

Photoelectrocatalytic treatment of *p*-nitrophenol using Ti/TiO₂ thin-film electrode

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Received 1 September 2004; received in revised form 24 February 2005; accepted 7 March 2005

Available online 3 May 2005

Abstract

The photoelectrochemical degradation of *p*-nitrophenol (PNP) was investigated using titanium dioxide thin-film photoelectrode. The effects of different supporting electrolytes, pH, applied potential and PNP concentration were examined and discussed. Complete photodegradation was obtained in perchlorate medium at pH 2 when the photoanode was biased at +1.0 V (versus SCE) during a 3-h experiment. Under these conditions, carbon removal of approximately 60% was achieved.

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Keywords: Photoelectrochemical; Photoelectrocatalysis; TiO₂ thin-film electrode; *p*-Nitrophenol

1. Introduction

The efficiency of photocatalytic processes using TiO₂, commonly utilized in the oxidative degradation of organic compounds in solution, has been improved by electrochemical means [1–4]. This technique combines UV illumination with the application of a controlled potential through a supported catalyst, resulting in a decrease in the recombination rate of photogenerated electrons and holes. Although this technique sheds greater light on catalytic processes, there are not too many detailed systematic studies of the photoelectrochemical behavior of the oxidation of organic substances on nanoporous film electrodes [5,6]. Such studies are crucial in the environmental area when one considers the degradation of these substances in water. Continually increasing quantities of different organic substances, including nitrophenolic compounds, enter the environment during manufacturing and processing. An important member of this group is *p*-nitrophenol, or 4-nitrophenol (PNP), which is applied in agriculture, dyes/pigments, engineering polymers,

and pharmaceuticals and is also used as a fungicide for leather, in the production of parathion and organic synthesis [7]. It breaks down readily in surface waters, but takes a long time to degrade in deep soil and ground water, being toxic to plant, animal and human health. In view of its toxic effects, efforts have been made to remove it from effluents. Although studies have been conducted to investigate the degradation and kinetics of *p*-nitrophenol and its pathways with pure and mixed cultures [8–11], no reports are available concerning its photoelectrochemistry. Therefore, this work focused on the study of the photoelectrocatalytic degradation of *p*-nitrophenol, using a titanium-supported titania electrode.

2. Experimental

Titanium dioxide suspensions were prepared by the sol-gel method, according to the following procedure: titanium(IV) isopropoxide (Ti(*i*-OPr)₄, Aldrich Chemical, 97%), was mixed rapidly with glacial acetic acid (Aldrich Chemical, 99.99%) under constant stirring to form complex (molar ratio H⁺/Ti = 4). Next, this solution was diluted with 2-propanol (Aldrich Chemical, >99.5%, reagent ACS) in 1:1

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Ti/alcohol ratio. Water and a nitric acid solution were then added to this mixture, still under continual stirring, keeping the molar ratios at $\text{H}_2\text{O}/\text{Ti} = 25$ and $\text{H}^+/\text{Ti} = 0.5$ [12].

The photoanodes were made of 1 mm thick titanium foil (Tibrasil Titânio). After cleaning them with oxalic acid 5%, they were dipped into the catalyst precursor suspension for 10 s and then removed at a constant speed mechanically controlled by a pulley. Finally, the electrode was thermally treated at about 400°C in an air atmosphere for 3 h. This procedure was repeated three times.

A 50 mL single-compartment Teflon cell having a 50 mm diameter circular quartz window was utilized as the electrochemical reactor. A circular opening in the cell opposite the quartz window allowed for the exposure of 3.8 cm^2 of the working electrode (photoanode of Ti/TiO_2) to UV illumination. A Pt gauze of $\sim 4\text{ cm}^2$ provided the counter electrode with a saturated calomel reference electrode (SCE), completing the cell assembly.

The electrochemical measurements were recorded using an Autolab PGSTAT 20 Eco chemie, potentiostat/galvanostat, its anode illuminated by a UV light from a 200 W Xe–Hg arc lamp (Oriel, model 6262). Photocurrent experiments were carried out in different supporting electrolytes in the presence and absence of PNP. The intensity of light beamed onto the electrode surface, which was measured with a model PMA2100 version 1.16 Solar Light Company Inc. photometer/radiometer, was 80 mW cm^{-2} . The solutions were oxygenated during the measurements.

