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A study of the photocatalytic and photoelectrocatalytic degradation of diclofenac sodium using nanocrystalline TiO_2 films

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Abstract

We study the photocatalytic and photoelectrocatalytic degradation of diclofenac sodium which is a widely used non-steroidal drug known for its anti-inflammatory and analgesic properties. For this purpose nanocrystalline titania (nc-TiO2) films are employed in the presence of NaOH under UVA irradiation. In particular upon application of a forward (anodic) bias (+1V) the photodegradation rate is decreased while a reverse (cathodic) bias (-1V) leads to rate increase. Furthermore, IV curves are obtained (5mV/sec scans) under black light (UVA) illumination at various concentrations of the pharmaceutical in the presence of 0.25M NaOH. The results show that currents of up to 8mA can be achieved in the case of 5×10^{-5}mol L^{-1} diclofenac concentrations.

Keywords: photocatalysis; photoelectrocatalytic; degradation; diclofenac; nc-TiO2

1. Introduction

The photocatalytic degradation of various organic pollutants using wide band gap semiconductors under UV or solar light, has been extensively studied [1-4]. Among them TiO_2 is an inexpensive semiconductor, which exhibits high photocatalytic activity, is non-toxic and has good stability in aqueous solutions with good applicability in environmental remediation [5]. An interesting approach to enhance photocatalytic properties of catalysts towards degradation of organic pollutants is the photoelectrocatalytic process [6-8]. This method is based on the application of an electric potential across a photoanode where the photocatalyst is deposited. Due to the applied bias, a more effective separation of the photogenerated charge carriers (electron/hole) is expected and may additionally facilitate formation of oxidative radicals [9].

In the present work, we have undertaken a study of the photocatalytic and photoelectrocatalytic degradation of a non-steroidal anti-inflammatory drug with anelgestic properties, namely diclofenac sodium (Fig.1) using nanocrystalline (nc-TiO2) titania films under UV irradiation. Diclofenac sodium is used both in human and veterinary medicine and as it is not completely metabolized it is carried into surface waters and soil [10-12]. In general, the presence of anti-inflammatory drugs in natural waters [13,14] may have serious consequences to the aquatic life especially due to their role as endocrine disruptors [15] and thus their elimination is important both for the environment and public health.

Our method is proposed as an alternative to current treatment methods which are most commonly physiochemical such as activated carbon adsorption [16-19] or biological processes [20] where microorganisms are involved in the removal mechanism with membrane bioreactors [21-23] and activated sludge processes [24,25] being the most common routes. Nevertheless, such conventional treatment methods do not always tend to be as effective as common pharmaceuticals tend to resist biological degradation as well as natural attenuation [26].

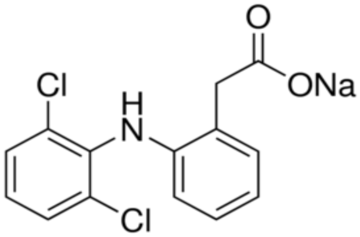


Figure 1. The chemical structure of diclofenac sodium

Currently there have been a number of efforts towards employing advanced oxidation processes (AOPs) in enhancing their elimination from the environment including both UV irradiation [27-29] or ozonation [30]. In particular, TiO2 assisted photocatalysis, which is also the focus of this work has also been previously showed promising results [31,32] towards the removal of analgesics and anti-inflammatory drugs including diclofenac sodium.

2. Materials and Methods

2.1 Materials

All reagents were obtained from Sigma-Aldrich. Diclofenac sodium was by Fluka according to the European Pharmacopoeia (EP) Reference Standards.Commercial nanocrystalline titania Degussa P25 was used in all reactor constructions and Millipore water was used in all experiments. SnO2:F transparent electrodes (FTO, resistance 8 Ω per square) were purchased from Pilkington.

