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Hydrogen bond interactions at the TiO_2 surface: Their contribution to the pH dependent photo-catalytic degradation of *p*-nitrophenol

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ABSTRACT

We have obtained pK_a values of *p*-nitrophenol–TiO_2 by measuring the adsorption equilibrium constants of *p*-nitrophenol (PNP) on the TiO_2 surface at different pH values. These values have been obtained from Langmuir isotherms and from a plot of 1/rate vs. $1/[PNP]_o$ obtained during TiO_2 catalyzed solar light photo-degradation of PNP. Two limit equilibrium constants are readily obtained depending on the solution pH: at pH 5 at which the TiO_2 surface is mainly positively charged and at pH 8 when it is negatively charged. With these and other adsorption equilibrium constants and the PNP pK_a value in solution, thermodynamic cycles are established in order to obtain the PNP pK_a when it is adsorbed on positively charged, neutral and negatively charged TiO_2 surfaces. From these pK_a values useful information on the PNP–TiO_2 interaction is readily obtained. For instance, the PNP nitro group interacts with the TiO_2 surface via a hydrogen bond, arising from the complex of water molecules with the Ti^{4+} ions on its surface. The weaker the hydrogen bond donor, the stronger the oxygen nitro group basicity. Therefore, pK_a changes on the phenolic hydroxyl group result from these interactions. Linear free energy correlations, maximum PNP adsorption capacity values (Q_L) and FTIR ATR, spectrum support this proposal. A k_{obs} vs. pH degradation profile of *p*-nitrophenol is also provided.

1. Introduction

For sometime we have been interested in finding favourable conditions for the degradation and mineralization of organic contaminants using heterogeneous photo-catalysis [1]. Among the methods currently available, TiO_2 photo-catalysis has been of great interest due to its efficiency [2] and its lower cost as compared, for instance, with degradation using the Fenton reagent [3–5]. In fact, we have been interested in optimizing the degradation and mineralization of contaminants from the oil industry [6,7] and fungicides and pesticides precursors [8]. In all cases, our main concern was to learn as much as possible from the reaction mechanism in order to improve reaction rates and selectivity toward contaminants. In order to pursue this objective, we have obtained rates and adsorption equilibrium constants from reactions under different initial conditions by using the Langmuir–Hinshelwood (L–H) relation (**1**), which, in the case of *p*-nitrophenol (PNP) as the organic contaminant, can be written as

$$r = \frac{d[PNP]}{dt} = \frac{kK[PNP]_o}{1 + K[PNP]_o} \quad (1)$$

where r is the PNP degradation rate, k ($[\ ]\,s^{-1}$) the apparent rate constant of the adduct phenol–TiO_2 degradation, K($[\ ]^{-1}$) the adduct formation equilibrium constant and $[PNP]_o$, the initial PNP concentration. Therefore, from a plot of $1/r$ vs. $1/[PNP]$, K can be obtained from the slope and k from the intercept. In cases in which the contaminant is present in solution as more than one species, for instance *p*-nitrophenol and its conjugate base (PNP^-), the Langmuir–Hinshelwood rate expression is transformed to Eq. (2):

$$r = \frac{kK\,[PNP] + k'K'[PNP^-]}{1 + K[PNP] + K'[PNP^-]} \quad (2)$$

where k' and K' correspond to de the degradation rate and the adsorption equilibrium constant of the PNP^-–TiO_2 adduct. This equation can be readily simplified for the case in which $1 \gg K[PNP] + K'[PNP^-]$, where Eq. (2) is reduced to

$$v = kK\,[PNP] + k'K'[PNP^-] \quad (3)$$

When Eq. (3) is rewritten in terms of the total phenol concentration ($[PNP]_T$), Eq. (4) is obtained:

$$r = \frac{kK[H^+]}{Ka + [H^+]} + \frac{k'K'Ka}{(Ka + [H^+])} \times [PNP]_T \quad (4)$$

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The last equation predicts that the observed rate constants, $k_{obs} = r/[\text{phenol}]_T$, can be obtained at each pH, to define a final k_{obs} vs. the pH sigmoid curve. In fact, we have obtained [9] such profiles for *p*-substituted phenols using a Hg lamp as light source.

Adsorption equilibrium constants can also be obtained from Langmuir isotherms according to Eq. (5):

$$q_e = \frac{Q_L K_L[\text{PNP}]}{1 + K_L[\text{PNP}]} \quad (5)$$

where q_e is the amount of PNP adsorbed, Q_L the maximum adsorption capacity of PNP on the TiO_2 surface and K_L the Langmuir equilibrium constant.