The photoelectrocatalytic degradation experiments were evaluated by absorption spectra in the ultraviolet and visible range, and based on removed organic carbon, using a ThermoSpectronic model Genesys 6 spectrophotometer and a total organic carbon analyzer (Shimadzu Instruments, model $\text{TOC-V}_{\text{CPH}}$).

3. Results and discussion

The results of the photoelectrocatalytic experiments in different supporting electrolytes, using the Ti/TiO_2 electrode, revealed that the PNP absorbance monitored at $\lambda = 315\text{ nm}$ decreased as a function of time. When $1 \times 10^{-4}\text{ mol L}^{-1}$ PNP solutions in HClO_4 ($\text{pH} \sim 5$) were used, employing only the electrocatalytic treatment and biasing the electrode with $+1.0\text{ V}$ versus SCE in dark conditions for 3 h, this reduction dropped to almost 7%. The photocatalytic treatment of the same solution using UV light without a bias potential showed that the absorbance decreased by $\sim 9\%$. However, the association of both UV light and $+1.0\text{ V}$ of bias potential promoted an almost 50% reduction of absorbance, indicating that the photoelectrodegradation was considerably more efficient than that expected sum of electrochemical and photocatalytic degradation.

In order to gain a better comprehension of the photoelectrocatalytic process and the method for optimizing phenolic compound degradation, we conducted studies as a function of

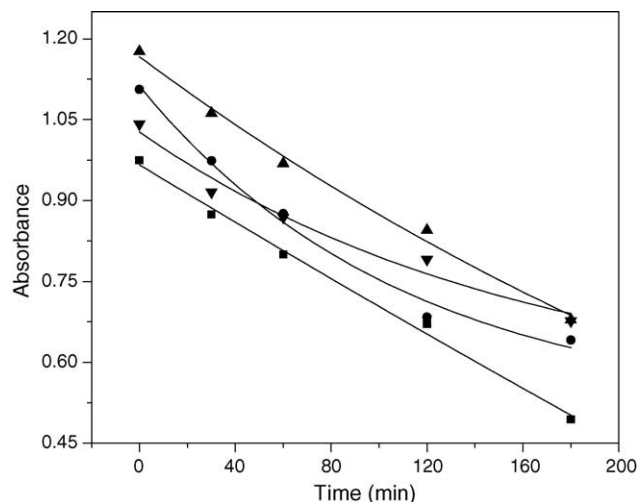


Fig. 1. Effect of supporting electrolyte on the photoelectrochemical degradation of $1 \times 10^{-4}\text{ mol L}^{-1}$ PNP solutions in: (■) HClO_4 ; (▲) Na_2SO_4 ; (●) KNO_3 ; and (▼) NaCl under the conditions of: $\text{pH} 5$, $E = +1.0\text{ V}$ vs. SCE, 200 W UV light.

the supporting electrolyte, the pH of the solution, the applied potential and the PNP concentration.

3.1. Effect of supporting electrolyte on photoelectrochemical degradation of PNP

The photoelectrodegradation of $1 \times 10^{-4}\text{ mol L}^{-1}$ PNP solutions was investigated in HClO_4 , 0.01 mol L^{-1} Na_2SO_4 , KNO_3 and NaCl at $\text{pH} 5$. Fig. 1 illustrates the reduction of absorbance, which was monitored for 3 h of photoelectrocatalytic degradation as a function of time. This reduction amounted to about 50%, 45%, 40% and 35%, respectively, for the HClO_4 , Na_2SO_4 , KNO_3 and NaCl electrolytes. Our studies revealed that, although the choice of electrolyte was not a critical factor, the better result was obtained when perchlorate was used. In addition, the photocurrent associated with the photoelectrode as a function of applied potential was investigated in solutions of the various supporting electrolytes by recording linear sweep voltammetry curves. The results indicated that the photocurrent in HClO_4 was the highest. Fig. 2 shows the profile of these curves at different pH values, as well as the dark current. As can be seen, under UV illumination the TiO_2 photoelectrode produced a photocurrent in HClO_4 at -0.49 V when the pH was 5. This profile was expected, for the application of potentials higher than the TiO_2 flat band potential across a photoelectrode increases the concentration of photogenerated holes (or hydroxyl radicals formed by subsequent oxidation of water) on the surface by decreasing the recombination rate of photogenerated holes and electrons [4,13]. As a result, the photocurrent is enhanced as the potential increases, improving the oxidative degradation process.

