ELSEVIER

Applied Catalysis B: Environmental 35 (2001) 117–124

APPLIED CATALYSIS B: ENVIRONMENTAL

www.elsevier.com/locate/apcatb

Influence of pH and chloride anion on the photocatalytic degradation of organic compounds Part I. Effect on the benzamide and *para*-hydroxybenzoic acid in TiO_2 aqueous solution

Antoine Piscopo, Didier Robert*, Jean Victor Weber

LCASPP-Environnement et Procédés Propres, Université de Metz, IUT — rue Victor Demange, 57500 Saint-Avold, France

Received 28 January 2001; received in revised form 22 July 2001; accepted 22 July 2001

Abstract

In the present work, we have studied the influence of pH (in the range 3–11) and chloride anions (in the range 0–0.8 mol/l) on the photocatalytic degradation (PCD), with titanium dioxide (TiO_2), in aqueous solution of two aromatic compounds: benzamide (BA) and *para*-hydroxybenzoic acid (4-HBZ). No significant adsorption is detected for the BA; further the pH input has a very low effect on this photodegradation rate. However, the pH effect on the adsorption of 4-HBZ on TiO_2 surface is significant and this is a factor to take into account in relation the photocatalytic decomposition of organic pollutants in water. For this compound, the degradation rate increases when the pH decreases. The effect of the pH on the degradation rate of 4-HBZ is not only dependent on the TiO_2 charge surface but also on the formation of hydroxyl free radicals. At low chloride concentration, the behaviours of BA and 4-HBZ are sensitively different ($[Cl^-] < 0.02$ mol/l). 4-HBZ is only weakly dependent on the chloride concentration. By contrast, the degradation of BA is strongly affected by the chloride ions concentration. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Titanium dioxide; Benzamide; *para*-Hydroxybenzoic acid

1. Introduction

The heterogeneous photocatalysis for total oxidation of organic and inorganic water and air pollutants has been studied extensively during the last 20 years [1–6]. Irradiation of semi-conductors like titanium dioxide (TiO_2) in suspension or fixed to various supports, in aqueous solutions containing organic pollutants, creates a redox environment which is able to destroy these pollutants. Many researchers [1–4] have shown that most organochloride compounds as well as many pesticides, herbicides, surfactants and colourings are completely oxidised into mineralised products like carbon dioxide, hydrochloric acid and water.

In the case of the biological treatment of groundwater from contaminated landfills some important problems are observed because of specific toxic substances (e.g. polysubstituted aromatic compounds) and/or biologically recalcitrant compounds (like humic acids, dyes, surfactants, polymers, ...) present in wastewater [7]. In order to avoid the failure of

* Corresponding author. Tel.: +33-3-87-939100; fax: +33-3-87-939101.
E-mail address: didier.robert@iut.univ-metz.fr (D. Robert).

0926-3373/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0926-3373(01)00244-2

biological process, a pre-treatment needs to be introduced to reduce the amounts of strong pollutants and to increase the level of biodegradable carbon in water. Photocatalytic degradation (PCD) (with solar or artificial irradiation) of the leachates could be used with this aim. However, the leachates from municipal landfills have changeable compositions depending on the age and construction of the landfills, the morphology of collected wastes and climate conditions [8]. In the beginning, when only the acid phase of waste decomposition occurs there are mainly volatile acids in leachates. These compounds are easily biodegradable. But after a few years, a methanogenic phase begins and volatile acids start to disappear. Their place is taken by humic and fulvic acids, and the non-biodegradable toxic xenobiotic substances are also present. These compounds are resistant to biodegradation.

Beside non-degradable organic compounds, the leachates contain very high concentrations of nitrogen ammonia, organic nitrogen, sulphates (amount depends on the age of the landfill) and chlorides [8]. For this reason, in the present work, we have examined the influences of pH (in the range 3–11) and chloride anions (in the range 0–0.8 mol/l) on the PCD with TiO_2 in aqueous solution of two representative aromatic compounds: benzamide (BA) and *para*-hydroxybenzoic acid (4-HBZ).

