

Selective solar photodegradation of organopollutant mixtures in water

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Abstract

Heterogeneous photocatalysis in a water solution is recognised as a method of totally eliminating most recalcitrant organic pollutants found in such solutions. Our current work has tried to show that the heterogeneous photocatalysis process can also be a selective elimination method in the case of the mixture: 4-hydroxybenzoic acid (4-HBz) and benzamide (Bz) at semi-pilot plant scale (190 dm³) under conditions of solar irradiation. The photocatalysis experiments performed by us were done at the “Plataforma Solar de Almería” and were carried out in the compound parabolic collectors’ CPC system. We investigated in particular the influence of TiO₂ loading, the effect of 4-HBz concentration and the effect of the presence of chloride anions and pH on the selectivity of the reaction process.

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1. Introduction

During recent decades, the photocatalytic degradation of various toxic organic compounds (particularly organochlorides and nitrogenous compounds) has been proposed as a viable process to detoxify drinking water (Mills and LeHunte, 1997; Bahnemann, 1999; Pichat, 1997; Robert, 2003). Consequently, the number of publication references and patents related to solar heterogeneous photocatalytic removal of toxic and hazardous compounds from water and air can be counted in thousands (Blake, 1999). Irradiating pulverulent semiconductors like TiO₂ in suspension or fixed to various support in aqueous solutions containing organic pollutants, has been shown to be capable of creating a redox environment which is able to destroy such pollutants.

Titanium dioxide has been demonstrated to be an excellent catalyst and its behaviour is very well documented in the literature. Since oxidation is governed by a free radical mechanism, it is expected to behave in a non-selective manner. Indeed, it was found (Matthews, 1986) that the degradation rate of a large variety of molecules is approximately the same, provided that these molecules are adsorbed on the surface of the photocatalyst. Our current work tries to show that such a heterogeneous photocatalysis can also be a selective elimination method of certain organic pollutants in water. This approach places us a little against the current of the present thinking, which regards photocatalysis as a method of total elimination of most recalcitrant organic pollutants.

In a previous paper (Robert et al., in press), we mentioned that a very small number of studies showed the selectivity of photocatalysis in water decontamination processes. More recent study has focussed upon selective physisorption of the contaminants in the vicinity of titanium dioxide micro-domains, followed by

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surface-diffusion of the contaminants to the photocatalytic sites (Ghosh-Mukerji et al., 2003).

At laboratory scale (volume of contaminated solution: 0.3 dm³) and under artificial irradiation (xenon lamp), we were able to demonstrate the feasibility of this approach in the case of a benzamide and 4-hydroxybenzoic acid mixture (Robert et al., in press; Piscopo, 2002). We showed, in the case of this binary mixture, that it was possible to degrade one molecule without any concentration change in respect of the other molecule. With appropriate modifications of two parameters (pH and TiO₂ concentration), it is also possible to improve the selectivity.

The aim of our current work is to demonstrate the selective photocatalytic degradation of organocompounds at semi-pilot plant scale (190 dm³) under solar irradiation for the mixture: 4-hydroxybenzoic acid (4-HBz) and benzamide (Bz). Photocatalysis experiments at “Plataforma Solar de Almería” were carried out in the compound parabolic collectors CPC system. In this experiment we looked particularly at: (1) the influence of TiO₂ loading; (2) the effect of 4-HBz concentration; and (3) the effect of the presence of chloride anions and pH on the selectivity of the reaction observed.

2. Configuration of experiment

The configuration of the photoreactor was one commonly-used in heterogeneous photocatalysis work, viz.: a plug flow reactor in a total recirculation loop with a non-reacting tank whose function is to provide aeration and samples for analyses. The photoreactor consisted of CPC modules in series (total irradiated surface: 6 m²) placed on fixed supports inclined 37° (latitude of the PSA site) from the horizontal plane and facing South, in order to maximise the daily absorption of solar radiation.