In further investigations of the photoelectrochemical degradation of PNP, a solution containing HClO_4 as the supporting electrolyte was selected.

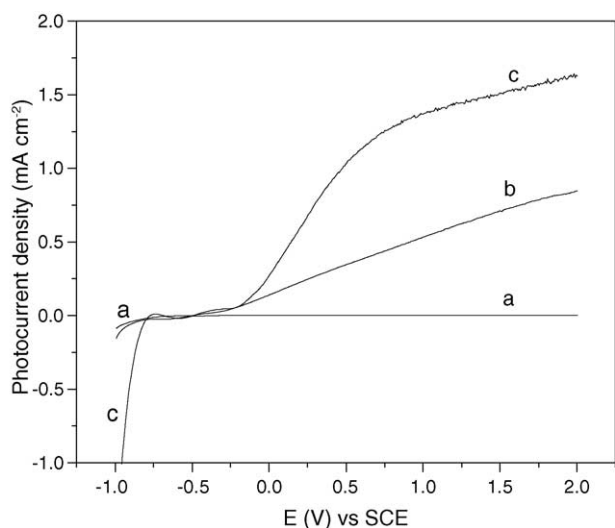


Fig. 2. Photocurrent–potential curves for TiO₂ thin-film electrode in $1 \times 10^{-4} \text{ mol L}^{-1}$ PNP/HClO₄ solutions under dark conditions (a) under UV illumination at pH 5 (b) and pH 2 (c). Scan rate = 10 mV s^{-1} .

3.2. Effect of pH on photoelectrochemical degradation of PNP

An investigation was made of the photoelectrocatalytic degradation of $1 \times 10^{-4} \text{ mol L}^{-1}$ PNP/HClO₄ solutions with different pHs. The UV–visible absorption spectra of the initial PNP solution and the solution after 3 h of photoelectrocatalytic treatment at pH 5 and 2 are depicted in Fig. 3a and b, respectively. The results indicate that the photoelectrocatalytic approach led to a decrease of all the PNP absorption peaks, with the maximum peak at $\lambda = 315 \text{ nm}$ decreasing by about 50% at a pH of 5 (Fig. 3a). This maximum disappeared completely, however, after the PNP degradation experiment at pH 2 (Fig. 3b). This response may be attributed to the surface

charge of the titanium dioxide electrode, which is influenced by the pH of the solution, and to the dissolved species [14]. Considering that TiOH₂⁺ are the predominant species in acid medium (pH < 3), as found in recent studies performed in TiO₂ suspensions (unpublished results), one can infer that, at pH 2, PNP is strongly adsorbed onto TiO₂, modifying its surface charge and leading to the complete degradation of the phenolic compound. However, at higher pH, e.g. pH 8, the adsorption spectra of the initial PNP solution changed, so additional photoelectrocatalytic experiments involving PNP degradation were investigated using perchlorate solutions at pH 2.

3.3. Effect of electrode potential on photoelectrochemical degradation of PNP

To verify the importance of selecting the best potential for phenolic compound degradation, experiments were carried out in $1 \times 10^{-4} \text{ mol L}^{-1}$ PNP solutions under the conditions described earlier herein. Different electrode potentials ranging from +0.4 V to +1.2 V were applied; the results are presented in Fig. 4. The fractional conversion in this figure was obtained by evaluating the ratio of the *p*-nitrophenol concentration change $C_0 - C_t$ at time t and the initial concentration C_0 in the solution, at $t = 0$, using the formula:

$$\text{Fractional conversion} = \frac{C_0 - C_t}{C_0} \quad (1)$$

The PNP concentration in the solution was determined by measuring the absorbance of the phenolic compound solution at $\lambda = 315 \text{ nm}$. In the calibration experiments in which the concentration ranged from $0.45 \times 10^{-4} \text{ mol L}^{-1}$ to $3 \times 10^{-4} \text{ mol L}^{-1}$, the absorbance at 315 nm was found to be proportional to the PNP concentration. The results indicate that the degradation rate increased as a function of biased