2. Experimental

2.1. Materials

BA and 4-HBZ were supplied by Fluka at highest available purity and TiO_2-P25 from Degussa Corporation (70% anatase, 99.8% purity, average particle size 30 nm and specific surface of 50 m^2/g) was used as received. The chemicals purchased to assist in high performance liquid chromatography (HPLC) analysis were obtained from Fluka. Milli-Q water was used throughout for the preparation of aqueous solutions or as a component of the mixed water–acetonitrile (HPLC grade) mobile phase in HPLC analysis.

2.2. Evaluation of the photocatalytic activity

Experiments were carried out in a Solar box ATLAS SUNTEST CPS+ simulating natural radiation. The light source was a vapour Xenon lamp (300 nm $< \lambda <$ 800 nm).

2.3. Procedure and analysis

For determining pH effect on the catalyst adsorption, all batch equilibrium experiments were conducted in the dark. Measurements were made on suspensions prepared by mixing 40 ml solutions of 4-HBZ or BA (with [pollutant] = 20 mg/l) at natural pH (between pH 5 and 5.5) with a fixed amount of TiO_2-P25 (1 g/l). Preliminary experiments [9] performed during 24 h under constant magnetic stirring have demonstrated that equilibrium is reached after 2 h. The equilibrium concentrations were determined using HPLC after centrifugation and filtration of the suspension through Millipore filters (0.45 μm diameter). The concentration of each compound in the clear filtrate was determined by HPLC (Waters 600 pump and 996 photodiode array detector, C-18 apolar column and acetonitrile (10%) water (90%) mixture as mobile phase). For the DRIFT experiments, the detailed procedure is shown in [9].

Concerning the determination of the PCD kinetic, the initial concentration of each organic compound was 20 mg/l and the time zero is the beginning of irradiation. For all experiments, the photocatalyst concentration is 1 g/l. The volume is 400 ml and 80 cm^2 for the illuminated surface at 20°C. The BA and 4-HBZ concentrations at different irradiation times were followed by HPLC after filtration. The pH of the solution was adjusted after TiO_2 addition with an appropriate volume of 0.1 mol/l NaOH or HCl solutions ($3 <$ pH < 11). For the experiments with chloride ions, we added a suitable amount of NaCl.

3. Results and discussion

3.1. Adsorption of BA and 4-HBZ on the TiO_2 surface

In previous works [9], we have demonstrated that the adsorption of phenols on the TiO_2 surface and at low concentrations followed the Langmuir equation (Fig. 1). However, increasing the concentration leads to a complex situation and for the multilayer adsorption to occur it has to be invoked as suggested by

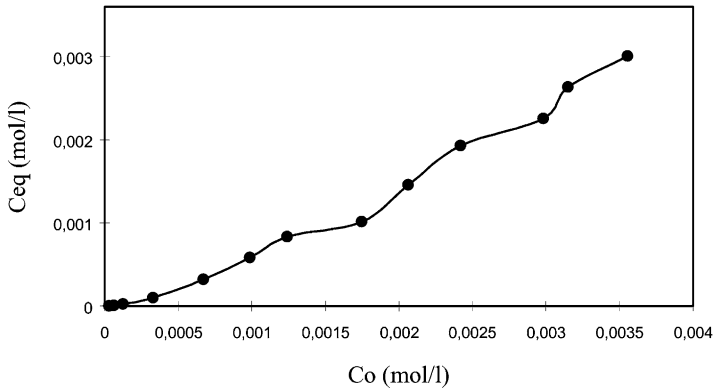

Fig. 1. Adsorption isotherm for 4-HBZ ($TiO_2 = 10$ g/l, natural pH (5.6), C_0: initial concentration of 4-HBZ, C_{eq}: equilibrium concentration of pollutant remaining in the bulk solution phase after equilibrium).

several authors [10–12]. For the 4-HBZ, the adsorption (chemisorption) is fast via titanium carboxylate and phenolate formation. It seems that this bifunctional compound gives a bidendate [10,11].