The plug flow photoreactor (PFP) consisted of UV-transparent glass tubes (i.d. 29.2 mm). All the tubes and the collectors were connected in series and the aqueous suspension was continuously fed to the PFP from the non-reacting tank by means of a centrifugal pump. The suspension flow rate, maintained constant for all of the runs, was 0.97 dm³ s⁻¹. The total volume of aqueous suspension loaded into the whole system was 190 dm³, whereas the irradiated volume, i.e. the volume of suspension contained in the glass tubes, was 72 dm³. The initial concentrations of 4-HBz and Bz were 0.2 mmol l⁻¹. For all the photoreactivity experiments polycrystalline TiO₂ (Degussa P25, ≈80% anatase and 20% rutile, BET surface area ≈50 m² g⁻¹) was used. The catalyst amount was in the 0.2–2 g l⁻¹ range.

The experimental runs were carried out by using the following procedure: firstly, the aqueous suspension containing the mixture of organic compounds and the

TiO₂ powder was made to circulate in the reacting system while keeping the collectors without irradiation by covering them with tarpaulins. After 30 min the tarpaulins were removed and the reactivity run was started. Samples were withdrawn at the start of irradiation and at fixed intervals of time from the non-reacting tank so that they were representative of the conditions at the inlet of the PFP. Further experiments were carried out by adding NaCl (10 g l⁻¹).

The quantitative determination of 4-HBz and Bz was routinely performed by reverse-phase liquid chromatography with UV detection (365 nm) using a HPLC-UV instrument (Hewlett-Packard, series 1050, standard deviation <2% of calibration curve) equipped with a C-18 column (LUNA 5 micron-C-18, 3×150 mm from Phenomenex). A mixture of acetonitrile and water 10/90 v/v, was used as the eluent. All the reagents were of analytical grade (Fluka).

A total organic carbon (TOC) analyser (5050A Shimadzu, standard deviation <2% of calibration curve) was used in order to determine the TOC content of the samples. Oxygen needed for the photoreaction was derived from the contact of the aqueous suspension with the atmospheric air in the non-reacting tank.

The results obtained in pilot scale testing, using the periods recorded as experimental time, are not to be considered indicative of real-life results because: (i) the reactor consists of exposed and non-illuminated elements and (ii) the intensity of solar radiation depends on the season, the time of day and the weather. Since it is not possible to work in conditions of constant illumination under sunlight, it is convenient to use a mathematical approach to process the data obtained in real solar experiments. In this work the relationships used were between experimental time (t_n), plant volume (V_i), collector surface (A_r) and the radiant power density ($UV_G = W_{UV}/m^2$) measured by the radiometer (KIPP & ZONEN, model CUV3, 2% accuracy (data of the supplier)). The kinetics of our outdoor experiments were determined by plotting the organic compound concentration as a function of accumulated energy ($Q_{UV,n}$) by photoreactor (instead of experimental time). Using bases established by Malato et al. (2000), the following Eqs. (1) and (2) were applied:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t \cdot UV_{G,n} \cdot \left(\frac{A_r}{V_i} \right) \quad [\text{J/l}] \quad (1)$$

$$\Delta t = t_n - t_{n-1} \quad [\text{s}] \quad (2)$$

3. Results and discussion

We chose the mixture Bz/4-HBz acid for different reasons: (1) we know the influence of the pH and C_{TiO_2}

on the reaction rate of each individual compound (Piscopo et al., 2001); (2) the affinity of these two compounds with the TiO_2 surface is very different from each other. In these experimental conditions no significant adsorption of Bz at the surface of TiO_2 was detected. On the contrary, in the case of 4-HBz, we observe a strong chemisorption at the semiconductor surface (Piscopo et al., 2001); and (3) the degradation rates are relatively fast and easy to measure.

3.1. Influence of C_{TiO_2} on the photodegradation of 4-HBz/Bz solutions

We observed the same effect of TiO_2 loading as in the laboratory scale testing (Figs. 1–3). For all experiments, the initial pH was in the range 5–6 and we noted few variations during the processes. For Figs. 2 and 3, the concentration of 4-HBz is less than 100% at the time point zero, because there is adsorption of acid at the surface of the TiO_2 .

At a low concentration of TiO_2 (0.2 g l^{-1}), the rates of photodegradation for both compounds are similar (Fig.