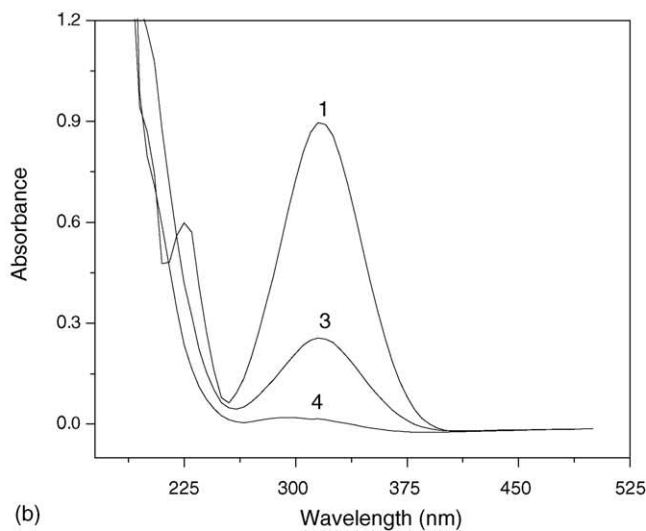
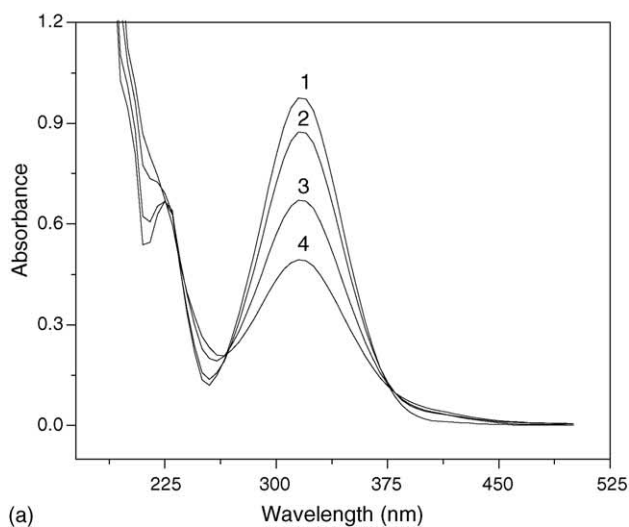


Fig. 3. UV–visible absorption spectra for $1 \times 10^{-4} \text{ mol L}^{-1}$ PNP/HClO₄ solution before (curve 1) and after photoelectrocatalytic degradation on the TiO₂ thin-film electrode biased at +1.0 V (vs. SCE) with aliquots removed (curves 2–4) at pH 5 (a) and pH 2 (b).

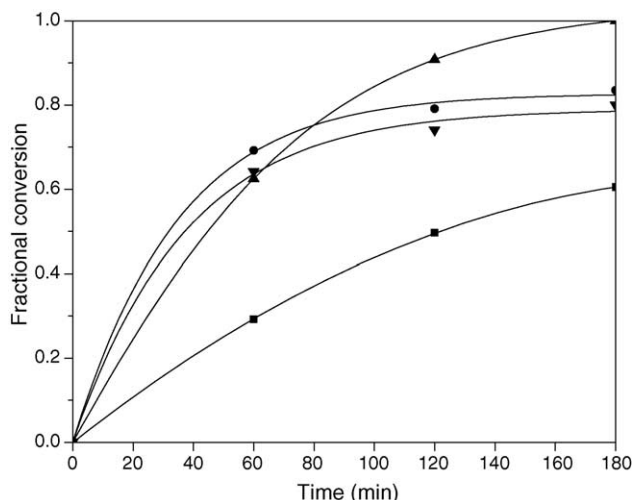


Fig. 4. Dependence of the photoelectrochemical degradation on applied potential for a TiO_2 thin-film electrode in $1 \times 10^{-4} \text{ mol L}^{-1}$ PNP/ HClO_4 solution (pH 2): (■) +0.4 V; (▼) +0.8 V; (▲) +1.0 V; and (●) +1.2 V (vs. SCE).

potential up to +1.0 V, at which point the PNP was completely degraded. However, at a more positive potential such as +1.2 V, the degradation declined slightly. These results were expected, since all the applied potentials were positive of the flat band potential for TiO_2 in PNP/ HClO_4 solution at pH 2, whose calculated value from the initial potential measurements was -0.27 V (Fig. 2). Under these conditions, a potential gradient was established within the titania film, which produced the same effect as band bending in single-crystal photoelectrodes [15]. As the positive potential increased, the resulting gradient separated holes and electrons, decreasing their combination rate, increasing the photocurrent, and accelerating the PNP degradation rate.

