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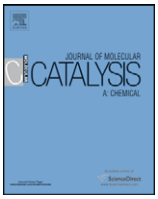

# Hydrogen bond interactions at the $TiO_2$ surface: Their contribution to the pH dependent photo-catalytic degradation of *p*-nitrophenol

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ABSTRACT

We have obtained p$K_a$ 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 p$K_a$ value in solution, thermodynamic cycles are established in order to obtain the PNP p$K_a$ when it is adsorbed on positively charged, neutral and negatively charged $TiO_2$ surfaces. From these p$K_a$ 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, p$K_a$ 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

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

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):

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

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

$$v = kK\,[PNP] + k'K'[PNP^-] \tag{3}$$

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

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

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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):

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

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 $TiO_2$ p$K_a$. In fact, in Eqs. (6) and (7), the p$K_a$ 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):

$$\text{TiOH}_2{}^{+} \overset{pK_{a1}=4.5}{\rightleftarrows} \text{TiOH} + \text{H}^{+} \qquad (6)$$

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

$$\text{pH}_{zpc} = \frac{1}{2}(pK_{a1} + pK_{a2}) \qquad (8)$$

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 p$K_a$ value of the phenol at the $TiO_2$ surface particularly useful, since any change of the phenol p$K_a$, as compared to its p$K_a$ 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 p$K_a$ 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–$TiO_2$ p$K_a$ values. Therefore, in this manuscript we deal with ways of finding those PNP–$TiO_2$ p$K_a$ 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-p$K_a$ 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