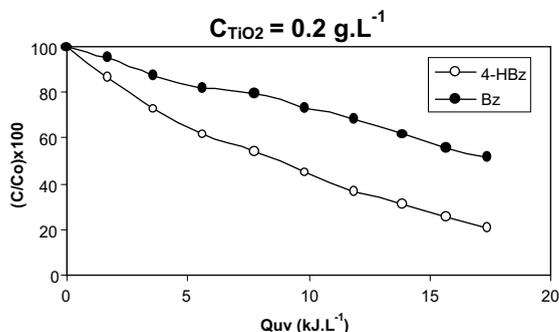


Fig. 1. Photodegradation of mixture of $[\text{Bz}] = [\text{4-HBz}] = 0.2 \text{ mmol l}^{-1}$ with $C_{\text{TiO}_2} = 0.2 \text{ g l}^{-1}$ versus accumulated energy.

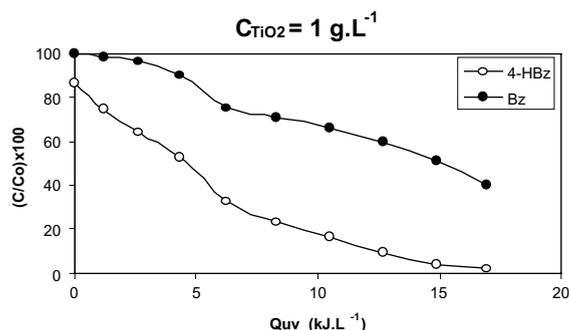


Fig. 2. Photodegradation of mixture of $[\text{Bz}] = [\text{4-HBz}] = 0.2 \text{ mmol l}^{-1}$ with $C_{\text{TiO}_2} = 1 \text{ g l}^{-1}$ versus accumulated energy.

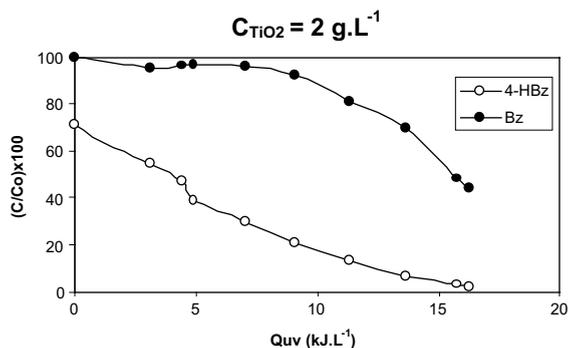


Fig. 3. Photodegradation of mixture of $[\text{Bz}] = [\text{4-HBz}] = 0.2 \text{ mmol l}^{-1}$ with $C_{\text{TiO}_2} = 2 \text{ g l}^{-1}$ versus accumulated energy.

1) and no selectivity is noted. If we increase the photocatalyst concentration (Figs. 2 and 3), we observe a significant difference in the behaviour of the organo-compounds in relation to the photocatalytic degradation.

At $C_{\text{TiO}_2} = 2 \text{ g l}^{-1}$, Bz degradation begins when 80% of the 4-HBz were eliminated. These results can be explained in the following way: the acid is adsorbed at the TiO_2 surface which will prevent the Bz degradation. If the TiO_2 concentration increases, the quantity of 4-HBz adsorbed increases as well as its photodegradation rate (For $C_{\text{TiO}_2} = 2 \text{ g l}^{-1}$, and for 8 kJ l^{-1} of accumulated energy, we eliminated 15 times more acid than Bz). In our case, these phenomena may be due to the competition between Bz and 4-HBz for surface sites of TiO_2 or free hydroxyl radicals, and 4-HBz proves to be a stronger competitor than Bz.

We determined the mineralisation kinetics of the mixture by Total Organic Carbon analysis for the three concentrations in TiO_2 . It is interesting to note that the evolution of the kinetics shows two distinct domains. At the beginning of the reaction, there is only degradation of the acid. The acid is quickly mineralized (decarboxylation, hydroxylation of aromatic ring and finally ring opening) (Pichat et al., 1992). In the second phase, there is a simultaneous degradation of Bz and acid. However the kinetic of amide mineralisation is slower, which explains the shallower slope (Piscopo et al., 2001).

