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Continuous photodegradation of naphthalene in water catalyzed by TiO_2 supported on glass Raschig rings

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Abstract

Polycyclic aromatic hydrocarbons (PAH's) are a class of persistent organic pollutants of special concern since they are carcinogenic and mutagenic. In this paper, the design of a continuously stirred tank reactor is reported for the photodegradation of the simplest and most water-soluble PAH, naphthalene, in water using TiO_2 (in the crystalline form of anatase), supported on glass Raschig rings as catalyst, with oxygen as electron acceptor. A first order kinetic rate constant has been calculated for this photodegradation. The irradiated solution after the reaction has been analysed and only traces of 1-naphthol, 1,4-naphthalenedione and phthalates have been found as intermediate products of the photodegradation.

Keywords: Naphthalene; Photodegradation; Continuous reactor; Titanium dioxide

1. Introduction

Polycyclic aromatic hydrocarbons (PAH's) are a class of persistent organic pollutants of special concern since they are carcinogenic and mutagenic [1]. This type of compounds frequently appears at the dump sites of coal mines, since PAH's are very abundant in coal. In the Asturias region (North of Spain), many old coal mines are being closed, leaving their dump sites heavily polluted with this type of contaminants [2]; moreover, since rainfall is very frequent in this region, the surface and ground waters are seriously affected by this pollution [3].

Solid TiO_2 (in the crystalline form of anatase) is a semiconductor that under ultraviolet irradiation can promote an electron (e^-) from the valence band (VB) to the conduction band (CB), leaving a positive hole (h^+) at the site where the electron was originally captured. When TiO_2 is suspended in water, both the electron and the hole can generate radicals (hydroxide and superoxide) very active in the oxidative degradation of organic pollutants in water [4–9] (Scheme 1).

The photodegradation of naphthalene, the simplest and most water-soluble PAH, in water solution catalyzed by TiO_2, has been extensively studied in the past few years with good results [10–14]. However, from the chemical engineering point of view, all these works were carried out in batch reactors, and only one work was undertaken in a catalytic recycle reactor with infinite recirculation ratio (the naphthalene solution was continuously recirculated without enter nor exit) [15].

Moreover, this technology has not been successfully commercialised, in part because of the costs and difficulties in separating TiO_2 nanoparticles from the suspension after degradation has occurred. In fact, the use of solid TiO_2 (anatase) as catalyst for the photodegradation of organic pollutants in water presents important operational problems. The nanosize of the TiO_2 crystals obtained by the sol–gel procedure [16] greatly hinders the filtration of the catalyst after the reaction. To avoid this problem, TiO_2 film photocatalysts have been supported in a variety of materials, although as a result of the immobilization, the surface area of the photocatalyst decreases greatly, and the TiO_2 film photocatalysts usually show poor performance. Some authors are supporting the TiO_2 on mesoporous materials [17] and stainless steel [18], but in our work the use of glass Raschig rings has been

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$$TiO_2 + h\upsilon \rightarrow e^-(CB) + h^+(VB)$$
$$H_2O + h^+(VB) \rightarrow OH^\bullet + H^+_{aq}$$
$$O_2(ads) + e^-(CB) \rightarrow O_2^{-\bullet}(ads)$$
$$h\upsilon \geq E_G$$

Scheme 1. Mechanism of formation of hydroxyl and superoxide radicals in water catalyzed by TiO_2 (E_G = gap energy).

preferred as supports for our TiO_2 photocatalyst. In this way, a high surface area is kept but at the same time the separation of the catalyst becomes an easy procedure. The aim of our research is to develop a methodology that could be operated continuously during long reaction times in natural water environments, but as a beginning a continuously stirred tank reactor (CSTR) has been developed for this purpose.

2. Experimental

2.1. Materials

TiO_2 nanoparticles were synthesized by the sol–gel process according to the method of Grätzel and co-workers [16], and were supported on glass Raschig rings (8 mm long × 7 mm o.d.) by the repeated dip-coating method, air drying and calcination at 400 °C for 10 min several times. This catalyst was analysed by X-ray powder diffraction (XRD, Philips PW 1820) resulting a monophase of anatase, and also by scanning electron microscopy (SEM, Hitachi S-570) coupled with energy dispersive X-ray microanalysis (EDX, Rontec M1). The catalyst Raschig rings were thoroughly washed with ultrapure MilliQ water (Millipore) under stirring prior to use, to avoid the leaching of TiO_2 particles to the irradiated solution during the reaction.

