Journal of Electroanalytical Chemistry 802 (2017) 33–39

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Enhanced photoelectrocatalytic performance of TiO_2 nanotube array modified with WO_3 applied to the degradation of the endocrine disruptor propyl paraben

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ARTICLE INFO

Keywords:
Mineralization
Photoactivity
Photoelectrocatalysis
Propyl paraben
TiO2-NT/WO3 electrode
Wastewater treatment
TiO2-nanotube
WO3
Electrodeposition
Degradation
Endocrine disruptor

ABSTRACT

We report on the photoelectrocatalytic degradation of the endocrine disruptor propyl paraben (PPB) using a TiO_2 nanotube (TiO_2-NT) electrode prepared *via* chemical anodization, and a TiO_2-NT electrode modified with WO_3 by electrodeposition. Solutions containing 50 mg L^{-1} PPB were subjected to the photoelectrocatalytic process in a 0.2 L one-compartment electrochemical cell under UV/VIS irradiation, and the effects of bias potential (+0.5, +1.0 and +1.5 V) and solution pH (3.0, 7.0 and 10) on the performances of the unmodified and modified electrodes were investigated. Scanning electron micrographs (SEM) showed that the nanotubes were highly organized and perpendicularly aligned with a mean length of 800 nm. According to energy dispersive X-ray and SEM analyses, the concentration of W in the TiO_2-NT/WO_3 electrode was ~0.75% and the distribution of the modifier was continuous and homogeneous on the surface, with pores uncovered and decorated with WO_3. The photocurrent of the TiO_2-NT/WO_3 electrode was improved by more than 20% in relation to its unmodified counterpart. The maximum degradation efficiencies were achieved at higher applied potentials and under acidic conditions for both electrodes. However, best results were obtained using the TiO_2-NT/WO_3 electrode with an applied potential of +1.50 V and at pH 3. Under these conditions, more than 99% of PPB was removed in 30 min and 94% mineralization was achieved in 60 min. The photoactivity of the electrode was highly stable even after exhaustive application, indicating that WO_3 deposition is an important method for improving the properties of TiO_2-NT electrodes as applied to organic oxidation.

1. Introduction

The parabens are a class of organic compounds comprising esters of 4-hydroxybenzoic acid with short chain alcohols. Members of this class are used widely as preservatives in the cosmetic and pharmaceutical industries and may be found in nearly all personal hygiene products [1]. Propyl paraben (PPB) is effective as a bactericide and is employed as a stabilizer of active ingredients in a wide range of formulations [2]. However, PPB exhibits a relatively high solubility in water (400 mg L^{-1} at 25 °C), as a result of which the compound can disperse readily within the environment [2] passing from industrial effluents and wastewaters into rivers and water treatment plants [3,4]. Additionally, it has been reported that PPB can cause adverse effects on the endocrine system even at low concentrations (μg L^{-1}) [5] and the preservative is classified as an endocrine disruptor. Moreover, long-term exposure to PPB can increase the risk of breast and testicular cancers [6]. For these reasons, the removal of PPB from aquatic environments would be expedient.

A number of alternative treatments, including a range of advanced oxidation processes (AOPs), have been described for the degradation of PPB and other parabens in aqueous suspension [7–9]. Typically, AOPs based on the generation of strongly oxidizing hydroxyl radicals (•OH) have been found to be highly efficient [10]. Moreover, in comparison with classical wastewater treatments, AOP methods such as ozonolysis, electrocatalysis (EC) and photocatalysis (PC) are particularly effective and can destroy the target molecule rather than just transferring it from one phase to another [10,11].

Photoelectrocatalysis (PEC) is an attractive development of AOP techniques and involves the combination of EC and PC methods in which •OH are generated in a semiconductor when activated by UV/VIS radiation. In the PEC strategy, application of an external bias potential to the semiconductor improves charge (electron-hole) separation and

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http://dx.doi.org/10.1016/j.jelechem.2017.08.040
Received 15 May 2017; Received in revised form 12 August 2017; Accepted 18 August 2017
Available online 19 August 2017

minimizes the recombination process, as a result of which there is an increase in •OH generation and, consequently, in photoactivity [12–13].

Over the years, titanium dioxide (TiO_2) supported on metallic titanium has been the main semiconductor studied in the PEC process. However, various studies have shown that application of the semiconductor in the form of hierarchical TiO_2 nanotubes (TiO_2-NTs) improves electron percolation at the TiO_2 interface by virtue of the enlarged surface area associated with the high structural organization [14]. This is translated into increased surface/solution reactions, lower levels of electron/hole recombination and better conversion of light energy [15]. TiO_2 nanotubes are readily synthesized *via* chemical anodization using methods that are well described in the literature [16–19], and the material affords a wide range of advantages including low toxicity, good stability and high efficiency [20,21].