3.2. Influence of 4-HBz concentration

We divided by 2 the molar concentration of the acid (0.1 mmol l^{-1}) compared to the Bz (0.2 mmol l^{-1}) concentration so as to evaluate the influence of the 4-HBz concentration. However the results obtained do not show any significant evolution of the “selectivity” of the treatment (Fig. 4) compared to an equimolar mixture (Fig. 2).

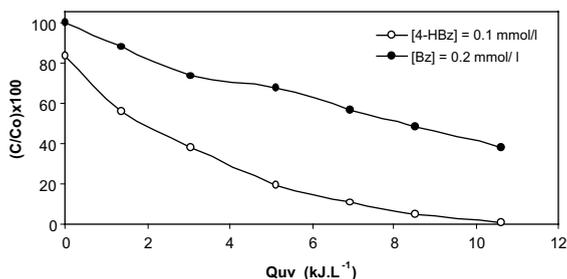


Fig. 4. Photodegradation of mixture of $[4\text{-HBz}] = 0.1 \text{ mmol l}^{-1}$ and $[\text{Bz}] = 0.2 \text{ mmol l}^{-1}$ with $C_{\text{TiO}_2} = 1 \text{ g l}^{-1}$ versus accumulated energy.

3.3. Effect of chloride anions

Many wastewaters contain a variable concentration of inorganic ions in particular chloride. For this reason we have determined the effect of the Cl^- concentration on the photocatalytic degradation of the 4-HBz/Bz mixture. In the previous works (Piscopo et al., 2001), we studied the influence of Cl^- at different concentrations in the case of each of 4-HBz and Bz alone in water solution. In our experimental conditions, the initial pH was in the range 5–6. In these conditions the pH is inferior to the pH_{zpc} of $\text{TiO}_2\text{-P25}$ (pH to the zero point charge = 6.3) and the photocatalyst surface is weakly positive due to the predominant species TiOH_2^+ . We showed that the rates of degradation of both Bz and 4-HBz are functions of chloride concentrations. It is interesting to note that the behaviours of Bz and 4-HBz are noticeably different.

The rate of degradation of 4-HBz is only slightly related to the level of chloride concentration in the aqueous solution. This observation can be explained by reference to the basis of adsorption of 4-HBz. It is well known that the presence of chloride leads to the desorption of organic acids (Chen et al., 1997). It can be assumed that degradation occurs on the adsorbed carboxylate (Robert et al., 2000; Cunningham and Al-Sayyed, 1990; Wang et al., 2000), in one way directly by holes or indirectly by OH° formed by reaction with adsorbed water molecules. To resume, the higher the amount of surface carboxylate, the higher the rate of degradation.

By contrast, the degradation of Bz is strongly affected by the concentration of chloride ions. At pH 5–6, TiOH_2^+ and TiOH were the main functional groups on the catalyst surface, and the chloride ions competed with organic species for active sites and reduced the reaction rate. Chloride ions competed with oxygen for electron, which reduced the formation of superoxide radicals and then blocked the chain reaction for hydroxyl free radicals.

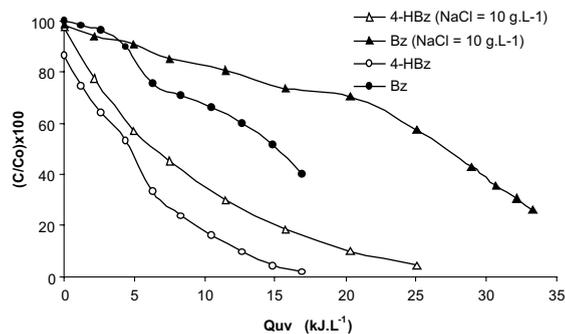


Fig. 5. Photodegradation of mixture of $[4\text{-HBz}] = [\text{Bz}] = 0.2 \text{ mmol l}^{-1}$ with $C_{\text{TiO}_2} = 1 \text{ g l}^{-1}$ with and without presence of $C_{\text{NaCl}} = 10 \text{ g l}^{-1}$ versus accumulated energy.