2.2. Photoxidation general procedure

The reactors used in the experiments were: (a) a 2 L spherical Pyrex glass tank stirred at 1000 rpm with a Teflon stirrer powered by an IKA RW 20 DZM engine (Fig. 1a); (b) a 2 L photochemical reactor stirred with a PTFE coated magnetic bar (Fig. 1b). Five litres of naphthalene solution of around 10–25 mg/L were prepared in ultrapure MilliQ water, and were fed to the reactor at a constant rate using a twin body Dosapro Milton Roy pump. The reactors were irradiated with different lamps, whose emission spectra are given in Fig. 2. Air was also fed to the reactors from a compressor Airblock through a mass flow controller Brooks TR-50E at a rate of 6 normal litres per hour (L_n/h) (higher air flows may result in naphthalene volatilisation without degradation). The irradiated solution was extracted from the reactor at the same constant rate using the twin body of the pump, thus keeping a constant solution volume (1.5 L) in the reactor during the experience. This solution was continuously analysed by UV spectroscopy at 275 nm (naphthalene, $\log \varepsilon = 3.76$) in a Lambda 3 Perkin-Elmer spectrophotometer. The last 1 L sample taken from the reactor, after around 7 h in steady state was extracted by solid phase extraction methods (SPE Supelco Supelclean ENVI-18SPE tubes, 6 mL, 0.5 g), and analysed by gas chromatography/mass spectrometry in a GC/MS Hewlett-Packard 6890-MSD 5973. The photodegradation products were identified by comparison of their mass spectra with the spectral library Wiley 275 using the software HP Chemstations.

3. Results and discussion

3.1. Preparation of the catalyst rings

The TiO_2 was synthesized from titanium isopropoxyde by acid hydrolysis with 70% (w/w) nitric acid after the Grätzel method [16]. The Raschig rings were immersed separately in the aqueous TiO_2 suspension obtained, dried with an air compressor and calcined at 400 °C for 10 min. This process was repeated several times with each ring to obtain a homogeneous TiO_2 film, and the rings were finally calcined at 400 °C for 4 h. The Raschig rings were thoroughly washed with distilled water under stirring, to avoid the leaching of TiO_2 particles during the experiments, and dried. This dip-coating process was carried out simultaneously with a Pyrex glass disk (1.30 mm thick × 26.35 mm o.d.), in order to analyze the TiO_2 film by XRD, which shows the presence of anatase as the only crystalline phase (Fig. 3). The XRD analysis allows also to calculate the TiO_2 characteristic crystal size t (in nm) by means of the Scherrer equation [19]:

$$t = \frac{0.9\lambda}{B\cos\theta_B} = 7.3\,\text{nm} \tag{1}$$

where λ is the X-ray wavelength of incident radiation (Cu $K\alpha_1 = 0.154$ nm), B the angular width of the peak at half maximum height (rad) and θ is the characteristic diffraction angle (0.221 rad for anatase).

The rings were also analysed by SEM coupled with EDX. The Fig. 4 shows the morphology of the TiO_2 film in a microphotography of one of the rings. The Fig. 5 shows the EDX analysis with the characteristic X-ray lines of titanium and small impurities of silicon, calcium, potassium and sodium from the glass support.

3.2. Photodegradation results

A concentrated (10–25 mg/L) solution of naphthalene in ultrapure water, prepared in our laboratory, was continuously fed to the CSTR reactor equipped with a catalyst consisting of 75 glass Raschig rings with TiO_2 supported; the reactor was irradiated with the appropriate lamp (Table 1), and air was fed to the system. The air flow should be carefully controlled below 6 L_n/h, since naphthalene can volatilise from the solution without degradation when using higher air flows. The solution flow entering (and exiting) the reactor was calculated after Pal and Sharon [10], which have reported that