However, the Langmuir equilibrium constants obtained may be different from the ones obtained from the Langmuir–Hinshelwood kinetic approach since, in the latter case, the TiO_2 surface is illuminated, for instance with solar light. Therefore, the substrate interactions at TiO_2 surface may change [10]. However, these changes are likely to be minimised at extreme pH since under these conditions the surface charge may then be mainly regulated by the TiO_2 pK_a. In fact, in Eqs. (6) and (7), the pK_a values of the two protonated TiO_2 species are shown. Therefore, a zero point charge pH 6.25 value is obtained from Eq. (8). These values [11] correspond to TiO_2 Degussa P25 (anatase:rutile 70:30%). A pH_{zpc} 6.8 has been reported [12] for TiO_2 (anatase):

$$TiOH_2^+ \overset{pK_{a1}=4.5}{\rightleftarrows} TiOH + H^+ \quad (6)$$

$$TiOH \overset{pK_{a2}=8.0}{\rightleftarrows} TiO^- + H^+ \quad (7)$$

$$pH_{zpc} = \frac{1}{2}(pK_{a1} + pK_{a2}) \quad (8)$$

An important aspect to be considered in TiO_2/solar UV light photo-degradation is the equilibrium constant for adsorption [13] of the PNP at the TiO_2 surface, since according to Eq. (1), a stronger adsorption will be translated into a higher degradation rate, unless $K[\text{PNP}] > 1$. In such a case, the adsorption equilibrium will not affect the rate. Therefore, we are interested in exploring the characteristics of the PNP–TiO_2 association. In this regard we found the measurement of the pK_a value of the phenol at the TiO_2 surface particularly useful, since any change of the phenol pK_a, as compared to its pK_a in water, will give us information about the PNP–TiO_2 interaction.

Moreover, since the charge on the TiO_2 surface also changes with pH, the interaction of PNP with the positively charged, neutral and negatively charged TiO_2 surface, should yield different pK_a values depending on the type of interaction. PNP is a very useful molecule in this regard due to the presence of the nitro group. In fact, it has been pointed out that, depending on the characteristics of the proton donor, the nitro group could form hydrogen bonds with –X–H molecules (X = O, N and C) of different strengths and orientations [11]. This difference in strength is likely to be manifested by changed PNP–TiO_2 pK_a values. Therefore, in this manuscript we deal with ways of finding those PNP–TiO_2 pK_a values, the type of interaction between PNP and the TiO_2 surface and its consequences for UV-TiO_2 catalyzed PNP degradation.

Thin-layer [14] electrochemical techniques have been used to take precise measurements of adsorbed amounts that define the orientations of adsorbed molecules by revealing the electrode (Pt) surface area required for formation of the adsorbed state. Photochemical measurement of phthalic acid adsorption on TiO_2 film electrodes has also been reported [15]. FTIR spectroscopy [16] has also been used, for instance with phenols, to determine the type of interaction on the TiO_2 surface. IR in diffuse reflectance mode (DRIFT) has been used [17] to study the chemisorption of phenols and acids on a TiO_2 surface. The results presented herein are based on the adducts-pK_a approach and provide additional and useful information to the understanding of the TiO_2 surface adsorption mechanism. Knowledge of the latter can be used to optimize reaction conditions for degradation.

2. Experimental

2.1. Reactants

Anatase, 99.9% TiO_2 was obtained from Aldrich; *p*-nitrophenol, spectrophotometric grade, from Sigma and *p*-chlorophenol from Merck 98%.

2.2. Equipment

Irradiations were conducted using a LS 1000 UV solar light simulator from Solar Light Co., equipped with a xenon lamp of 1000 W and filters that simulate solar light intensities in the UVB and UVA (290–400 nm) regions. Radiation intensity was measured with a PMA 2100 radiometer from Solar Light Co. [PNP] kinetics were followed using a 8452A diode array Hewlett Packard (HP) UV–vis spectrophotometer. Millipore filtration equipment provided with cellulose and nitrocellulose 0.45 μm filters and a digital pH meter, model P211, Hanna Instruments were also used.

FTIR ATR (Fourier transform infra red attenuated total reflection) spectra were taken on a Nicolet Magna-IR 750 serie II spectrometer with an ATR accessory with a ZnSe window and a software Omnic versión 4.1.

2.3. Langmuir isotherms

Langmuir isotherms, at 25 °C and pH 5.0, 6.0, 6.8 and 8.0, were obtained using 100 mg of TiO_2 and PNP in the concentration range of 2–35 mg/L in a total volume of 100 mL of distilled water. The general procedure consisted of mixing 100 mg of TiO_2 with the appropriate amount of PNP. To this mixture concentrated HCl or NaOH was added to obtain the desired pH. No buffer was used in order to avoid its competition for the active sites at the TiO_2 surface. Once the desired pH was obtained, the mixture was stirred until the adsorption equilibrium was reached. This equilibrium was monitored by measuring the PNP absorbance of sample aliquots previously filtered using micro-pore filters on a UV–vis spectrometer. No changes in pH were observed during the experiments. In all cases equilibrium was reached in <5 h. The amount of PNP adsorbed on the TiO_2 surface at each [PNP] was calculated from the difference between the total [PNP] and the [PNP] remaining in solution. [PNP] were obtained by using calibration curves (absorbance vs. [PNP]) at 318 nm (acid pH) or 402 nm (basic pH). Plots of [PNP] adsorbed on the surface, per gram of TiO_2 added vs. the [PNP] in solution gives the Langmuir isotherms. From best fitting of the obtained experimental points to Eq. (5), the adsorption equilibrium constant (K_L) and the maximum amount of PNP adsorbed (Q_L) were obtained.