For the reasons, stated above, TiO_2-NTs represent an ideal material for application in the removal of organic pollutants from wastewater. However, TiO_2 exhibits low absorption (~7%) of visible solar radiation [22], a disadvantage that jeopardizes its study and application as a photocatalyst in solar wastewater treatment plants. Additionally, TiO_2 has a wide band gap (3.2 eV) such that more energy is required to excite electrons from the valence band (VB) to the conduction band (CB) in the semiconductor [22]. In order to improve these properties, and to increase the efficiency of the semiconductor, new strategies have been investigated, many of which involve modification of the TiO_2-NT surface [17,23,24] with metals such as V [25], Fe [26], Ag [27], Co and Pt [28]. Nanotubes of TiO_2 doped with WO_3 are of particular interest because the energy bands of the modifier are relatively close to those of the substrate and band coupling at the heterojunction of the metal oxides is possible [29]. However, it is important to note that the method of deposition employed and the amount of WO_3 deposited can exert a strong influence on the PEC performance of the modified TiO_2-NTs [30]. In particular, a disproportionate amount of WO_3 can increase charge recombination in the bicomponent, thereby reducing photoactivity [31].

In a previous study [32], we established the appropriate amount of WO_3 that should be deposited electrochemically on the surface of TiO_2-NTs in order to improve PEC responses, including enhancement of light absorption, reduction of band gap energy and, more importantly, better photocurrent performance. To our knowledge, the PEC degradation of propyl paraben has not been reported. In order to verify the effectiveness of TiO_2-NT/WO_3, the purpose of this work is to investigate the effect of WO_3 modified in the TiO_2-NT array electrodes with respect to the PEC degradation of the preservative PPB comparing to the performance of the non-modified TiO_2-NT. Electrode efficiencies were evaluated by monitoring the levels of PPB and total organic carbon (TOC) during degradation reactions carried out at different bias potentials with electrolytes at pH values of 3, 7 and 10, while electrode stabilities were established by comparing performance prior to and after 20 h of process time.

2. Methods

2.1. Preparation of TiO_2-NT/WO_3 electrodes

TiO_2-NT electrodes were produced by chemical anodization using a published method [33]. The electrochemical cell comprised a stainless steel counter electrode and a working electrode (2.4 × 2.4 mm) prepared from Ti foil (1 mm thick) that had been polished with a series of fine silicon papers (400, 600 and 1200 grit). The electrolyte solution contained 1 mol L^{-1} NaH_2PO_4 and 0.3% HF, and a bias potential of 20 V was applied to the system for 120 min using a DC power supply. Electrodes were subsequently modified with WO_3 by electrochemical deposition [34] using a standard three-electrode cell comprising a TiO_2-NT working electrode, a stainless steel counter electrode and a saturated calomel electrode (SCE) as reference. The electrolyte solution contained 0.075% (v/v) H_2O_2 and 5 mmol L^{-1} Na_2WO_4, as the precursor of WO_3, with pH adjusted to 1.4 by addition of HNO_3. The electrochemical reactions were performed with the cell connected to a Metrohm Autolab (Utrecht, The Netherlands) model PGSTAT 302 potentiostat/galvanostat, controlled by NOVA software and with the potential set at − 0.45 V *vs* SCE. In accordance with our previous study [32], a process time of 5 min was selected to allow the deposition of an appropriate amount of WO_3 onto the TiO_2-NT electrode. The modified electrode was subsequently washed in ultrapure water, dried in a stream of nitrogen gas and calcinated at 450 °C for 120 min.

2.2. Characterization of electrodes

Electrode composition was established using an Oxford Instruments (Abingdon, UK) model 7060 energy dispersive X-ray (EDX) detector coupled to the Zeiss/Leo (Cambridge, UK) model LEO 440 scanning electron microscopy (SEM) that was employed in the morphological evaluation of the materials.

PEC characterization of the electrodes was performed using the electrochemical cell described above with UV-VIS radiation (350–450 nm) provided by an Osram 125 W low pressure mercury vapor lamp (without bulb) located inside a quartz tube placed vertically within the reactor. Activation times of the electrodes under irradiation were established by pulsed chronoamperometry through application of alternate potentials of − 0.5 and + 1.5 V *vs* SCE. Photocurrents under constant irradiation were measured *via* linear sweep voltammetry at 10 mV s^{-1} in an electrolyte containing 0.1 mol L^{-1} Na_2SO_4 adjusted to pH 6.

2.3. PEC degradation of PPB

Degradation reactions were carried out in a single compartment, three-electrode glass reactor (200 mL), the electrochemical configuration and radiation source of which were similar to those adopted for the photoactivity measurements. Reactions were performed at 25 °C, with constant magnetic stirring (250 rpm), using unmodified TiO_2-NT or modified TiO_2-NT/WO_3 as the working electrode. The reaction mixture comprised 50 mg L^{-1} PPB (Sigma-Aldrich, St Louis, MO, USA) in a support electrolyte containing 0.1 mol L^{-1} Na_2SO_4 in ultrapure water (1.3 μS cm^{-1}), the pH of which was monitored using an Orion (ThermoFisher Scientific, Waltham, MA, USA) digital pH meter and glass electrode and adjusted by the addition of dilute H_2SO_4 or NaOH prior to and during the experiments.