In our conditions, no significant adsorption of BA is detected in the pH range of 3–11. On the contrary, the pH seems to be a critical parameter for the adsorption of 4-HBZ (Fig. 2). In the pH range 4 to 5, the adsorption is at a maximum close to 0.02×10^{-3} mol g of TiO_2. At lower pH values, due to HCl addition, chloride ions compete with 4-HBZ and logically the adsorption decreases [13]. At pH higher values, thus, 5 unit, 4-HBZ ($pKa = 4.48$) is in ionic form and lead to a decrease of adsorption. Furthermore, at pH values higher than the pH_{zpc} of TiO_2 (6.3), the adsorption decreases drastically. In these conditions, the TiO_2 surface is globally negative and the ionic repulsion could explain these results [14]. The DRIFT study of TiO_2 after equilibrium (without illumination) in different pH lead to the following conclusions (see Fig. 3).

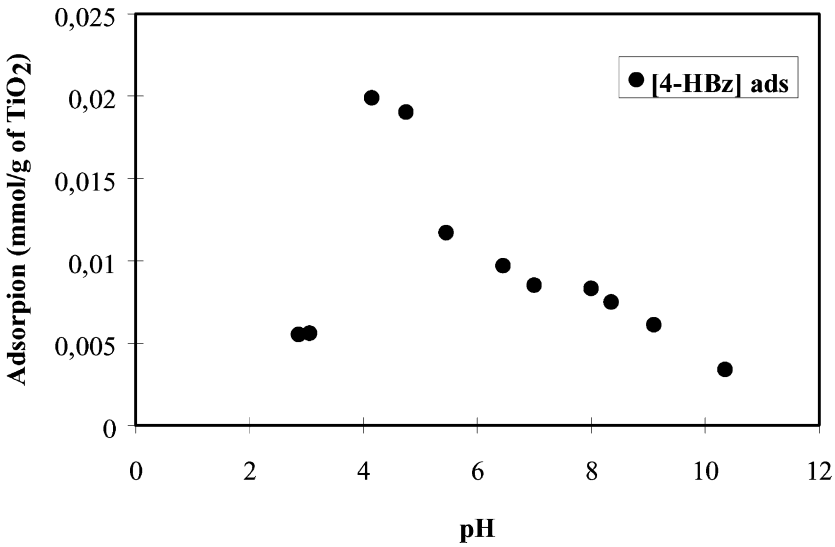

Fig. 2. Influence of the pH on the adsorption of 4-HBZ with an experimental condition of photodegradation (4-HBZ = 0.14 mM and $TiO_2 = 1$ g/l).

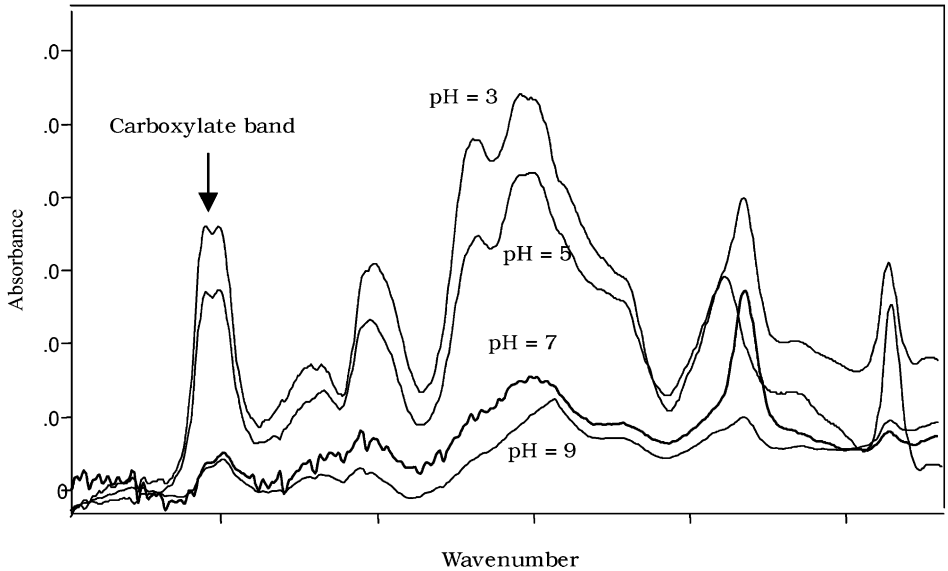

Fig. 3. DRIFT spectra of 4-HBZ at different pH.