Additionally, Langmuir isotherms of PNP and *p*-chlorophenol were obtained at pH 3 and 40 °C. A molar adsorption coefficient of 1500 M^{-1} cm^{-1} at 282 nm was obtained for *p*-chlorophenol.

The sample for the FTIR ATR spectrum was prepared by using 300 mg/kg of TiO_2, 300 mL of water solution at pH 3 and 20 mg/L of PNP. This mixture was stirred overnight. The solid was filtered and dried at room temperature for 12 h.

2.4. Langmuir–Hinshelwood (L–H) kinetic measurements

L–H kinetics were performed at 25 °C and at pH 6 or 8. In a typical experiment, 100 mg of TiO_2 and 10–30 mg of PNP were added to 1 L of distilled water. To this solution NaOH or HCl were added

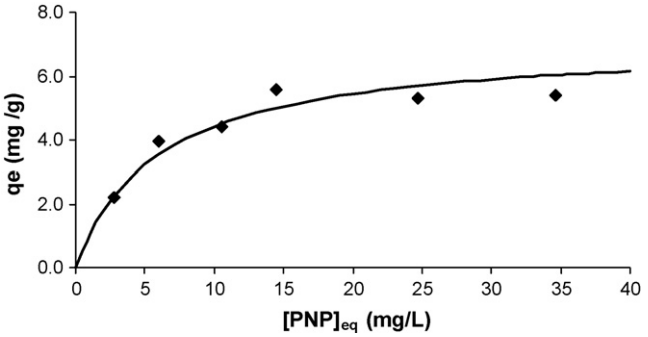


Fig. 1. Langmuir isotherm for the adsorption of PNP on the TiO_2 surface at pH 5. Solid line: best fitting of the experimental points using Eq. (5): Q_L = 7.07 mg/g and K_L = 0.14 L/mg.

to adjust pH to the desired value. This solution was irradiated with simulated UVB and UVA light (22 μW/cm^2) while stirred mechanically. Reaction aliquots were taken at different reaction times. These aliquots were filtered and their [PNP] was obtained by measuring the PNP absorbance at 318 nm or 402 nm in an UV–vis spectrometer. The absorbance values were transformed into the actual [PNP] from calibration curves previously prepared. The rates (r) at each [PNP] were obtained from the initial slope of a [PNP] vs. t plot. From a plot of $1/r$ vs. $1/[PNP]_o$ the k and K values of Eq. (1) were obtained. Alternatively, the PNP degradation k_{obs} values were obtained from the slope of a plot of ln [PNP] vs. t.

Additionally, L–H kinetics were measured for PNP and p-chlorophenol at pH 3 and 40 °C. For p-chlorophenol, a calibration curve of absorbance at 282 nm vs. [p-chlorophenol] was used to obtain the initial rates and the k_{obs} value.

2.5. Accumulated irradiation and quantum yield

The accumulated radiation (I) at 300–387 nm, and the quantum yield (Q), were calculated as follows: a direct UV radiation (300–387 nm) of 22 W/m^2 that corresponds to 6×10^{-5} eisntein/(m^2 s) (6×10^{-9} einstein/(cm^2 s) was used. For a solar simulator cannon diameter of 14 cm the light intensity per unit of time is: 6×10^{-9} einstein/(cm^2 s) $\times$ 3.14 $\times$ 49 = 9.2×10^{-7} einstein/s (5.52×10^{-5} einstein/min).

From this value the quantum yield can be obtained from: $Q = (d[\ ]/dt \times 1\,L)/I = 5.89 \times 10^{-4}$ mmole/min/5.22×10^{-2} meintein/min = 0.01, where d[ ]/dt is the PNP degradation rate (a value of 8×10^{-2} mg/L is used in the calculation), 1 L is the solution volume used and I the light intensity. In this calculation of the quantum yield the total incident light has not been corrected by the fraction that is actually absorbed by the TiO_2. This fraction has been determined, ca. 0.1, via spectrophotometric integrating sphere technique [18]. When this fraction is taken into account, a quantum yield of 0.1 is obtained. This quantum yield is in agreement, for instance, with values obtained [18] for phenol.

3. Results

The Langmuir isotherm for the adsorption of PNP on the TiO_2 (anatase) surface at 25 °C and pH 5 is shown in Fig. 1. The corresponding Langmuir isotherm parameters at 25 °C and pH 5, 6, 6.8 and 8 are shown in Table 1 (second and third columns). In this table the Langmuir isotherm parameters for PNP at pH 3 and 40 °C are also shown.