Samples of electrolyte were collected during 60 min of process time, and the decay of PPB and concomitant formation of intermediates monitored by high performance liquid chromatography (HPLC) using a Shimadzu (Kyoto, Japan) 20A LC system with UV-VIS detector set at 210 nm. Separations were performed at 45 °C on a Phenomenex (Torrance, CA, USA) C18 column (250 × 4.60 mm i.d.; 5.0 μm) eluted isocratically with a mobile phase containing acetonitrile/water (65:35 v/v) supplied at a flow rate of 0.6 mL min^{-1}. The rate of mineralization of organic material in the reaction mixture was established by measuring TOC using a Shimadzu TOC-V_{CPN} analyzer.

3. Results and discussion

3.1. Morphology, composition and activity of electrodes modified and non-modified

We have previously shown the synthesis of TiO_2-NT electrodes by chemical anodization and its successfully modification with WO_3 [32]. The ideal process time (5 min) to electrodeposition of WO_3 provided excellent properties that motivated the application of such electrodes. The concurrence of monoclinic phase WO_3 and anatase phase TiO_2-NT gives rise to a noticeable decrease in band gap energy, an increase in absorption in the UV/VIS region and low flat potential potential - E_{fb} (+ 0.11 and + 0.15 V to TiO_2-NT and TiO_2-NT/WO_3, respectively).

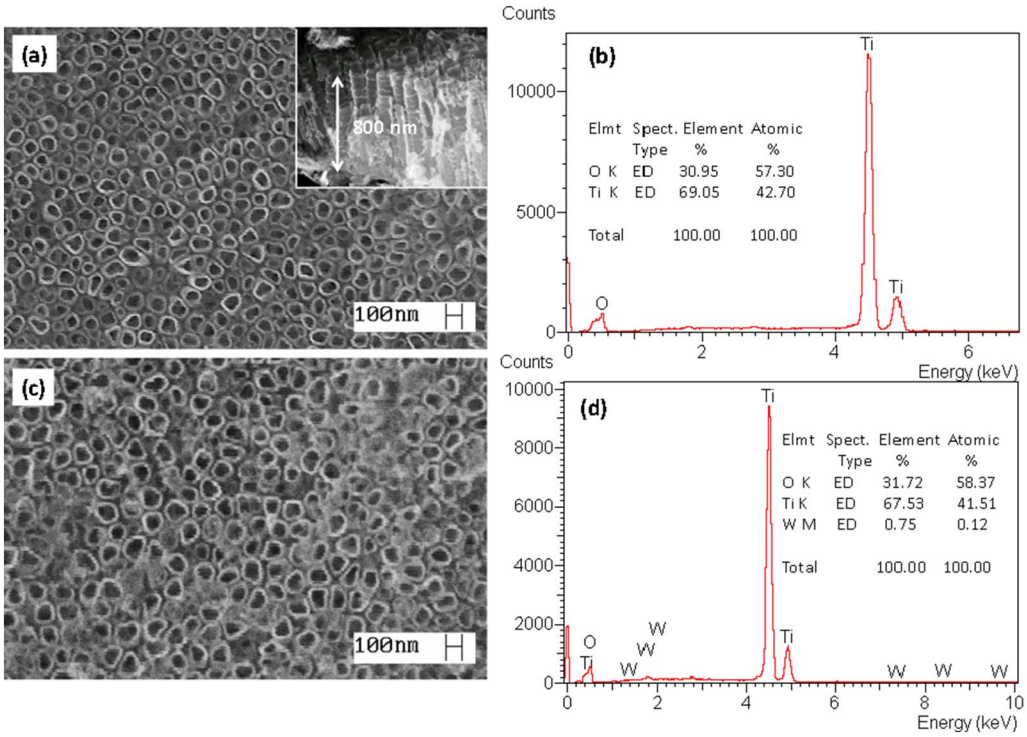

Fig. 1. Scanning electron micrographs showing: (**a**) top and cross sectional (insert) views of the TiO_2-NT electrode, and (**c**) top view of the TiO_2-NT electrode modified with WO_3. The energy dispersive X-ray spectra of: (**b**) the TiO_2-NT electrode, and (**d**) the TiO_2-NT/WO_3 electrode were recorded over the respective geometric areas chosen for the micrographs.