3.4. Effect of electrode potential on Faradaic efficiency

In photoelectrochemistry, Faradaic efficiency is used to explain the electrons' efficiency in degrading the compound under investigation. In this study, the percentage of Faradaic efficiency (η) was calculated as follows:

$$\eta = \frac{26x \text{ moles of PNP degraded}}{\text{the moles of electrons crossed through electrode}} \times 100 \quad (2)$$

where 26 is the number of moles of electrons needed to completely degrade 1 mol of PNP to CO_2 . Both the moles of degraded PNP and those of the electrons were measured at the same applied potential. The results are presented in Table 1. The Faradaic efficiency of over 100% can be explained by the fact that not all the degraded PNP moles are related to the electrons moles that pass through the electrode. In photoelectrocatalytic experiments, the bias potential is intended to separate the photogenerated charges, i.e. electron-hole pairs. At low potentials (+0.4 V and +0.8 V)

Table 1

Faradaic efficiency of PNP degradation by the titanium dioxide thin-film electrode as a function of applied potential under conditions of: $1 \times 10^{-4} \text{ mol L}^{-1}$ PNP/ HClO_4 solution (pH 2)

E (V) vs. SCE	η (%)
0.4	121.6
0.8	129.9
1.0	94.5
1.2	117.4

this effect is not completely attained, so not all the photo-generated electrons pass through the electrode because some are trapped by scavengers, such as oxygen or are consumed by electron-hole recombination. However, as the bias potential increases, most of photogenerated electrons reach the electrode back contact leading to the external circuit, thus contributing to the photocurrent and causing the Faradaic efficiency to decline [4,16]. It seems, however, that the optimal applied potential is around +1.0 V because at higher potentials, the Faradaic efficiency returns to values above 100%. Electron-consuming processes, such as oxygen reduction and recombination, may be favored under these conditions.

3.5. Effect of PNP concentration on its degradation rate

The influence of the initial PNP concentration on the photoelectrochemical degradation of phenolic compound was studied, keeping all the other previously optimized factors identical. The photoelectrocatalytic decomposition of the PNP concentration ranging from $1 \times 10^{-4} \text{ mol L}^{-1}$ to $3 \times 10^{-4} \text{ mol L}^{-1}$ in perchlorate (pH 2) was followed by measurements of the absorbance decay at $\lambda = 315 \text{ nm}$ over 3 h. Experiments involving monitoring of the total organic carbon (TOC) removal under the same conditions were also conducted, since the main purpose of using the photoelectrocatalytic method is to discover the degree to which the organic compound is mineralized. The results are presented in Table 2, which indicates that PNP degradation decreased as the initial concentration increased. This was attributed to the fact that, at higher PNP concentrations, the light intensity reaching the TiO_2 film surface is reduced. In addition, considerable mineralization of PNP (about 60%) was observed at $1 \times 10^{-4} \text{ mol L}^{-1}$ of the substrate under the best conditions of the method.

Table 2

Absorbance decay, A ($\lambda = 315 \text{ nm}$) and total organic carbon (TOC) removal by photoelectrocatalytic oxidation of PNP/ HClO_4 at pH 2 and $E = +1.0 \text{ V}$ (vs. SCE) on TiO_2 electrode over a 3-h experiment

PNP concentration $\times 10^4$ (mol L^{-1})	Absorbance decay (%)	TOC removal (%)
1	100	57
2	62	40
3	41	27

4. Conclusions

Our findings indicate that the efficiency of the photochemical procedure can be significantly improved by simultaneously applying an electrochemical process. The best conditions for maximum photoelectrocatalytic degradation of PNP were found to be in perchlorate medium at pH 2 with +1.0 V of applied potential on Ti/TiO₂ over a 3-hour experiment. Under these circumstances, using a 1×10^{-4} mol L⁻¹ PNP solution, approximately 60% of mineralization of the organic compound was achieved. In view of these results, the use of Ti/TiO₂ in an electrochemically assisted photochemical process appears to be a promising alternative for degradation of phenolic compounds, which are toxic and relatively resistant to biological degradation.

Acknowledgements

The financial support of FAPESP, CNPq and FUNDUNESP are gratefully acknowledged.

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