2.1.1 Description of the reactor

A batch reactor was used consisting of a pyrex cylinder that could accept 100 ml of an aqueous solution of the photodegradable substance [33]. A nanocrystalline titania (nc-TiO2) photocatalyst was deposited on four FTO slides, covering in total an area of 2.5 cm × 6.5 cm. The four slides were introduced into the reactor at an upright position, which in turn was introduced into a home-made cylindrical construction carrying 4 black light tubes giving radiation peaking in the UVA, ideal for titania excitation. The tubes were placed at four symmetrical positions around the reactor and were covered with a metallic reflecting cylinder. The intensity of radiation at the position of the sample was approximately 1.5 mW cm^{-2}. Cooling of the reactor was ensured by means of air flow using an incorporated fan. The concentration of the photodegradable substance was monitored by absorption spectrophotometry using 2 ml aliquots, which were returned to the reactor after each measurement was completed.

Photoelectrocatalytic measurements were made by using a (3) electrode set up: an FTO (working) electrode covered on the conductive side with nc-TiO2 as well as a counter electrode (Pt foil 2.5 cm × 2.5 cm) and an Ag/AgCl reference electrode which were accommodated within the same reactor as in Fig. 2. In all cases the reactor was exposed to an ambient atmosphere. The electrolyte concentration (NaOH) was kept at a concentration of 0.25M.

2.1.2 TiO_2 thin film preparation

The TiO2 nanocrystalline thin films (nc-TiO2) were deposited both on FTO and microscope slides for all purposes as follows: the nc-TiO2 photocatalyst was deposited in two layers, a bottom compact layer and a top open structure **[**34]. The bottom layer was prepared using a sol–gel method while the top layer was deposited by using a paste made of Degussa P25 nanoparticles. Deposition of a compact bottom layer is common practice in making titania photoanodes since it facilitates upper layer attachment and increases electrical contact with the FTO electrode.

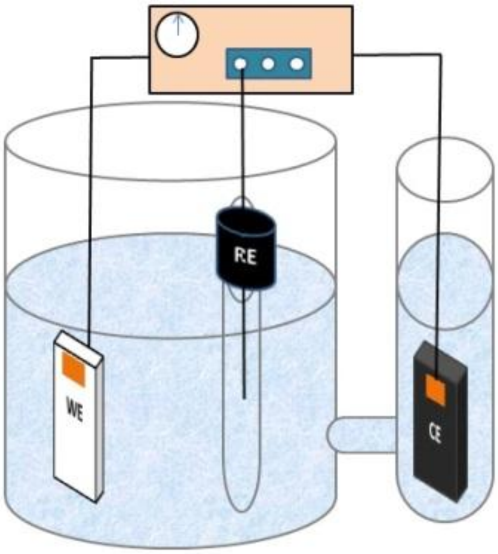


Figure 2. *A schematic representation of the photoreactor*

The bottom dense layer was deposited by the following procedure: 3.5 g of the non-ionic surfactant Triton X-100 was mixed with 19 ml ethanol. Then 3.4 ml glacial acetic acid and 1.8 ml titanium tetraisopropoxide were added under vigorous stirring. After a few minutes of stirring, the film was deposited by casting a thin layer of the sol and then it was left to dry in air for a few minutes. Finally, it was calcined at 550 °C. The temperature ramp was 20 °C per min up to 550 °C and the sample was left for about 10 min at that temperature. The final compact film was about 300–350 nm thick. On the top of this compact nanostructured layer, commercial Degussa P25 was deposited. For this purpose, we used a paste which was applied by screen printing. It was finally calcined again at 550 °C. This last sequence was repeated in order to obtain a top layer of about 10 μm thickness. The thickness of the films was measured using their SEM profiles. The geometrical area of the film as previously mentioned was 2.5 × 6.5 = 16.25 cm^2 and the quantity of the photocatalyst in each film was approximately 35 mg.