1. Whatever the pH values, the adsorption is characterised by surface carboxylate formation.
2. Depending on the pH value, the amount of adsorbed 4-HBZ changes, but no evolution of IR spectra is observed.

To summarise, in the studied pH range 3–11, the adsorption of BA cannot be evidenced (in our conditions) and the adsorption of 4-HBZ is strongly connected with the pH values. In this last case, whatever the pH adsorption proceeds via carboxylate formation.

3.2. Photocatalytic degradation of BA and 4-HBZ with TiO_2

Whatever the pH value in the range 3–11, we verify that illumination without TiO_2 does not lead to BA or 4-HBZ degradation.

3.2.1. Influence of pH on the photodecomposition

The evolutions of pseudo-first-order rate constant for BA and 4-HBZ according to the pH are given in Figs. 4 and 5 and Table 1. In the case of BA, there is a slight increase of the rate of degradation commensurate with the increase in pH value. On the contrary, the kinetic of 4-HBZ degradation is strongly affected by the pH. There are two fundamental differences in the behaviour of BA and 4-HBZ:

1. BA is in the molecular form in all the studied pH range, on the contrary 4-HBZ is in the dissociated state at pH higher than pH = 4.48.
2. BA is not adsorbed on TiO_2.

It is well known that the surface of TiO_2 is amphoteric and consequently, the charge of surface is pH-dependant [15]. For the TiO_2-P25, the pH_{zpc} is close to 6.3.

The mechanisms of BA degradation are described in the literature [16]. The first step is the hydroxylation of BA by reaction with $OH^{\bullet}$. Whatever the pH, it seems that the hydroxybenzamides are always produced (as evidenced by HPLC), consequently, $OH^{\bullet}$ is the oxidant and $OH^{\bullet}$ production is not a function of the surface state of TiO_2.

The opposite behaviour of 4-HBZ can be explained both by the evolution of adsorption (versus pH) and the change of the molecular form (according to the pH). It was observed that the degradation of 4-HBZ is a function of specific area of TiO_2 for pH lower than the p*K*a (and pH_{zpc}) [9]: the higher the degradation, the higher the degradation in similar conditions. The evolution of the degradation at pH lower than pH_{zpc} can be explained on this basis. At higher pH, the pH_{zpc}, a second factor plays an important role:

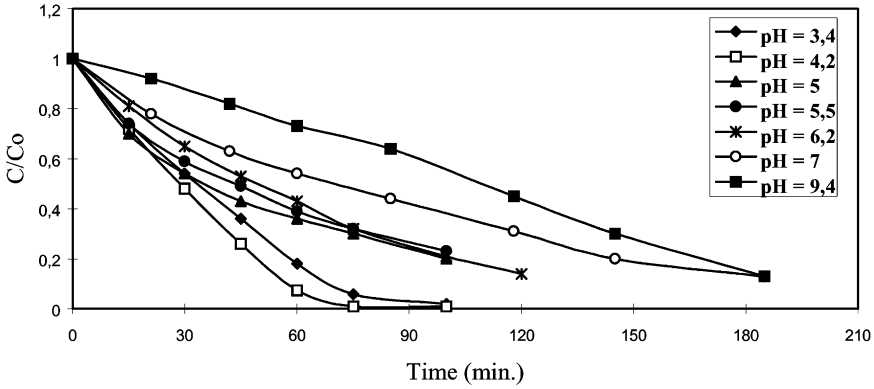

Fig. 4. Photodegradation of 4-HBZ at different pH (4-HBZ = 0.14 mM and TiO_2 = 1 g/l).