The top view scanning electron micrograph (Fig. 1a) of the unmodified TiO_2-NT electrode showed tubes with a mean diameter of 100 nm, while the cross sectional view (Fig. 1a, insert) revealed that the tubes were highly organized and perpendicularly aligned with a mean length of 800 nm. The modified TiO_2-NT/WO_3 electrode exhibited a continuous and homogeneous distribution of WO_3 on the surface of the nanotubes (Fig. 1c) although most of the pores remained uncovered, which may be interpreted as an increase in the surface area of the electrode. Its cross sectional was not possible to measure since to this characterization is destructive and the tubes are scratched of the substrate, thus the WO_3 deposited is scraped from the top of surface. The EDX spectra shown in Fig. 1b and d were recorded over the geometric areas corresponding to those chosen for SEM imaging. The elementary composition profiles showed similar proportions of Ti in both electrodes, while W was detectable in low concentration (~0.75%) in the TiO_2-NT/WO_3 electrode indicating that this element decorated the surface of the material.

In order to evaluate the PEC activities of the electrodes under constant irradiation, photocurrent densities were measured at potentials of − 0.5 and + 1.5 V *vs* SCE applied alternately which are lower and higher than the flat band potential, respectively, as depicted in Fig. 2. It is desirable that the electrodes exhibit a constant current to both potentials that translates in a good stability due to stable generation of charges. At the negative potential ($< E_{fb}$) both electrodes exhibited the same behavior with currents that were low and indistinguishable. Although TiO_2 and WO_3 electrodes typically generate high anodic currents when exposed to UV–Vis radiation, an applied potential of − 0.5 V was clearly insufficient to promote charge excitation and, therefore, the separation of the photogenerated charges has not been begun [35–36]. However, when the electrodes were exposed to a potential of + 1.50 V ($> E_{fb}$) the photoactivities increased instantaneously. Moreover, modulations in photocurrent densities between potentials were consistent over consecutive cycles confirming the high stability and reproducibility of the photoactivities of the studied materials. The unmodified TiO_2-NT electrode presented a high and constant photocurrent of ~17 mA cm^{-2}, while that of the WO_3-modified electrode was ~21 mA cm^{-2}, corresponding to an improvement of a further 20%. This increase can be attributed to the formation of the TiO_2/WO_3 heterojunction and appropriate coupling of the VB/CB of the two semiconductors. Since the CB of WO_3 is of lower energy than that of TiO_2, electrons excited from the VB to the CB of TiO_2 would be effectively directed to WO_3 and, subsequently, to the external circuit. In this manner, the rate of charge recombination would be reduced and the half-life prolonged, reflecting in higher PEC activity.

3.2. PEC degradation of PPB

The pH of the reaction mixture plays an important role in PEC degradation since it affects the key factors that determine the effectiveness of the system [37–39], namely the adsorption of electroactive species and the oxidation of H_2O/OH^- to •OH. For this reason, we have evaluated the PPB degradation in alkaline (pH = 10), acid (pH = 3) and neutral solution (pH = 7). The influence of pH on the PEC oxidation of PPB carried out at + 1.50 V *vs* SCE is presented in Fig. 3a and b. For both electrodes, the removal of PPB was most efficient at pH 3, with analyte being undetectable in the reaction solutions after 30 min. At pH 7, the decay of PPB proceeded at a moderate rate, while at pH 10 the removal of analyte occurred relatively slowly over a 60 min process time. Based on the above, pH 3.0 was selected as the most appropriate condition for all further investigations.

Plots of ln [C]/[C_0] as a function of process time for PEC degradations performed at pH 3 with TiO_2-NT and TiO_2-NT/WO_3 electrodes (Fig. 3c) indicate that the reactions followed pseudo first-order kinetics. Values of the apparent kinetic constants (k_{ap}) presented in Fig. 3d confirm the significant improvement in efficiency of PPB degradation observed under acid conditions. Furthermore, the performance of the modified TiO_2-NT/WO_3 electrode at pH 3 was clearly enhanced in comparison with that of the unmodified electrode.

Since the isoelectric point of TiO_2 is 6.5 and the pKa of PPB is 8.2 [40,41] both species would be positively charged under acidic conditions and, therefore, the adsorption of PPB on the surface of the electrode is reduced and it does not influence the higher acidic efficiency. In this way, the direct oxidation by holes generated in the anode can exert more influence on the oxidation. In fact, the pH of solution also can