In the case of the aqueous mixture, we observed a significant decrease of degradation rate for both molecules (Fig. 5). However, it seems surprising to note that the “selectivity” of the reaction is very little influenced by a strong concentration of chloride anions. We showed that the kinetics of Bz degradation were much more sensitive to the presence of chlorides (Fig. 5), but this is not sufficient to improve the selectivity of the process.

3.4. pH effect at the laboratory scale

Before studying the influence of the pH on the selectivity, it is necessary to recall the pH effect on the photodegradation rate of pure solution of Bz or 4-HBz (Piscopo et al., 2001, Table 1). In the degradation of 4-hydroxybenzoic acid, the pH has a strong effect. Two phenomena have to be taken into account: (1) the adsorption via surface carboxylate or phenolate formation, because at pH levels lower than the pH_{zpc} of TiO_2 , the higher the adsorption, the higher the degradation; (2) at higher pH values, the change of surface charge of TiO_2 leads to a supplementary repulsive phenomenon lowering the degradation of the ionic state of 4-HBz in the carboxylate form. However, for a non-adsorbed molecule like Bz, the rate of degradation increases very

Table 1
Pseudo-first-order rate constants k' (min^{-1}) for Bz and 4-HBz at different pH with $[\text{TiO}_2] = 1 \text{ g l}^{-1}$

Benzamide		4-Hydroxybenzoic acid	
pH	k'	pH	k'
3.4	0.0298	4.2	0.0352
5.7	0.0313	5	0.0178
7.8	0.0323	5.5	0.0160
9	0.0329	6.2	0.0146
		7	0.0110
		9.4	0.0089

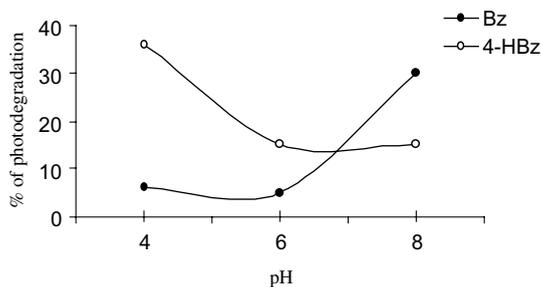


Fig. 6. pH effect on the photodegradation of mixture of [4-HBz]=[Bz]=0.2 mmol⁻¹ with C_{TiO_2} = 1 g l⁻¹ after a 60 min irradiation.

little across the range of pH levels (Table 1). In conclusion, the pH effect on both molecules is very different.

The pH effect on the selectivity of the reaction has been studied only at the laboratory scale with a xenon lamp. It is summarized in Fig. 6.

At pH 4, we obtain a good selectivity (after a 60 min irradiation, 6 times more acid than Bz is degraded). At pH 6, the degradation rates for both products are similar. At pH 8, there is an inversion of the selectivity since Bz degrades at twice the speed of the acid. We can explain this situation by the fact that if we change the pH, the surface charge of TiO₂ also changes. Between pH 4 and 8, there is no variation of the degradation rate of Bz pure solution. However, for the pure solution of 4-HBz the degradation rate is divided by 3.5 (Table 1). In the aqueous mixture, the presence of pH at different ranges affects only the 4-HBz degradation. Theoretically in this case, we will be able to choose the molecule that we want to eliminate.

4. Conclusion

These results, at the semi-pilot scale under natural irradiation, are very promising. We showed that the selective treatment of wastewater is possible in defined conditions. In the case of the binary mixture of Bz and 4-HBz, we can draw the following conclusions:

- If we increase C_{TiO_2} , the selectivity increases.
- By altering the pH range it is possible to prioritise the degradation of one or the other of the two products.
- If we added chloride anion, we observed a significant decrease of degradation rate for both molecules, but no influence on the selectivity of the reaction.

These results confirm our first study at the laboratory scale using artificial illumination. The perspectives for the follow-up to this study are to evaluate the influence of other parameters like the crystalline structure of

photocatalysts and their specific surface properties. In the case of a possible semi-industrial application of this process, it will be necessary to evaluate the effect of the supported titanium dioxide on different supports.

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