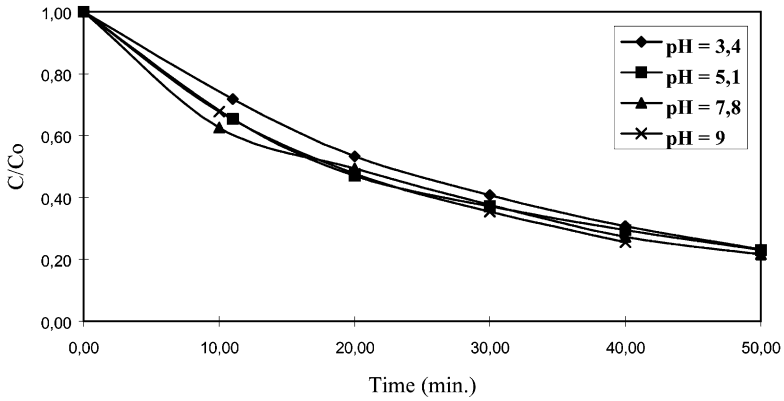

Fig. 5. Photodegradation of BA at different pH (BA = 0.16 mM and TiO_2 = 1 g/l).

Table 1
Pseudo-first-order rate constants k' (min^{-1}) for BA and 4-HBZ at different pH

BA		4-HBZ	
pH	k'	pH	k'
3.4	0.0298	3.4	0.0256
5.7	0.0313	4.2	0.0352
7.8	0.0323	5	0.0178
9	0.0329	5.5	0.0160
		6.2	0.0146
		7	0.0110
		9.4	0.0089

the repulsion of carboxylate ion by the TiO_2 surface [17]. This leads to the observed decrease of the photodegradation (Fig. 6).

To summarise, if no adsorption occurs, no change in molecular state versus pH, there is slight evolution of degradation kinetic. Apparently, the mechanisms do not change and $OH^{\bullet}$ production is independent of TiO_2 surface state. Having in mind, that $OH^{\bullet}$ production can be explained by several ways, and is in some cases pH-dependent, it is difficult to propose a balance between all the pathways proposed in the literature [1–5].

For acidic organic molecule (acids or phenols), two phenomena have to be taken in account: (1) the adsorption, via surface carboxylate or phenolate [9,10,17] formation: at pH lower than the pH_{zpc} of TiO_2, the higher the adsorption, the higher is the degradation; (2) at higher pH values, the change of surface charge of TiO_2 leads to a supplementary repulsive phenomena lowering the degradation of the ionic state of 4-HBZ.

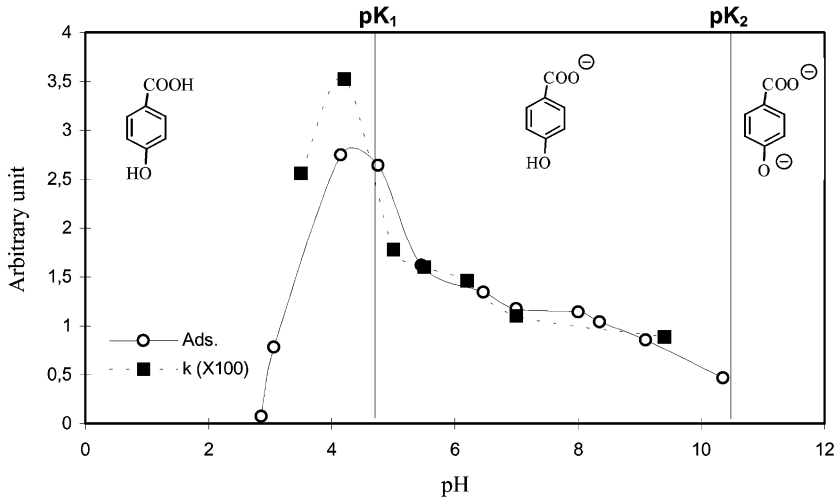

Fig. 6. Comparative evolution of adsorption and rate constant according to the pH.

