300 ppb is about 85% for either catalyst and it drops to 60–65% at 600 ppb.

At a constant catalyst loading, performance will be dictated by the catalyst sites to substrate molecules ratio. At relatively low BPA concentrations (i.e. in the range 150–300 ppb at the experimental conditions of this study), catalyst particles are in excess and they can accommodate all BPA molecules. The fact that degradation decreases at higher initial concentrations may be explained by (i) an increase of the molar extinction coefficients due to the formation of several reaction by-products at considerable concentrations, thus absorbing a substantial portion of the emitted radiation, and (ii) less active sites are available at higher BPA concentrations, thus triggering a competitive adsorption onto the catalyst surface which thereby decreases the concentration of hydroxyl radicals and other reactive species attacking BPA [21].

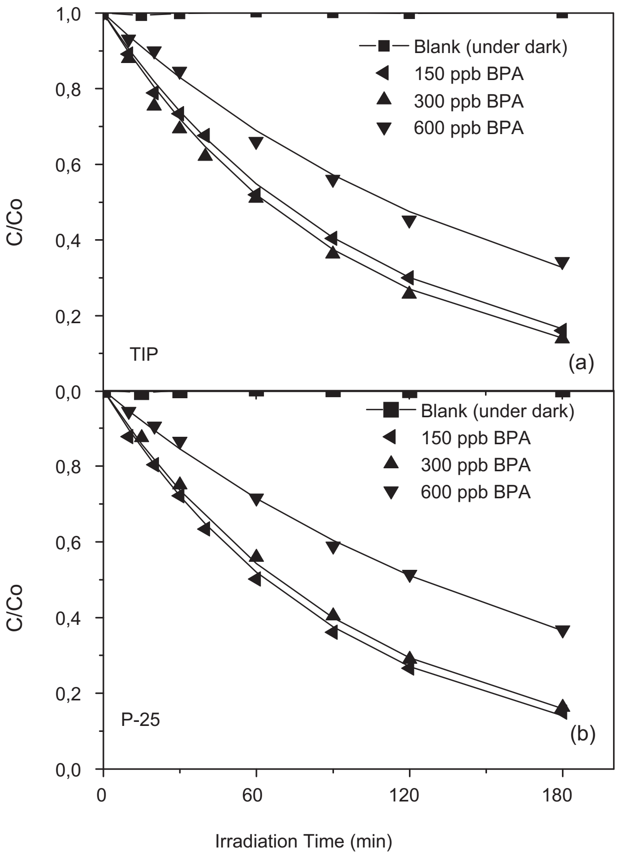

Fig. 5. Variation of normalized BPA concentration in the dark (■) and under solar irradiation with 0.65 mg of (a) TIP and (b) P-25 catalyst at various initial BPA concentrations (150 ppb (◄), 300 ppb (▲) and 600 ppb (▼)). Other conditions: $T = 25\,^{\circ}\mathrm{C}$; pH: inherent.

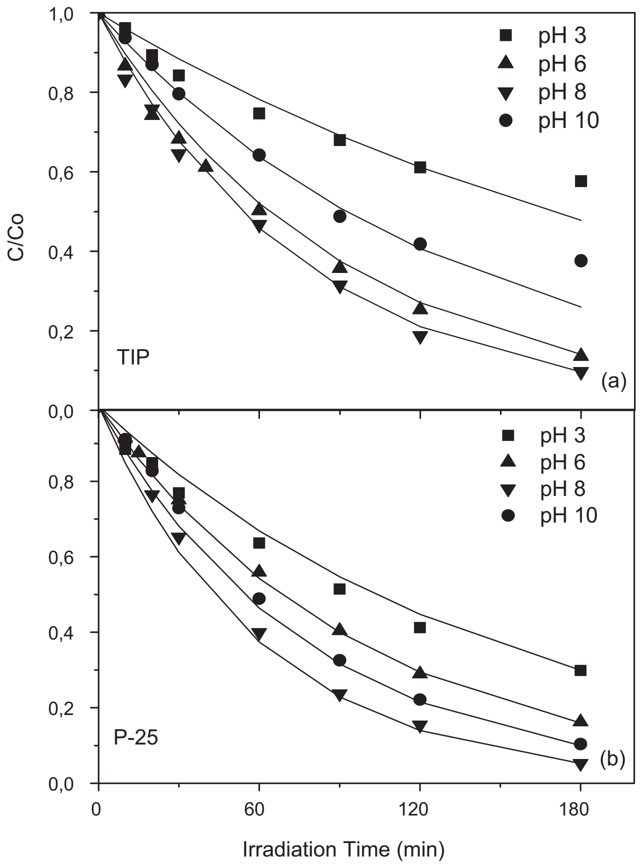

Fig. 6. Variation of normalized BPA concentration under solar irradiation with 0.65 mg of (a) TIP and (b) P-25 catalyst at three different pH values (3 (■), 6 (▲) 8 (▼) and 10 (●)). Other conditions: initial concentration of BPA = 300 ppb; $T = 25\,^{\circ}\mathrm{C}$.