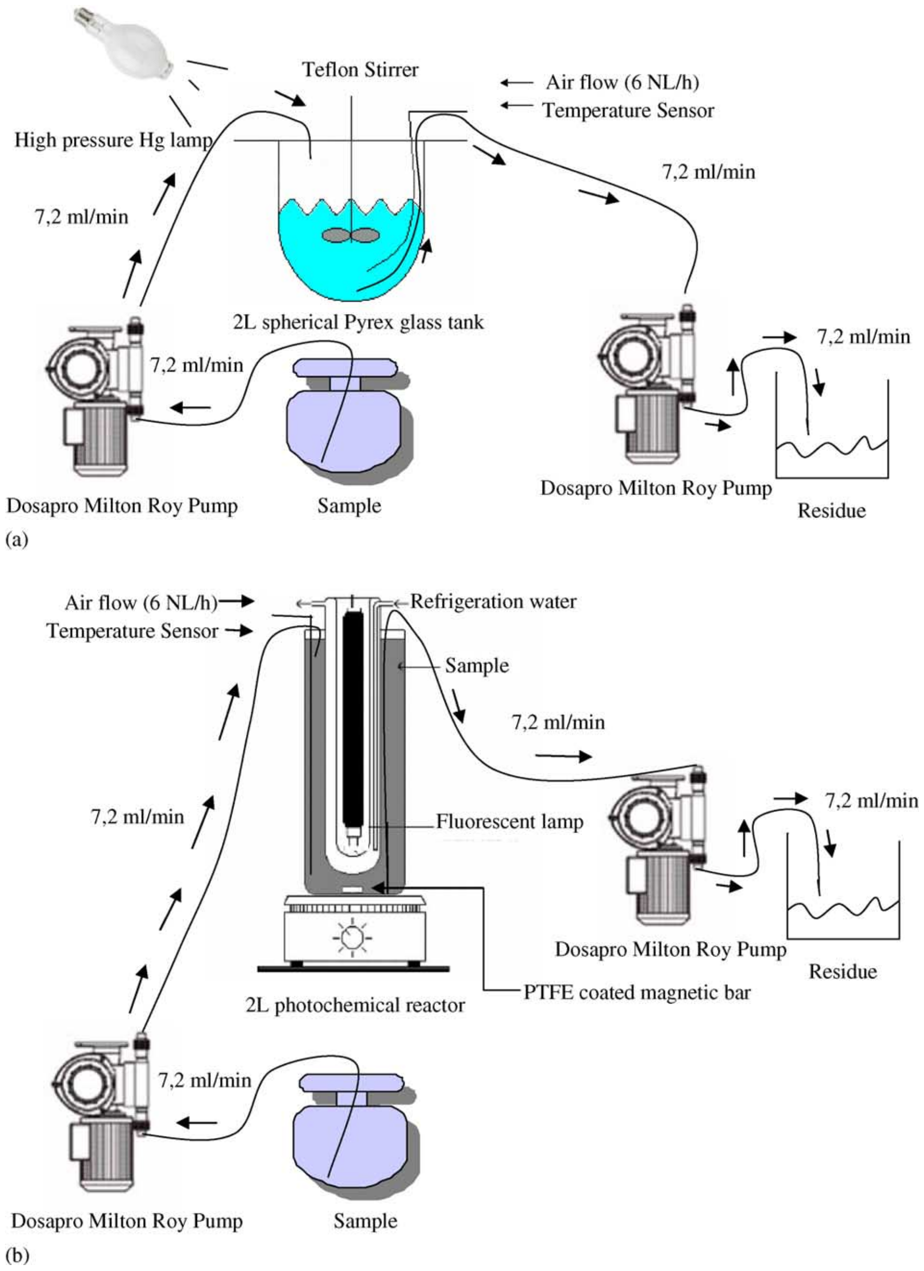


Fig. 1. (a) Two litre spherical Pyrex glass tank and (b) 2 L photochemical reactor.