In Fig. 2, a Langmuir–Hinshelwood plot of 1/rate vs. $[PNP]_o$ at pH 8 and 25 °C is shown and in Fig. 3, the corresponding plot of ln [PNP] vs. t is shown. Similar plots are obtained at pH 6 (not shown). In

Table 1
Langmuir isotherm experimental values for the PNP adsorption on the TiO_2 (anatase) surface at different pH values.

pH	Q_L (mg/g)	K_L (L/mg)	K_{LH} (L/mg)	k_{LH} (min^{-1} mg/L)	k_{obs} (min^{-1})
3[a]	7.47	0.13	0.10(0.012[b])	0.19(0.83[b])	0.028(0.012[b])
5	7.07	0.14(−6.4)[c]			
6	7.79	0.10	0.17	0.087	0.015
6.8	16.4	0.13			
8	26.9	0.07	0.09	0.26	0.023

The experimental Langmuir–Hinshelwood (L–H) values and the k_{obs} values at [PNP] = 5 mg/L at pH 6, 8 and 3 (40 °C) are also shown.

[a] Experiments performed at 40 °C.

[b] p-Chlorophenol values.

[c] $\Delta\Delta G^\circ$ (kJ mol^{-1})value at 25 °C calculated from $\Delta\Delta G^\circ = -RT \ln K_L(PNP)/K_L(phenol)$ [15].

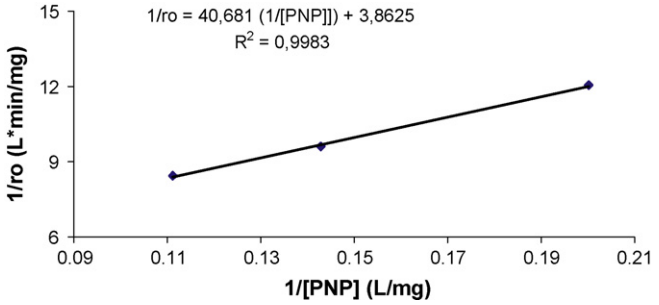


Fig. 2. Langmuir–Hinshelwood (L–H) plot of 1/rate vs. $1/[PNP]_o$ at pH 8; 100 mg TiO_2. Lamp intensity: 22 μW/cm^2.

Table 1 (the fourth column to the last one), the corresponding k, K and k_{obs} values obtained from the last plots at pH 6 and 8, can be seen. In this table, the corresponding Langmuir–Hinshelwood parameters for PNP and p-chlorophenol at pH 3 and 40 °C are also shown.

FTIR ATR spectrum of the surface-modified TiO_2 with PNP is shown in Fig. 8.

4. Discussion

As shown in Table 1, the adsorption equilibrium constants obtained kinetically from Eq. (1) in the catalyzed photodegradation of PNP at pH 6, 8 and 3 (40 °C) (the fourth column) are quite similar to those obtained from the Langmuir isotherms (the third column) in which no light was used during the adsorption. Therefore, the presence of light does not appear to modify the PNP–TiO_2 interaction.

Under pH 7, most of the PNP (pK_a = 7.14) exists as its protonated form so that the K values obtained at pH 3, 5 and 6, represent

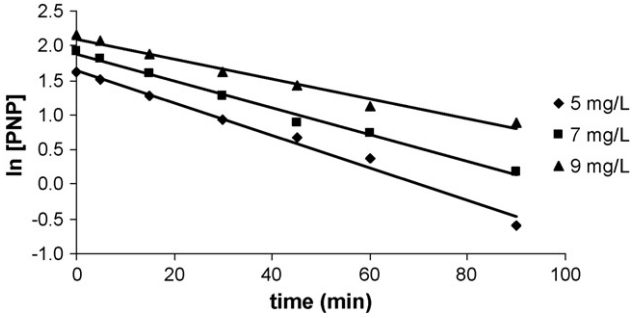


Fig. 3. Plot ln [PNP] vs. time at three different $[PNP]_o$. In agreement with Eq. (1), the k_{obs} values depend on the $[PNP]_o$. In fact, at 5, 7 and 9 mg/L the k_{obs} = −slopes = 0.023, 0.019 and 0.014 min^{-1}.