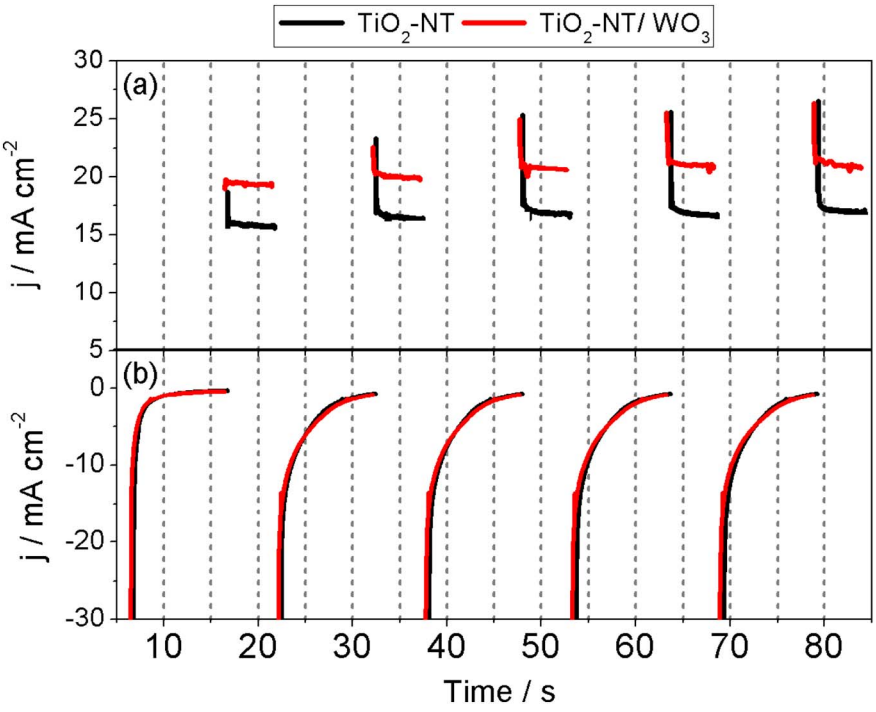

Fig. 2. Plots of photocurrent density *vs* time obtained by applying alternate potentials of (**a**) + 1.5 and (**b**) -0.5 V *vs* SCE to TiO_2-NT and TiO_2-NT/WO_3 electrodes. Experimental conditions: electrolyte, Na_2SO_4 0.1 mol L^{-1} at pH 6; radiation source 125 W low pressure mercury vapor lamp.

govern the PEC efficiency under others aspects. The oxidative power of the •OH generated in the surface is influenced by the pH. The redox potential of •OH, calculated by Nernest equation (E^0(•OH_{aq}/H_2O) = 2.59–0.059pH), shows that the redox potential of •OH in acid condition presents higher oxidative potential and therefore, the PPB oxidation is favorable [42]. Furthermore, the CO_2 produced during the oxidation can be dissolved in the alkaline solutions generating HCO_3^- and CO_3^{2-} which are strong •OH scavengers and inhibit the degradation of PPB in pH 10 [42].

Based on the experimental results described above, we propose that the initialization of PPB degradation proceeds in a different manner under acidic and basic conditions (Fig. 4). Acid pH favors the generation of a region in the PPB molecule with high positive charge density [43], as a result of which the analyte becomes more susceptible to nucleophilic attack by •OH. In contrast, the conjugate base of PPB is generated at basic pH [43], and this species is more stable and less susceptible to radical attack. Thus, the photoelectrochemical process is strongly dependent on the pH of the solution and is more efficient under acidic conditions. Although the efficiency of degradation is related to the pH of the solution, it is not significantly influenced or limited by the