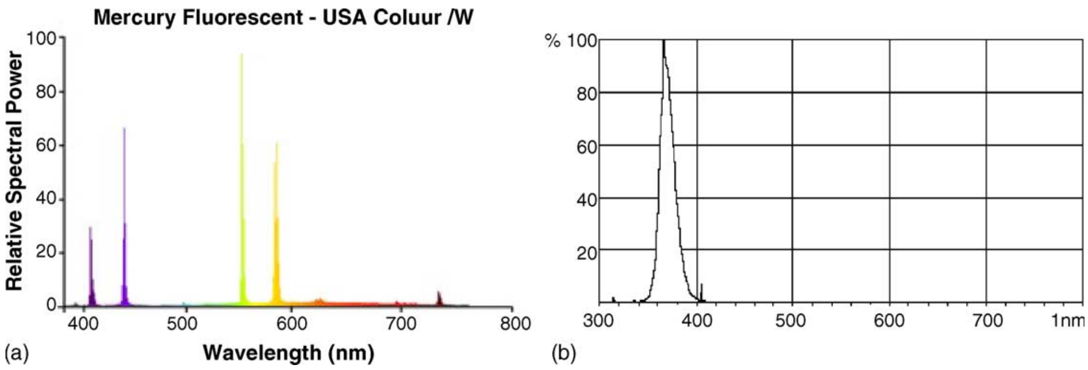


Fig. 2. (a) High-pressure mercury lamp emission spectrum (b) low-pressure mercury lamp emission spectrum.

Table 1

Reactor	Lamp	C_{N_0} (mg L^{-1})	v_0 (mL min^{-1})	χ_N	k (min^{-1})
Stirred tank	High-pressure Hg 18000 lm	21.3	7.2	0.408	3.31×10^{-3}
Photoreactor	Low-pressure Hg 400 lm	13.3	7.2	0.247	6.26×10^{-4}

C_{N_0}: initial concentration of naphthalene; v_0: volumetric flow rate; χ_N: fractional conversion of naphthalene; k: FOK rate constant.

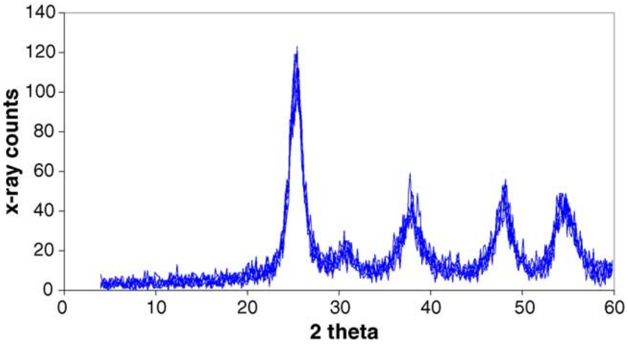


Fig. 3. X-Ray diffraction pattern of the TiO_2 catalyst supported on glass.

the photodegradation of naphthalene catalyzed by TiO_2 films follows a first order kinetic (FOK) rate in batch reactors, with $k = 0.0479\,\text{min}^{-1}$ and a naphthalene final conversion $\chi_N = 0.91$. These data were introduced in the CSTR design Eq. (2), assuming also a FOK model [20]:

$$k\tau = \frac{\chi_N}{1 - \chi_N} \tag{2}$$

obtaining the spatial time τ. The volume of liquid in the reactor (V in L) and the initial concentration of naphthalene (C_{N_0} in mg/L) were used together with the spatial time to calculate the molar flow rate of naphthalene (F_{N_0} in mol/min), and the volumetric solution flow (v_0 in mL/min):

$$\tau = \frac{VC_{N_0}}{F_{N_0}} = \frac{V}{v_0} \tag{3}$$

The irradiated solution exiting at the same rate from the reactor was continuously analysed by UV spectroscopy at 275 nm ($\log \varepsilon = 3.76$) to follow the photodegradation of naphthalene.

The Fig. 6 shows the decreasing of the concentration of naphthalene with time in two of the experiments. As can be seen in this figure, after a short induction period of around 30 min, the concentration of naphthalene exiting from the reactor is stabilized for the rest of the experiment that lasted for about 7 h in steady state. The conversion of naphthalene for the experiments shown in Fig. 6 is summarized in the Table 1. These values allow to calculate the FOK rate constants for the photodegradation of naphthalene, using the equation of a CSTR [20] (Table 1). These rate constants are much lower that the constant calculated in a batch reactor ($47.9 \times 10^{-3}\,\text{min}^{-1}$) [10]. This may suggest that the rate constants for the photodegradation of other PAH's in continuous systems may be significantly lower than the values reported for discontinuous experiments.