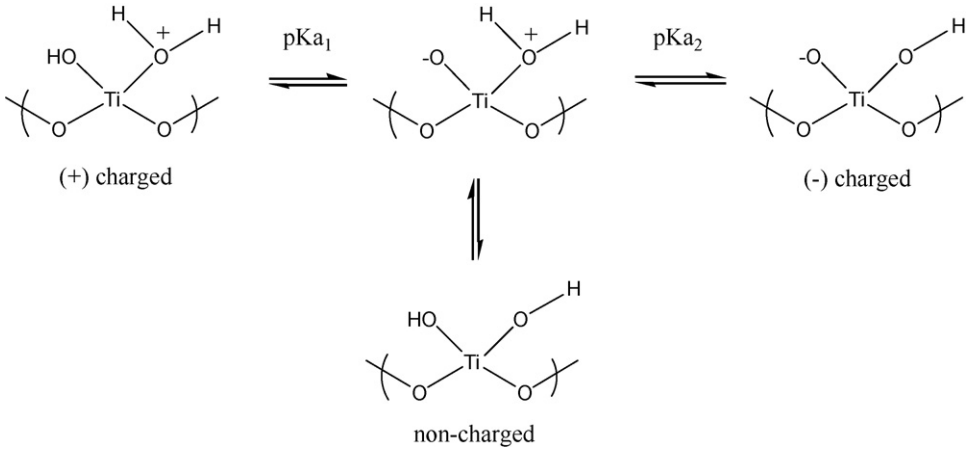


Fig. 4. Water and OH interactions with Ti (IV) at the TiO_2 surface. As shown (+) charged, uncharged and/or (−) charged species may act as proton donors to form hydrogen bonds.

Table 2
PNP and PNP' adsorption equilibrium values for their interaction with positively (+) charged, uncharged and (−) charged TiO_2 surface.

	TiO_2 surface		
	(+) Charged	Neutral	(−) Charged
PNP, K_L (L/mg)	0.14[a]	0.06[b]	0.02[b]
PNP^-, K'_L (L/mg)	0.21[b]	0.13[a]	0.07[a]
PNP, pK_a	6.9[c]	6.8[c]	6.6[c]

$PNP–TiO_2$ pK_a values, obtained using Scheme 1 thermodynamic cycle, are also shown. In water, PNP pK_a = 7.1.

[a] Experimental values.

[b] Obtained from linear regression of the experimental points (see text).

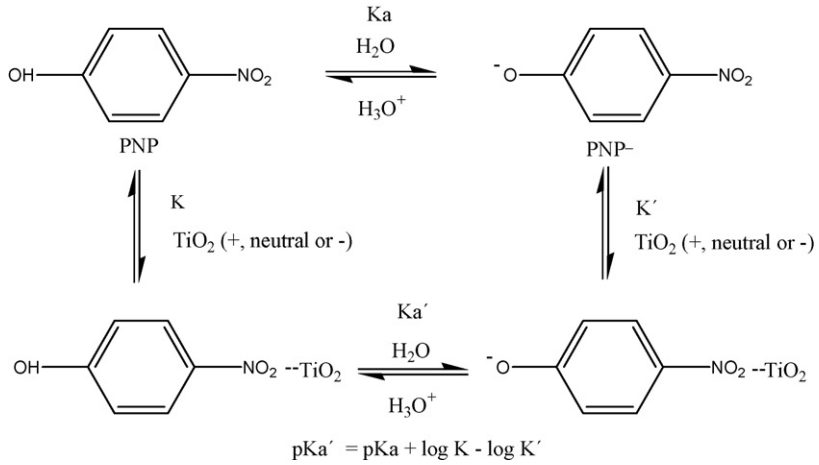
[c] Obtained from Eq. (8): $pK_a = 7.14 + \log K - \log K'$.

the PNP interaction with the TiO_2 surface. These equilibrium constants are similar but different since when pH is increased, the TiO_2 surface becomes less positively charged (see Eqs. (6) and (7)). By linear regression of the two points at 25 °C (pH 5 and 6), the interaction of PNP with the TiO_2 surface at pH 6.8 and 8.0 can be estimated. These values are shown in Table 2. The experimental K value (0.13) obtained at pH 6.8 is double that estimated based on only the $PNP–TiO_2$ interaction. Therefore, PNP^- (PNP conjugated base) may also be contributing as adsorbed species. It has been previously suggested [19] that both PNP^- species might participate in the adsorption at the TiO_2 surface and in the photo-degradation process. In fact, since PNP = PNP^- interconversion is fast compared to the rate at which the adsorption equilibrium is established, the observed high adsorption constant may be attributed to the interaction of the PNP^- form with the neutral TiO_2 surface. In the same table, the experimental K equilibrium adsorption at pH 8 is shown. Since at this pH PNP exists mainly as its PNP^- form, this K value corresponds to the adsorption of PNP^- on the negatively charged TiO_2 surface. By using this value and the one estimated for the $PNP^–$–TiO_2 interaction, the PNP^- adsorption with the positively charged (pH 5) TiO_2 surface is found by linear regression. This value is also shown in Table 2.