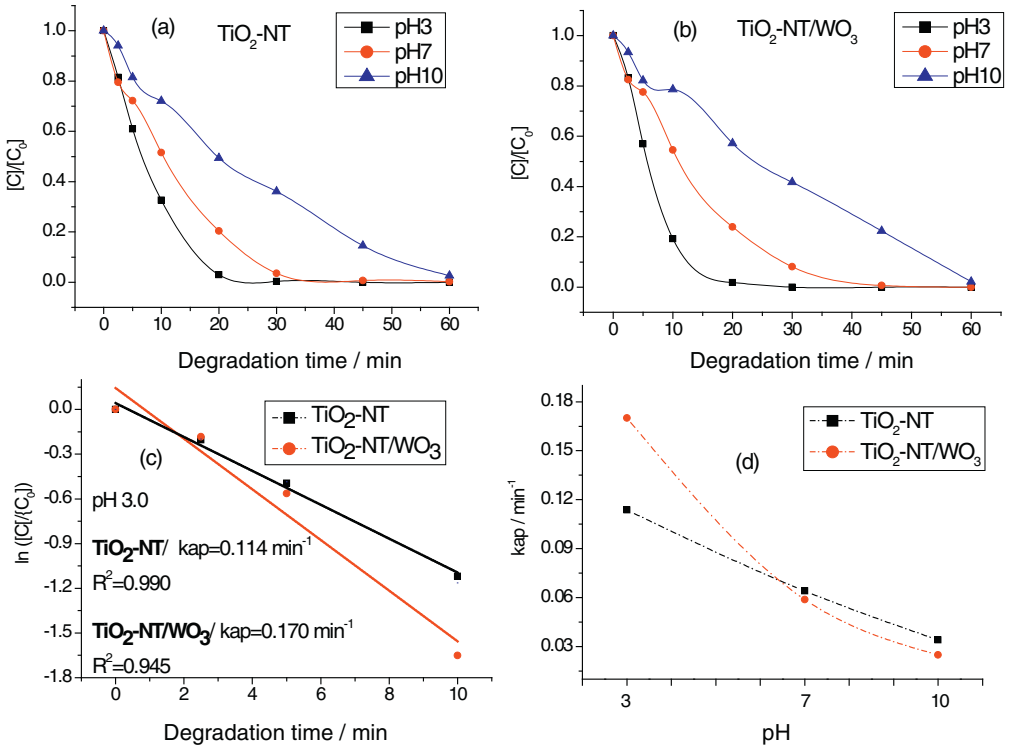

Fig. 3. The effect of pH on the rate of photoelectrocatalytic (PEC) degradation of propyl paraben (PPB) performed with an applied potential of + 1.50 V *vs* SCE using: (**a**) the TiO_2-NT electrode, and (**b**) the TiO_2-NT/WO_3 electrode. Panel (**c**) presents the kinetic parameters of PEC degradation of PPB by the two electrodes at pH 3.0, while (**d**) shows the influence of pH on the kinetics of the degradation reaction under similar conditions.

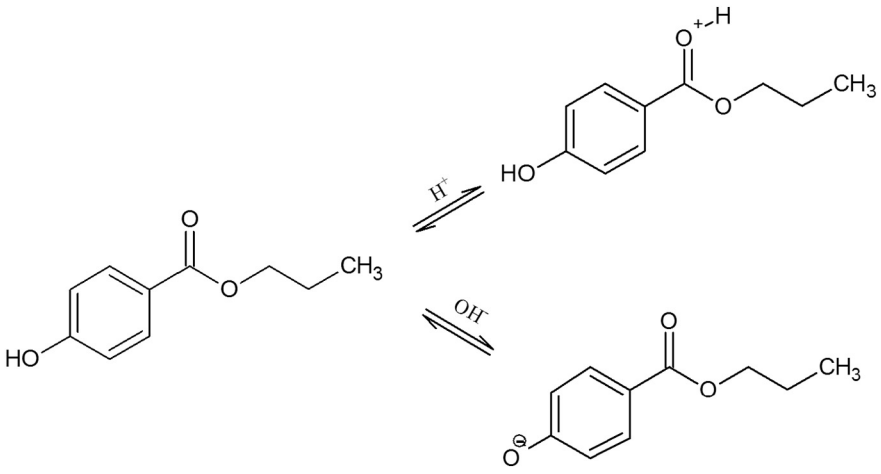

Fig. 4. Protonation and deprotonation of propyl paraben under acidic and basic conditions.

mass transport and permeability, since the convection of solution (magnetic stirring) is held constant in 250 rpm in all the experiments.

The effects of applied bias potential on the PEC degradation of PPB carried out at pH 3 using TiO_2-NT and TiO_2-NT/WO_3 electrodes are presented in Fig. 5a and b. Since the potentials applied, *i.e.* + 0.5, + 1.0 and + 1.5 V, were higher than the flat band potentials of the electrodes, the electrons would be photoexcited and directed to the counter electrode while the holes would be enriched at the surface of the electrodes, thereby generating an electric field. In the higher bias potentials was observed the oxygen evolution which could compete to the generation of hydroxyl radical in the surface and reduces the PPB oxidation rate. The removal of PPB from the reaction mixture was high with both electrodes at all applied potentials, and the analyte was undetectable after 45 min process time under all conditions. These results indicate that sufficient •OH radicals are generated to promote the oxidation of PPB even at the low potential of + 0.5 V. Moreover, the potentials applied did not favor competitive reactions such as oxygen evolution or the formation of other radicals that could decrease the efficiency of degradation. Values of K_{ap} for the PEC degradation of PPB carried out using TiO_2-NT and TiO_2-NT/WO_3 electrodes at different applied potentials are compared in Fig. 5c. The oxidation rate of PPB increased continuously with increasing positive potential, verifying that better electron/hole separation is achieved at more positive potentials, resulting in an improvement in process performance. Moreover, the modified TiO_2-NT/WO_3 electrode presented higher efficiencies at all applied potentials. In this case, the TiO_2-WO_3 heterojunction reduced the level of charge recombination and, more importantly, ensured the correct direction of charge flow even at low potential, with a consequential increase in the generation of •OH.

The mineralization rate of organic compounds is an important parameter in the evaluation of PEC efficiency since byproducts of the degradation process may remain in solution. Under the experimental conditions of the study, the behavior of the TOC removal profile was similar to that of PPB oxidation but, surprisingly, exhibited an augmented response to pH and applied potential. Although the pH effect is a complex issue associated with the byproducts, it influences the electrostatic interaction and consequently may favor the reactions by holes in the anode surface that increases the TOC removal rate. After 60 min