3.2.2. *Influence of the chloride anions*

The leachates from contaminated landfills contain a variable concentration of inorganic ions in particular chloride. For this reason, we have determined the effect of the Cl^- ion concentration on the photocatalytic rate of organic compounds degradation. In the previous works, the authors have shown that the influence of the anions are dependent on the pH of the aqueous solution [13,14]. The study by Wang et al. [17] indicated that at pH 3, the Cl^- ions are strongly adsorbed on the TiO_2 surface and reduce the photodegradation rate. At neutral or alkaline conditions, the addition of Cl^- ion did not influence the reaction. The authors report that the main explanation is the acid/base properties of TiO_2-P25 surface (adsorption with $TiOH_2^+$ at low pH and repulsion of Cl^- ion by TiO^- at basic pH). But Wang et al. [17] worked with a low concentration of anions (0.01 M). In the real water (leachates for example), the concentration of chloride can reach more than 0.8 mol/l. That is

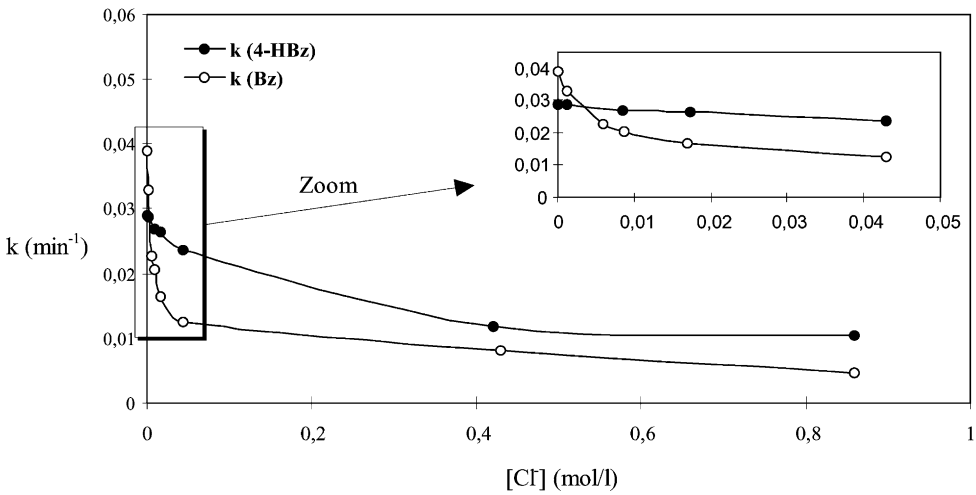

Fig. 7. Influence of the chloride concentration on the photocatalytic degradation of the BA and 4-HBZ (natural pH).

why, we have used chloride solutions in the range 0–0.8 mol/l to study the influence of the chloride concentration on the PCD of BA and 4-HBZ (Fig. 7).

In our study, the pH was in the range 5–6 (pH < pH_{zpc}) and the TiO_2-P25 surface is weakly positive, due to predominant species $TiOH_2^+$. Considering Fig. 7, it is clear that the rate constants of the degradations of both BA and 4-HBZ are functions of the chloride concentrations. Furthermore, an effective degradation is observed even for high chloride concentrations. It is interesting to note that the behaviours of BA and 4-HBZ are sensitively different at low chloride concentrations ($[Cl^-] < 0.02$ mol/l). 4-HBZ is only weakly dependent on the chloride concentration at low concentration. The evolution can be explained on the basis of adsorption of 4-HBZ, and it is well known that chloride leads to the desorption of organic acids [13]. It can be assumed that degradation occurs on the adsorbed carboxylate [9,10,17] in one way directly by holes or by $OH^\bullet$ 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 BA is strongly affected by the Cl^- ions concentration, especially at low chloride concentrations ($[Cl^-] < 0.02$ mol/l). The decrease of degradation rate according to chloride concentration has been described [18] and could explain the results obtained in the BA degradation: (1) at pH 5 to 6, $TiOH_2^+$ and TiOH were the main functional groups on the catalyst surface, and the Cl^- ions competed with organic species for active sites and lowered the reaction rate; (2) Cl^- ions competed with oxygen for electron, which reduced the formation of superoxide radicals and then blocked the chain reaction for hydroxyl free radicals [19]; (3) according to Abdulah et al. [20], chloride recombines with free radicals during reaction, and thus, decreases the reactive change between pollutant and free radicals.