With PNP and PNP^- adsorption equilibrium values in Table 2, three thermodynamic cycles can be established. These cycles take into account the interaction of the PNP species with the positively, neutral (uncharged) and negatively charged TiO_2 surface. Moreover, from each of these cycles the pK_a values for the $PNP–TiO_2$ adducts can be found (see Scheme 1) from the thermodynamic relations:

$$pK_a \text{ adduct} = pK_a + \log K - \log K' \quad (9)$$

The three pK_a values obtained are shown in Table 2. In the three cases, the pK_a values are lower than the pK_a of PNP in water (7.14). This tendency can be explained in terms of the PNP interaction with the TiO_2 surface through the PNP nitro group. In fact, in the PNP molecule it is the site with higher charge density. Moreover, it has



Scheme 1. Thermodynamic cycle showing the interaction of PNP and PNP^- with the positive (+), neutral and negatively (−) charged TiO_2 surface. Using the corresponding K and K' values of Table 2, and the pK_a of PNP in water (7.14), the pK_a' values are obtained. These values correspond to the $PNP–TiO_2$ adducts acidity constants.

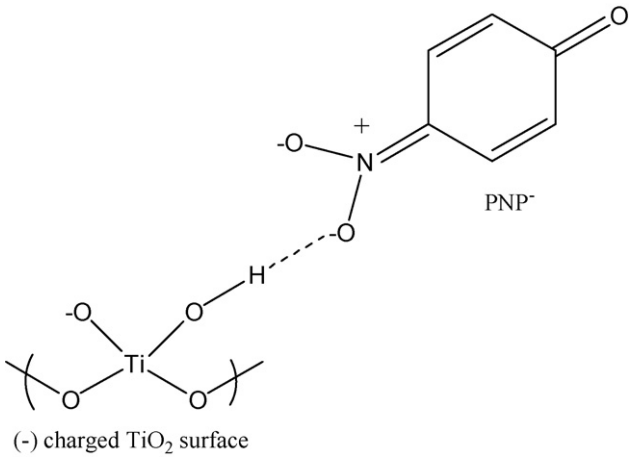


Fig. 5. Hydrogen bond interaction between the Ti–OH donor and the proton acceptor PNP^- at pH 8.

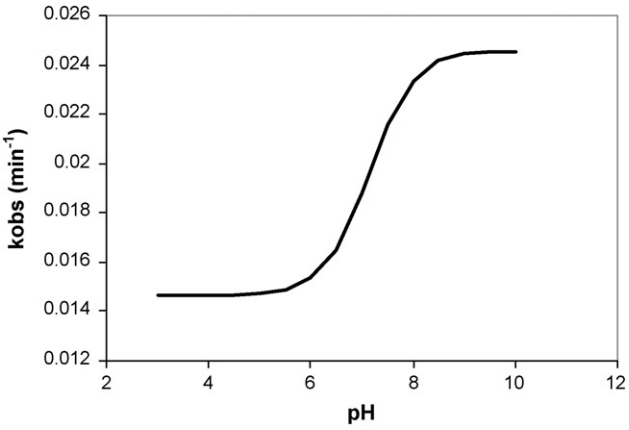


Fig. 6. Plot k_{obs} vs. pH for PNP TiO_2 photo-degradation according to Eq. (4). Experimental kK and $k'K'$ at pH 6 and 8, respectively, were used to obtain the profile.

been pointed out that the nitro group forms hydrogen bond with –X–H species and that the strength of that hydrogen bond depends on the electron density on the nitro group acceptor and the acidity of the –X–H donor. Since the donors at the TiO_2 surface are $–H_2O^+$ or –OH that act as ligands on the Ti (IV) (see Fig. 4), a change in the interaction strength is expected. Furthermore, the nitro group donor also changes in going from PNP to PNP^- since, in the last case, there is more negative charge density delocalized at the nitro group through its resonance form. Therefore, the hydrogen bond acceptor becomes stronger and in turn, the hydrogen bond interaction. Thus, the strongest interaction in the $PNP^–$–TiO_2 adduct is expected to occur when PNP^- interacts with the positively charged TiO_2 surface (low pH, see Fig. 4 and Table 2). However, the weakest, is not at high pH since a strong acceptor (e.g. like PNP^-) can still form a hydrogen bond with –OH on the TiO_2 surface (see Fig. 5). The last statement is in agreement with the experimental and estimated adsorption equilibrium constants and estimated pK_a values reported in Table 2.

We have discounted the PNP interaction with TiO_2 surface through the –OH group since this interaction has been reported [16] for resorcinol, phenol and cresols and the obtained K_L values are one order of magnitude lower than the reported in this work. Only in the case of catechol (0.06 mg/L) is the interaction of the same order of magnitude as the PNP values but still lower than the values reported in Table 2. Moreover, *ab initio* molecular calculations [11] at the MP2/TZV level show directional hydrogen bond interaction between the nitro group and water with potential wells with depths greater than 4 kJ mol^{-1}. In agreement with these calculations, the $\Delta\Delta G^\circ$ values, obtained from the K_L (PNP)/K_L (phenol) at pH 5, is 6.4 kJ mol^{-1} (see column 3, Table 1). The K_L (phenol) value has been reported [16] previously. In fact, from FTIR studies it has been concluded that phenol interacts with the TiO_2 surface through the phenol oxygen and does not form a hydrogen bond with water molecules at the surface as PNP does. Therefore, the K_L (PNP)/K_L (phenol) ratio and the associated $\Delta\Delta G^\circ$ value, may be considered as the excess of free energy stabilization due to the hydrogen bond formed between the water molecule at the TiO_2 surface and the PNP nitro group.