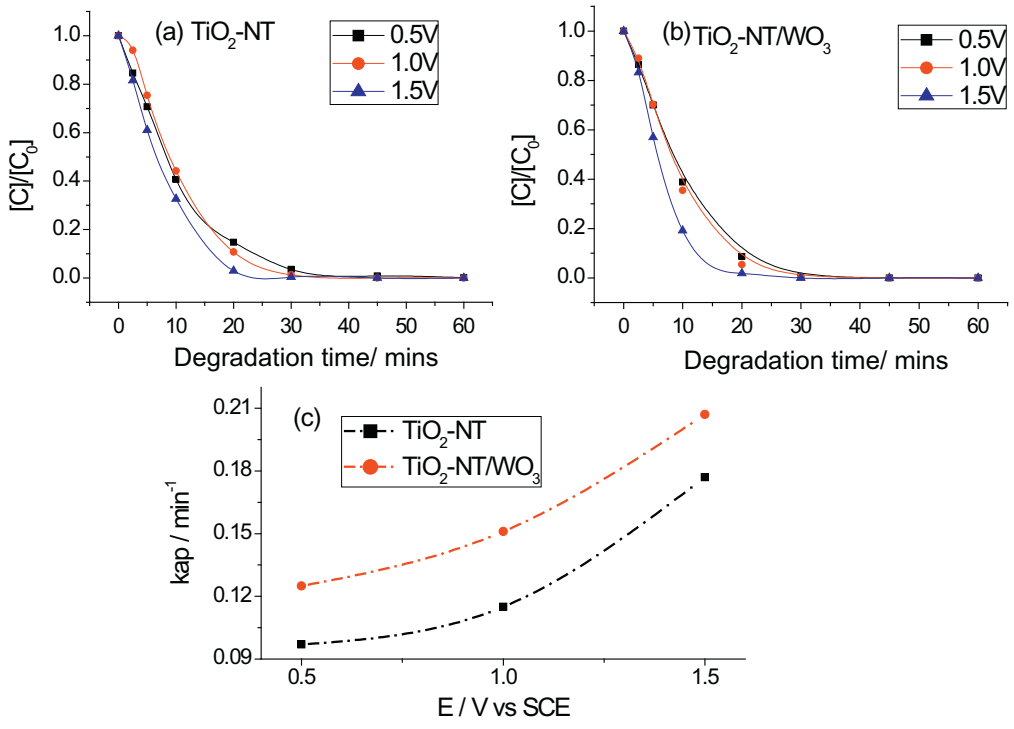

Fig. 5. The effect of bias potential on the rate of photoelectrocatalytic (PEC) degradation of propyl paraben (PPB) performed at pH 3 using: (**a**) the TiO_2-NT electrode, and (**b**) the TiO_2-NT/WO_3 electrode. Panel (**c**) presents the influence of bias potential on the kinetic parameters of the PEC degradation of PPB by the two electrodes at pH 3.0.

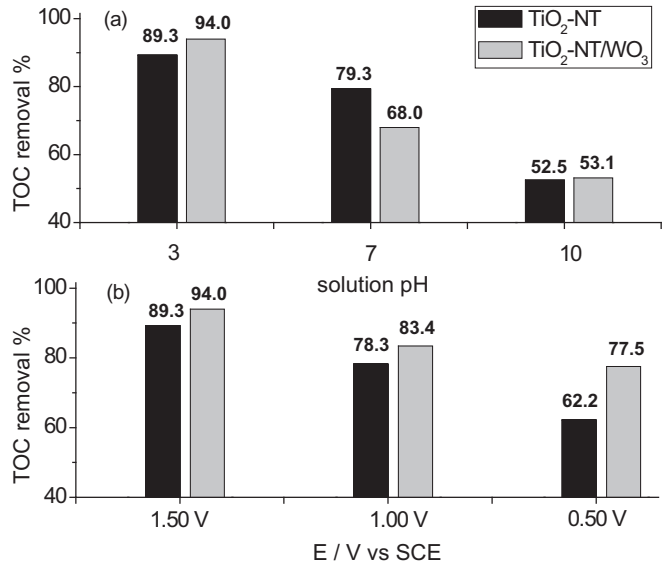

Fig. 6. Percentage removal of total organic carbon (TOC) after 60 min photoelectrocatalytic degradation of propyl paraben using TiO_2-NT and TiO_2-NT/WO_3 electrodes: (**a**) at different pH values and a bias potential of + 1.50 V *vs* SCE, and (**b**) at different bias potentials and a pH of 3.