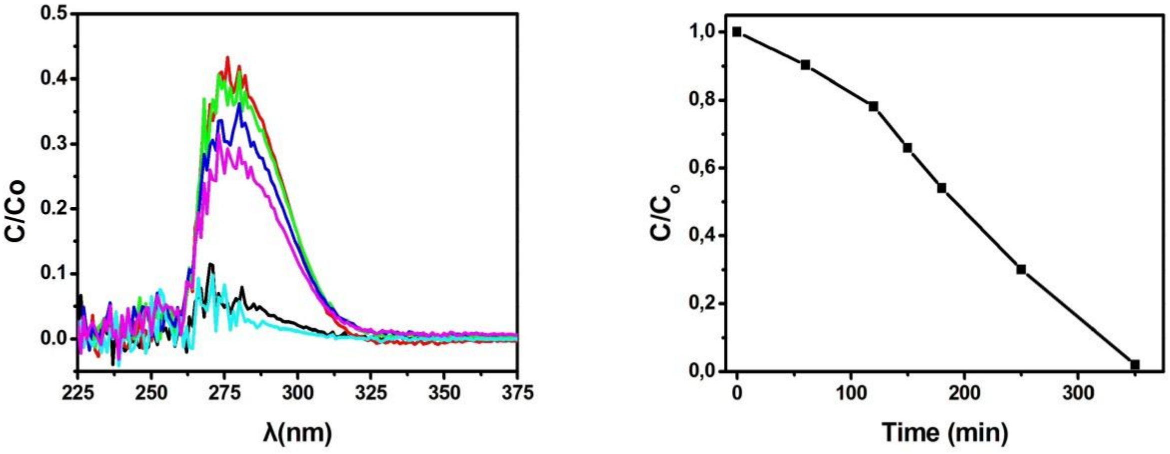
2.2 Methods

Absorption measurements were made with a Cary 1E spectrophotometer. Percent degradation was calculated relative to the initial absorbance (C/C0) of the untreated sample. Linear voltammetry curves were traced with an Autolab potentiostat PGSTAT128N and the same was used for applying bias. All current–voltage curves were traced at 5 mV s−1.

3. Results and discussion

At a first instance the absorption spectra of diclofenac sodium (3mg/100mL) were monitored in the presence of NaOH (0.25M) both under black light (UVA) illumination and in the dark. In particular, no photocatalyst, i.e. nc-TiO_2 was used. In both cases NaOH showed to have little influence on the degradation of diclofenac sodium, which was practically unaffected even after 24 hours of irradiation with black light of approximately 1.5 mW cm^{-2}. It should be noted that quantity of the pharmaceutical tested (3mg/100mL) is much higher than the usual quantities of diclofenac sodium detected in surface waters. Nevertheless, higher concentrations were chosen in order to test the photocatalytic capacity at elevated pollution levels [10,15] and to facilitate monitoring by absorption spectrophotometry.

Following that the degradation of diclofenac sodium was studied in the presence of NaOH 0.25M using a 4 titania films (nc-TiO_2) deposited on microscope glass, providing 140mg of photocatalyst. The films were placed at four diametric positions in from of four black light tubes used for excitation and the absorption spectra were detected (Fig. 3a). The decay of the relative concentration C/C_0 of diclofenac sodium was minimized after 5 hours and all material was degraded (Fig. 3b).



a. **b.**

Figure 3 (a)The absorption spectra of diclofenac during nc-TiO2 photocatalysis (b) The reduction of the relative concentration C/Co of diclofenac during a 5h period

Additionally, the degradation of diclofenac sodium was studied in the presence of NaOH 0.25M using a (3) electrode set up as described in Fig. 2 under black light. The nc-TiO2 was deposited on the working electrode (FTO) in 2 layers of sol-gel and 2 layers of Degussa P25 paste, while the counter electrode was made of Pt foil. The reference electrodes were Ag/AgCl. A static bias was applied (+1V, 0V, -1V) using a potentiostat for the study of photodegradation while the concentration of diclofenac sodium was kept constant at 3mg/100mL. It is noted that the forward (anodic) bias (+1V) decreased the photodegradation rate in the presence of NaOH while a reverse (cathodic) bias (-1V) increased the photodegradation rate. In Fig 4. below we present the variation of the relative absorbance (C/Co) in all cases.