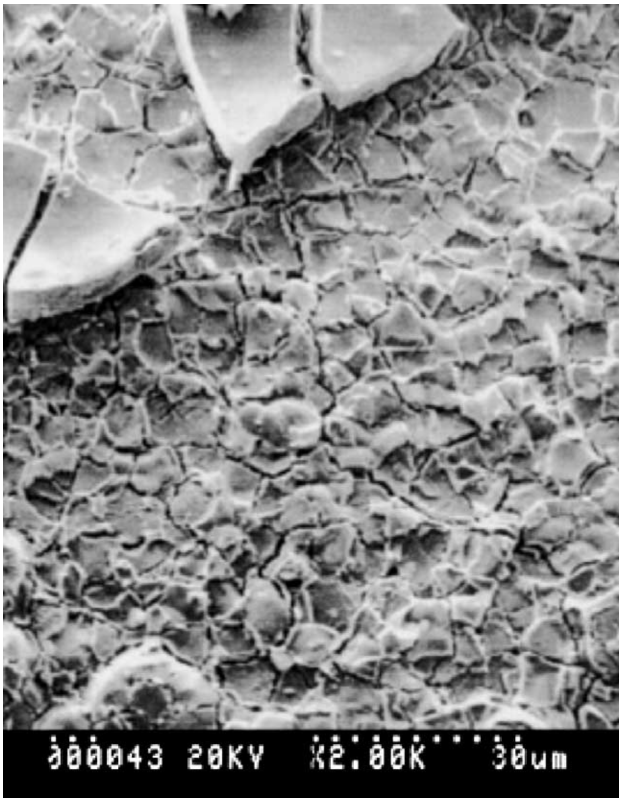


Fig. 4. Scanning electron microphotography of the TiO_2 film supported on the glass rings.

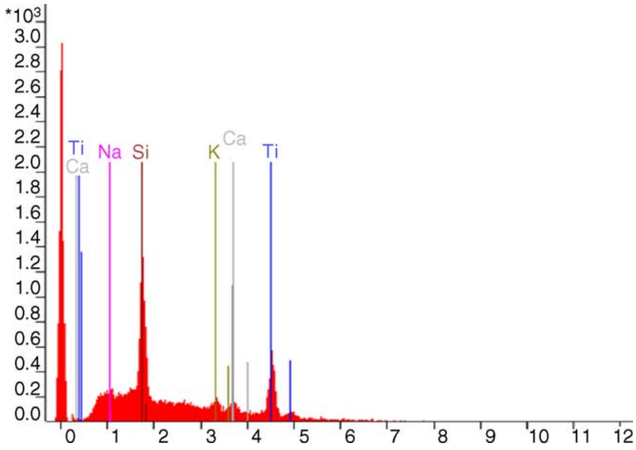


Fig. 5. Energy dispersive X-ray microanalysis of the TiO_2 film supported on the glass rings.