We found it interesting to correlate our results with the results published [20] on the Hammet study on the TiO_2-catalyzed photooxidation of para-substituded phenols. In that manuscript, K_{LH} are plotted vs. Hammet parameter σ_I. Two kind of straight lines are found: One with a negative slope (all substituents, including X = H (phenol)) and the other with a positive slope for X = halogens. Therefore, they suggest different adsorption modes for the halogenated and nonhalogenated para-monosubstituted phenols; *p*-nitro phenol is not included in the study. Therefore, we have measured K_L and K_{LH} values under the same conditions as the one reported [20]: pH 3 and 40 °C. To verify that this result is comparable to the previously reported [20], we have also measured, under the mentioned conditions, K_{LH} value for *p*-chlorophenol. As shown in Table 1, the K_{LH} for the last compound is very similar (1609 M^{-1}) to the one previously reported [20] (1600 M^{-1}) Therefore, we feel confident to add the PNP K_{LH} value obtained in this work (Table 1) to the reported [20] Hammet correlation. This PNP K_{LH} high value (0.10 L/mg (13,900 M^{-1}) at pH 3) does not fit at all the non-halogenated para subtituent in which the constants decrease with σ_I; however, it fits better the halogenated ones in which a positive slope is found. This result supports our proposal of a hydrogen bond interaction with the nitro group. It is quite probable that a similar mechanism is operating with the halogen substituents, although through a weaker hydrogen bond. In fact, molecular calculations [21] performed on *p*-halophenol show that in the case of *p*-fluorophenol, an important density charge is developed on the F atom. It is also quite important that the reactivity order ($k \times K$) of *p*-halophenols is quite higher than other *p*-substiturted

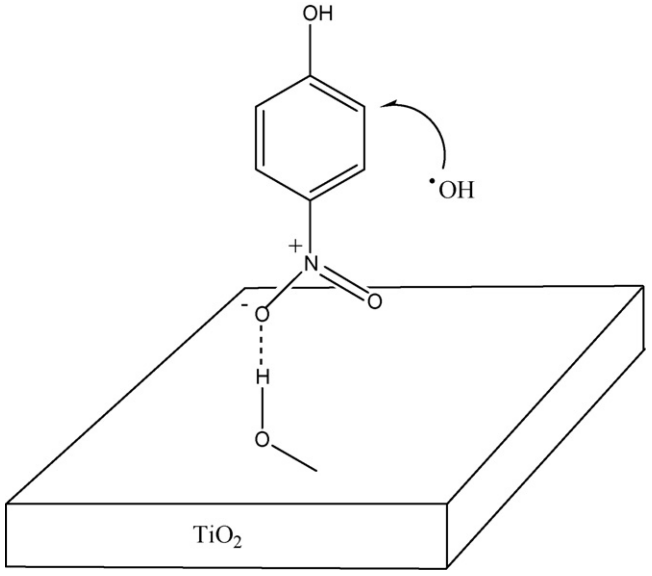


Fig. 7. PNP is adsorbed perpendicularly to the TiO_2 surface and the OH radical attack occurs on carbon 2 or 6 as depicted.

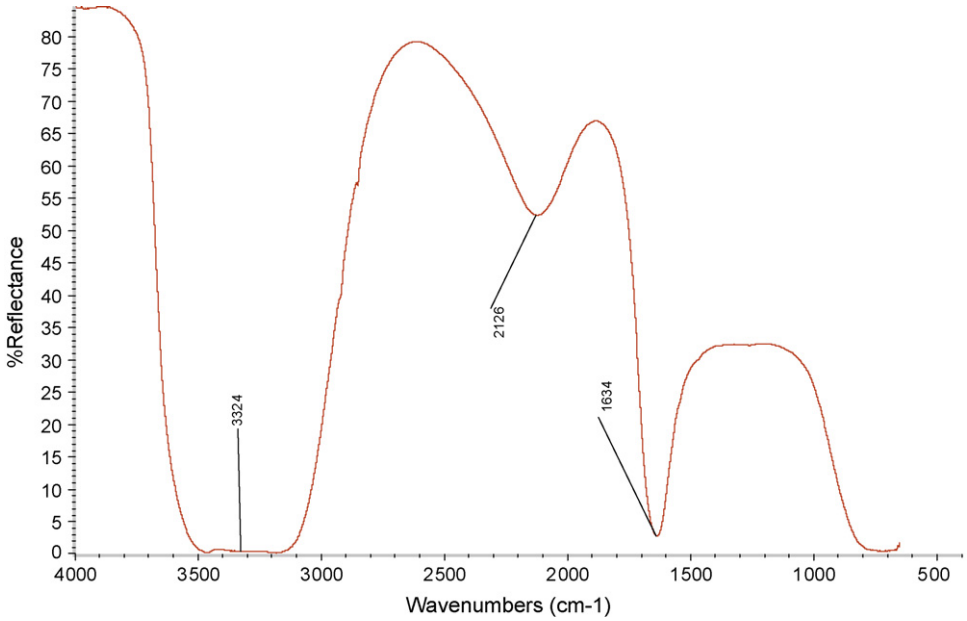


Fig. 8. FTIR ATR spectrum of TiO_2–PNP.