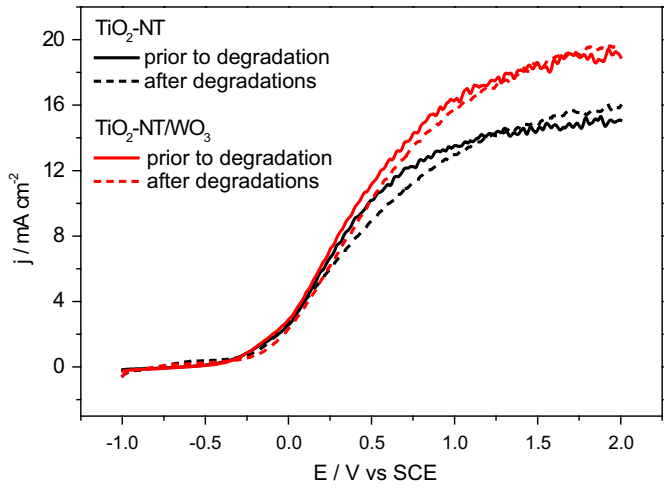

Fig. 7. Plots of photocurrent *vs* potential for TiO_2-NT and TiO_2-NT/WO_3 electrodes evaluated prior to (solid lines) and after more than 20 h (dashed lines) of process time. Experimental conditions: scan rate, 10 mV s^{-1}; electrolyte, Na_2SO_4 0.1 mol L^{-1} at pH 6; radiation source 125 W low pressure mercury vapor lamp.

of PEC at + 1.50 V and pH 3, the modified TiO_2-NT/WO_3 electrode produced almost complete mineralization of PPB with 94.0% TOC removal, while the unmodified TiO_2-NT electrode achieved 89.3% TOC removal under similar conditions (Fig. 6a). Although PPB oxidation was high under neutral (pH 7) and alkaline (pH 10) conditions, such efficiencies were not reflected in the removal of organic matter with the TiO_2-NT/WO_3 electrode achieving TOC removal levels of only 68.0 and 53.1%, respectively. As pointed out to other parabens [44], the route to PPB degradation may follow different steps to the oxidation in relation to pH and therefore generate intermediates with different stabilities. Thus, acidic conditions are not only required for the efficient oxidation of PPB but are particularly important for the removal of recalcitrant intermediates formed during the degradation process.

As shown in Fig. 6b, the effect of bias potential on the rate of mineralization was less marked in comparison with that of pH. Nevertheless, the modified TiO_2-NT/WO_3 electrode presented a better performance than the unmodified TiO_2-NT electrode at all applied potentials. Thus, the TiO_2-NT/WO_3 electrode achieved TOC removal values of 77.5 and 83.4% even at the low potentials of + 0.5 and + 1.0 V, respectively. These results verify that, at pH 3 and under an applied potential of 1.50 V, the modified TiO_2-NT/WO_3 electrode is more effective than the unmodified electrode in the oxidation of PPB and the removal of intermediates generated during the degradation process.

3.3. Stability of electrodes

In order to evaluate the durability of the electrodes, we determined their photoactivities prior to degradation studies and after 20 h of process time. The photoactivity is considered a crucial factor that influences the stability of the electrodes and, therefore, affects the PEC degradation performance. Fig. 7 shows plots of photocurrent *vs* applied potential, determined in 0.1 mol L^{-1} Na_2SO_4 electrolyte in the presence of UV/VIS irradiation, for TiO_2-NT and TiO_2-NT/WO_3 electrodes before and after use in degradation experiments. Modification of TiO_2-NTs with WO_3 generates a remarkable increase in electrode photoactivity of around 20% at an applied potential of + 2.0 V and, according to the results for PPB degradation, gives rise to a substantial improvement in the performance of the unmodified electrode. Moreover, plots relating to the used electrodes (dotted lines in Fig. 7) verify that both electrodes were highly stable even after exhaustive application in PEC. These findings substantiate the excellent durability and stability of the electrodes and, consequently, their applicability in PEC processes.

4. Conclusions

A comparative study on the photoeletrochemical oxidation of PPB by TiO_2-NT unmodified and modified with WO_3 was conducted. TiO_2 nanotubes were successfully decorated with WO_3 electrodeposited using a simple electrochemical deposition method. The photocurrent density of the modified TiO_2-NT/WO_3 have excellent activity and durability, it was found to be 20% higher than that of its unmodified counterpart. The enhancement in the photoactivity is related to the improvement of electronic transfer between VB and CB of WO_3 and TiO_2. As a result, there is an increase of half-life of holes directed to the anode surface and, therefore, an increase of the photocurrent. The rate of degradation fit a pseudo first order kinetics regarding PPB concentration and it is controlled by the applied potential and the pH of solution. Using the modified electrode, PPB was removed almost completely within 20 min of PEC performed at pH 3.0 with an applied potential of 1.50 V. Organic matter was efficient removed from the reaction solution under these conditions, almost the complete mineralization was attained in 60 min with 94% of TOC removal. The enhanced photoactivity was highly stable and reproducible, even after constant cycling between potentials, exhibiting excellent durability. In summary, this novel electrode modified with WO3 represents an important method for improving the properties of TiO2-NT and provides a promising application for degradation of parabens and other phenolic compounds.

Acknowledgments

The authors are grateful to the São Paulo Research Foundation (FAPESP), grants #2013/08543-3, #2014/50945-4 and #2016/01937-4, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq; grant no. 301492/2013-1 and 465571/2014-0 (INCT-DATREM)) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

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