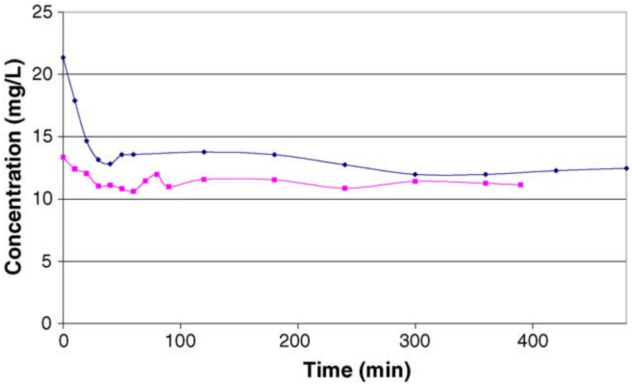
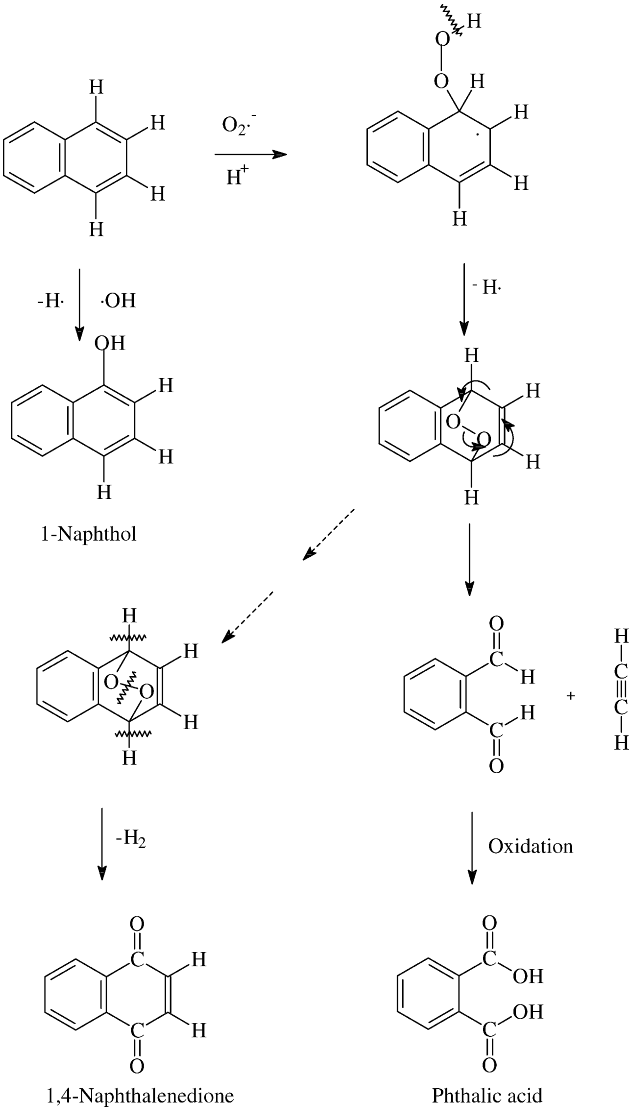


Fig. 6. Concentration of naphthalene (mg/L) vs. time (min) in the photodegradation experiments: (♦) 2 L stirred tank reactor and high-pressure Hg lamp; (■) 2 L photochemical reactor and low-pressure Hg lamp.



Scheme 2. Mechanism of formation of 1-naphthol, 1,4-naphthalenedione and alkyl phthalates by photoxidation of naphthalene.

We measured continuously the temperature and the pH of the naphthalene solution during all the experiments. With the high-pressure mercury lamp in the 2 L stirred tank, the temperature raises from the initial 26 °C to final 32 °C as a consequence of the unavoidable heating effect of the irradiation; in the photochemical reactor, the temperature was kept constant around 22 °C. The pH ranges from 7.39 at the beginning of the experiments to 7.82 at the end, since the proposed mechanism of naphthalene photodegradation consumes H^+ (see Scheme 2).

The analysis of the irradiated solutions at the end of the experiments by GC/MS shows only the peak of unreacted naphthalene and traces of 1-naphthol, 1,4-naphthalenedione and alkyl phthalates as intermediate products of the photodegradation. The formation of these photoxidation products could be explained by the attack of the hydroxyl ($^\bullet$OH) and superoxide ($O_2^{\bullet -}$) radicals to the naphthalene molecule and posterior evolution to the final products found (Scheme 2). Although several mechanisms have been published in the literature to explain the photodegradation of 1-naphthol, 1,4-naphthalenedione and alkyl phthalates to CO_2 [10–14], we could not identify any of the reported intermediate products in our experimental solutions.

4. Conclusions

Experiments for TiO_2 photocatalytic degradation of naphthalene in water solution were carried out in a continuously stirred tank reactor (CSTR). The results are summarized as it follows:

(1) TiO_2 was supported on glass Raschig rings to facilitate filtration of the catalyst after the experiment without essential loss of active catalytic surface.
(2) Naphthalene photodegrades continuously in water solutions with conversions ranging from 25 to 40% depending of the type of lamp and of CSTR, leaving no intermediate products, only traces of 1-naphthol, 1,4-naphthalenedione and alkyl phthalates.
(3) The FOK rate constants for this continuous process were 3.31×10^{-3} min^{-1} (high-pressure mercury lamp) and 6.26×10^{-4} min^{-1} (low-pressure mercury lamp), 15 and 76 times lower, respectively, than this same constant in batch reactors under similar experimental conditions.

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