phenols except for *p*-nitrophenol that has the highest reactivity. From the mechanistic point of view, we could propose that the radical OH generated on the TiO_2 surface interacts easily with the *p*-substituted phenol adsorbed perpendicularly at the TiO_2 surface, as shown in Fig. 7, than with the one adsorbed parallel via π interaction. Although a perpendicular interaction as the one shown in Fig. 7 is certainly operating at high pH, at low pH an additional interaction between the hydrogen-bonded PNP may be acting between the aromatic π electrons and the positive charged TiO_2 surface. This interaction may twist the molecule from the perpendicular position toward a nearly planar one. This argument is supported by the Q_L values reported in Table 1 where at low pH these values are significantly lower than at high pH. That is, at low pH there is less space on the surface to adsorb PNP molecules than at high pH, although the adsorption is stronger at low pH than at high pH.

A profile of k_{obs} vs. pH for the solar light TiO_2 catalyzed degradation of PNP is shown in Fig. 6. This profile has been obtained using Eq. (4) and the experimental values of Kk and $K'k'$ obtained at pH 6 and 8, respectively. Degradation is faster at higher pH due to the relative efficiency of the PNP^-–TiO_2 interaction and the high k value (efficient degradation rate constant) at high pH due to the increase in the [$OH^\bullet$]. In fact, the k_{LH} value at pH 8 is considerably higher than the one at pH 6. Therefore, besides the additionally formed hydroxyl radicals, the electron deficiency on the aromatic ring, due to the electron delocalization toward the nitro group (see Fig. 5), may also be contributing to the high observed rates at this pH.

A mechanism of the photodecomposition of PNP at the TiO_2 surface is proposed in Fig. 7. The OH radical formed at the surface, as a consequence of water molecule oxidation, diffused to the perpendicularly adsorbed PNP molecule to produce the dihydroxycyclolhexadienyl radical to probably yield *p*-nitrocathecol, an intermediate detected [22] in the electrophilic addition of hydroxyl radicals. This attack is favoured as compared to a parallel adsorbed molecule due not only to the charge density at the aromatic ring, but also statistically since only one molecule face is available for the electrophilic radical attack when the molecule is attached in a planar manner.

Finally, from the FTIR ATR of PNP–TiO_2 adduct shown in Fig. 8, three main bands are detected. A broad one at 3324 cm^{-1} typical of a hydrogen bonded OH group (TiO_2), an aromatic one at 2126 cm^{-1} and a band at 1634 cm^{-1} that could be attributed to the nitro group bands that have been blue shifted due to the hydrogen bond formed with the TiO_2–OH groups. Two bands at ca. 1537 and 1360 cm^{-1} are the typical asymmetric and symmetric stretch bands of the nitro group. However shifts of these bands (approaching each other) have been observed [23] due the coordination of the nitro group to cations. It is then possible that the observation of only one band at 1634 cm^{-1} is due to the overlapping of these band that are further blue shifted due to the strong hydrogen bond formed between the nitro group and the TiO_2–OH groups at its surface.

5. Conclusions

The pK_a of *p*-nitrophenol adsorbed on three types of TiO_2 surfaces: positively, neutral and negatively charged, have been estimated from experimental PNP adsorption equilibrium constants measured by using the Langmuir isotherm. These equilibrium constants are quite similar to those obtained kinetically from the Langmuir–Hinshelwood approach. Therefore, it appears that there is no important perturbation of the PNP–TiO_2 interaction when the TiO_2 surface is illuminated with solar UV light.

PNP is more acidic when adsorbed at any of the above TiO_2 surfaces than in water. PNP interaction at the TiO_2 surface occurs through the PNP nitro group which forms a hydrogen bond with Ti–H_2O complexes at the TiO_2 surface. This interaction becomes stronger when the electron density on the nitro group and the acidity of the donor (water molecules) are increased. Therefore, even at high pH, the PNP^- adsorption at the negatively charged TiO_2 surface is relatively strong (K_L = 0.07 L/mg).

The k_{obs} vs. pH profile predicts a more efficient PNP photo-catalytic degradation at pH > 8. For environmental water decontamination purposes, degradation at pH > 8 can be achieved at a rate = 0.023 min^{-1} $[PNP]_T$, at $[PNP]_T$ < 10 mg/L.

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