3.4. *Effect of pH*

Several experiments were carried out to investigate the effect of initial solution pH on the photocatalytic degradation of BPA and the results are shown in Fig. 6. For both catalysts, an increase of pH from 3 to 8 results in a substantial increase of BPA degradation. In contrast, a further pH increase from 8 to 10 induces a reduction of the photocatalytic activity. Specifically, the 180 min conversion becomes 42%, 86%, 90% and 62% at initial pH values of 3, 6, 8 and 10, respectively with the TIP catalyst, while the corresponding values with P-25 are 70%, 84%, 95% and 90%. These results are indicative of the significant role of the TiO_2 surface properties. The acid–base property of the metal oxide surface has a considerable influence on the photocatalytic activity with varying pH. The pH effect can be explained on the basis of the zero point charge (zpc) of TiO_2, which generally varies between 3.5 and 6.7 [22]. As a consequence of this amphoteric behavior, the TiO_2 surface is predominantly positively charged below zpc and negatively charged above it. Furthermore, the pK_a value of BPA is 9.6–10.2 [23] which implies that BPA is in its molecular form below pH 9.6, while its ionization to form the bisphenolate anions, BPA^- and BPA^{2-}, occurs at pH values close to 10. Therefore, the low photodegradation rates recorded in highly acidic and alkaline conditions (i.e. pHs 3 and 10) may be due to the adsorption capacity of BPA associated with the electrostatic interactions between BPA and the charged TiO_2 surface. At pH 10, both the catalyst and BPA are negatively charged, and therefore, repulsion will occur. At pH 3, BPA is not charged and this would not facilitate its attraction on the catalyst surface. In addition to the aforementioned arguments, the increased performance recorded at pH 8 may partly be due to the fact that hydroxyl radical formation is favored at alkaline conditions [10].

3.5. *Degradation kinetics*

The Langmuir–Hinshelwood kinetic model has been widely used to describe the kinetics of heterogeneous photocatalytic reactions in aqueous phase [24]:

$$r = -\frac{dC}{dt} = k\frac{KC}{1+KC} \qquad (1)$$

where r is the rate of substrate degradation, k is the intrinsic reaction rate constant and K is the Langmuir adsorption equilibrium constant. For those systems where the substrate concentration, as well as its adsorption onto the catalyst are relatively low (as in the case of BPA), Eq. (1) is reduced to:

$$-\frac{dC}{dt} = kKC = k_{\mathrm{app}}C \Leftrightarrow \ln\frac{C_o}{C} = k_{\mathrm{app}}t \qquad (2)$$

where k_{app} is a pseudo-first order kinetic constant.

If the results of Figs. 2, 5 and 6 are plotted in the form of Eq. (2), straight lines passing through the origin (not shown) fit the experimental data very well (the coefficient of linear fitting, r^2, is always greater than 0.99). From the slopes of the resulting lines, k_{app} values can be computed and they are summarized in Table 1. Depending on the reaction conditions, the rate constant takes values between 6×10^{-3} and $2 \times 10^{-2}\ \mathrm{s}^{-1}$.

The photocatalytic degradation of BPA is likely to occur through the formation of intermediate compounds that will eventually be mineralized to carbon dioxide and water. With the analytical protocols used in this work (i.e. UV and fluorescence

Table 1
Pseudo-first order kinetic constants (k_{app} in s^{-1}) for the photocatalytic degradation of BPA over immobilized TiO_2/Ti-films at various conditions. ND: not determined due to the dissolution of the catalyst.

TiO_2 loading, m_{sp} (mg)	$pH_o = 6/C_o = 300$ ppb	
	TIP	P-25
0.65	0.011	0.01
1.3	0.02	ND

C_o (ppb)	$pH_o = 6/m_{sp} = 0.65$ mg	
	TIP	P-25
150	0.01	0.011
300	0.011	0.01
600	0.006	0.006

pH_o	$m_{sp} = 0.65$ mg$/C_o = 300$ ppb	
	TIP	P-25
3	0.004	0.007
6	0.011	0.010
8	0.013	0.016
10	0.008	0.013

detectors), the determination of reaction by-products was not feasible.

4. Conclusions

The photocatalytic degradation of bisphenol-A, an emerging aqueous phase pollutant, has been investigated by means of solar irradiation over immobilized TiO_2/Ti catalysts. The proposed process is conceptually advantageous since (i) it utilizes renewable energy, thus promoting sustainability, and (ii) catalyst immobilization on a solid matrix enables its easy recovery at the end of the treatment. The major conclusions drawn from this study are summarized as follows:

(1) Semiconductor photocatalysis driven by solar light is an efficient method for the degradation of BPA in aqueous solutions. Process performance is affected by several factors, namely irradiation time, photocatalyst type and loading, BPA concentration and the solution pH.
(2) The stability of immobilized catalysts is a key parameter and it is affected by the preparation method, as well as the active phase loading. A catalyst prepared by a sol–gel method was highly stable regardless the active phase loading (i.e. 0.65 or 1.3 mg) employed, while a catalyst prepared by deposition of a commercially available Degussa P-25 precursor suffered serious leaching at increased loadings. The latter not only compromises catalyst integrity but also alters the kinetics due to the contribution of the dissolved catalyst.
(3) BPA degradation follows pseudo-first order kinetics. Higher conversions are achieved at lower concentrations. Since the levels of BPA in environmental samples are relatively low (even lower than those employed in this work), degradation is likely to occur readily at mild operating conditions. Moreover, BPA degradation is favored in the pH range 6–8 which is typical of real water/wastewater matrices.

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