4. Conclusion

In this work, we have studied the influence of the pH (3–11) and chloride ions ($[Cl^-] = 0$–0.8 mol/l) on the photocatalytic degradation (PCD) of BA and 4-HBZ in aqueous solution of TiO_2. BA is not adsorbed on TiO_2, and is present in aqueous solution in their molecular form. On the contrary, 4-HBZ is adsorbed. It should be noted that in the pH range 3–11, DRITF's investigation suggests that adsorption proceeds via carboxylate formation. Furthermore, 4-HBZ is found in the ionic state for pH >4.8. The following conclusions can be stated.

1. For nonadsorbed molecule (BA), the rate of degradation varies weakly in the pH range. Considering that the first intermediate observed in the degradation is hydroxybenzamides, we can conclude that $OH^\bullet$ production is not affected by the surface state of TiO_2-P25. There are certainly several ways of $OH^\bullet$ production, some of them are pH-dependant and probably a balance occurs between these pathways.
2. For the influence of the pH on the PCD of 4-HBZ there is adsorption via surface carboxylate or phenolate formation. At pH lower than the pH_{zpc} of TiO_2, the higher the adsorption, the higher is the degradation. When the pH increases, the rate of degradation decreases, because the change of surface charge of TiO_2 leads to a supplementary repulsive phenomenon.
3. At low chloride concentrations ($[Cl^-] < 0.02$ mol/l), 4-HBZ is only weakly dependent on the chloride concentration at low concentration, when BA is strongly affected at this concentration. However, at high chloride concentrations, the behaviours of both compounds are the same and there is a stability of the rate constant degradation after $[Cl^-] = 0.4$ mol/l.

References

[1] M. Schiavello (Ed.), Heterogeneous Photocatalysis, Wiley, New York, 1997.
[2] D. Bahnemann, in: P. Boule (Ed.), Handbook of Environmental Photochemistry, Springer, Berlin, 1999, p. 285.
[3] D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat, N. Serpone, in: G.R. Helz, R.G. Zepp, D.G. Crosby (Eds.), Aquatic and Surface Photochemistry, Lewis, Boca Raton, Fl, 1994, p. 261.
[4] P. Pichat, in: G. Ert, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Photocatalysis, VCH–Wiley, Weiheim, 1997, p. 2111.
[5] D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993.
[6] D. Robert, J. Lede, J.V. Weber (Eds.), Special Issue in Entropy, No. 228, 2000.

[7] E.M.C. Lo, Environ. Int. 22 (1996) 433.
[8] N. Ragle, J. Kissel, J.E. Ongerth, F.B. Dewall, Water Environ. Res. 67 (1995) 238.
[9] D. Robert, S. Parra, C. Pulgarin, A. Krzton, J.V. Weber, Appl. Surf. Sci. 167 (2000) 51.
[10] J. Cunningham, G. Al-Sayyed, J. Chem. Soc., Faraday Trans. 86 (1990) 3935.
[11] U. Stafford, K.A. Gray, P.V. Kamat, A. Varma, Chem. Phys. Lett. 205 (1993) 55.
[12] R.P. Hansen, R.P. Graig, J. Phys. Chem. 58 (1954) 212.
[13] H.Y. Chen, O. Zahraa, M. Bouchy, J. Photochem. Photobiol. A: Chem. 108 (1997) 37.
[14] F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizzetti, N. Serpone, Appl. Catal. B: Environ. 15 (1998) 147.
[15] Y. Suda, T. Morimoto, Langmuir 3 (1987) 786.
[16] P. Pichat, C. Maillard, C. Guillard, New J. Chem. 16 (1992) 821.
[17] K.H. Wang, Y.H. Hsieh, C.H. Wu, C.Y. Chang, Chemosphere 40 (2000) 389.
[18] K.H. Wang, Y.H. Hsieh, M.Y. Chou, C.Y. Chang, Appl. Catal. B: Environ. 21 (1999) 1.
[19] K. Okamoto, Y. Yamamoto, H. Tanaka, M. Hanaka, A Italian Bull. Chem. Soc., Jpn. 58 (1985) 2015.
[20] M. Abdulah, G.K. Low, R.W. Matthews, J. Phys. Chem. 94 (1990) 6820.