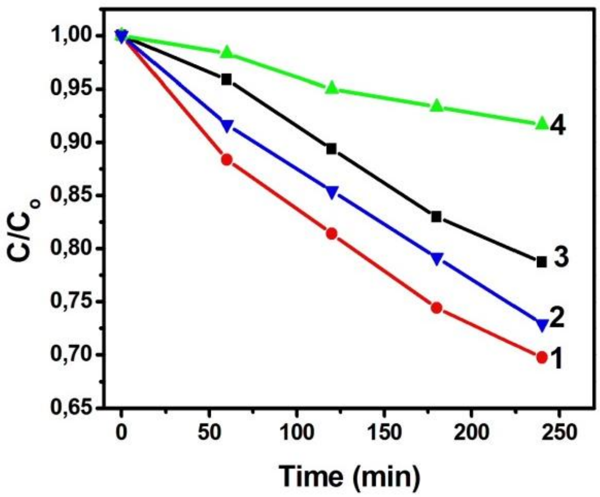


Figure 4. The application of reverse (cathodic) bias (-1V) increased the photodegradation rate as can be seen by comparing the relative absorbance in all cases: (1) -1V, (2) 0 V, (3) no-bias, (4) +1V

Furthermore, I–V curves (Fig.5) were obtained with a nc-TiO2/FTO photoanode (3 electrode system) in the presence of NaOH (0.25 M) in all the following cases: (1) in the dark, (2) under illumination and at two different diclofenac concentrations again under black light, i.e. at (3) 2.5 × 10^{-5}mol L^{-1} and finally at (4) 5 × 10^{-5}mol L^{-1}. All current–voltage curves were traced at 5 mV s−1 using a potentiostat.

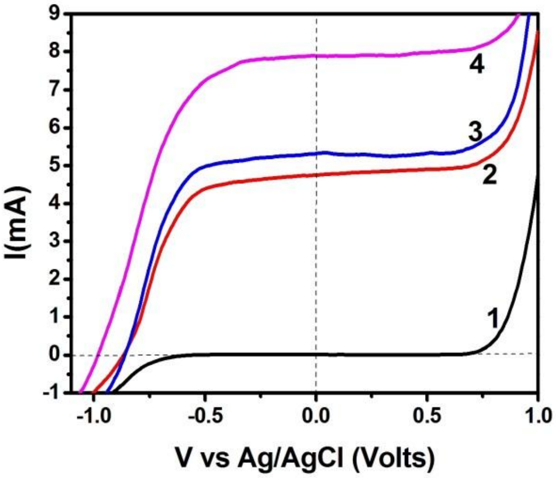


Figure 5. I-V curves in the presence of NaOH (0.25M) in the casesof :(1) no illumination (2) black light and (3) 2.5 × 10^{-5}mol L^{-1}diclofenac and (3) 5 × 10^{-5}mol L^{-1}diclofenac, both under black light illumination.

The presence of diclofenac sodium resulted in a substantial increase of the anodic photocurrent, indicating that an important interaction has taken place between the photoanode and the photodegradable target. Obviously, diclofenac was oxidized by consuming photogenerated holes thus liberating electrons and causing a current increase.

Conclusions

The photocatalytic degradation of diclofenac can be achieved using nanocrystalline titania films. In the presence of an alkaline electrolyte (NaOH) it was observed that photocatalytic degradation was slower than in pure water, which could be explained due to the fact that alkaline environments do not encourage the adsorption of the pharmaceutical to the surface of the nc-TiO_2 films. It was further noted that the rate of degradation of diclofenac was increased by application of a reverse bias which assisted in the electron–hole separation and diclofenac attraction to the photoanode. IV curves traced at 5 mV s−1 using a potentiostat showed that currents of up to 8mA can be achieved in the case of 5 × 10^{-5}mol L^{-1} diclofenac concentrations under black light illumination again in the presence of NaOH.

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