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Biosensor-based real-time monitoring of paracetamol photocatalytic degradation

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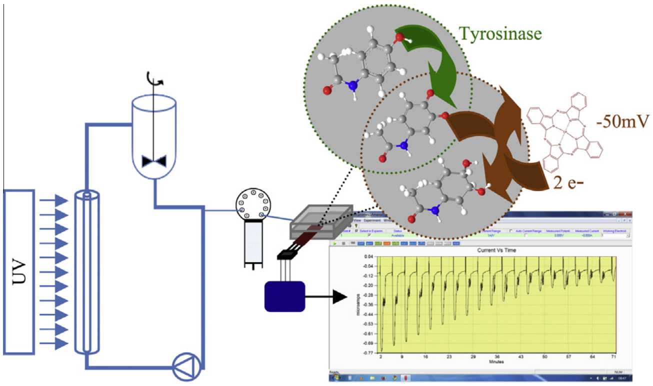
HIGHLIGHTS

- A flow-cell biosensor was developed for monitoring a photocatalytic process.
- The biosensor was based on tyrosinase immobilization on CoPC-modified SPCE.
- The photocatalytic degradation of paracetamol was successfully monitored.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents for the first time the integration of a biosensor for the on-line, real-time monitoring of a photocatalytic degradation process. Paracetamol was used as a model molecule due to its wide use and occurrence in environmental waters. The biosensor was developed based on tyrosinase immobilization in a polyvinylalcohol photocrosslinkable polymer. It was inserted in a computer-controlled flow system installed besides a photocatalytic reactor including titanium dioxide (TiO_2) as photocatalyst. It was shown that the biosensor was able to accurately monitor the paracetamol degradation with time. Compared with conventional HPLC analysis, the described device provides a real-time information on the reaction advancement, allowing a better control of the photodegradation process.

1. Introduction

Pharmaceuticals, personal care products and their degradation compounds are organic contaminants that have been detected in wastewater and surface waters throughout the world (Benotti et al., 2009). These emerging pollutants, like many other anthropogenic compounds, are continuously introduced into the aquatic environment from several sources like industries, urban and hospital wastes (Langford and Thomas, 2009). Paracetamol (4-acetaminophen) is commonly used as analgesic and antipyretic drug for human beings. At therapeutic doses, it is considered a safe drug. Therefore, in most countries, paracetamol can be purchased in retail stores as an over-the-counter preparation, and it is

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currently the most widely used drug worldwide (An et al., 2009). This molecule is easily accumulated in aquatic environments; it has been shown to be present in surface waters, wastewaters, and drinking waters throughout the world (Wu et al., 2012).

Paracetamol-contamined waters are mainly treated by usual oxidation processes (Tunay et al., 2010) e.g. H_2O_2/UV (Vogna et al., 2002; Andreozzi et al., 2003) and ozonation (Andreozzi et al., 2003). In 2004, Sirés et al. have described the use of UV light associated to electrochemical methods for paracetamol mineralization in water by catalytic action of Fe^{2+} and Cu^{2+} on electrogenerated hydrogen peroxide (Sirés et al., 2004, 2006). Although these methods may be efficient for treating this pollutant, the harsh reaction conditions, the generation of secondary products, and the high operational cost associated with these techniques have often made them not a desirable choice (Wu et al., 2012). Recently, the photocatalytic oxidation of paracetamol has been investigated (Yang et al., 2008) and main reaction intermediates have been identified (Zhang et al., 2008). Heterogeneous photocatalysis appears as a promising alternative to degrade organic micropollutants in a non-selective manner. In photocatalysis, the excitation of a photocatalyst with UV rays allows the creation of electron–hole pairs that triggers the formation of hydroxyl radicals, thus enabling chemical species to be broken down and finally, mineralized into CO_2 and water (Galvez et al., 2003). The use of solar radiations as UV source would allow obtaining energetically-autonomous, self-sufficient water treatment processes (Malato et al., 2009). An efficient use of UV light thus represents a major challenge in the conception and the development of this technology adapted for a sustainable water treatment (Bahnemann et al., 2004). Basically, such efficiency is highly dependent of the photocatalytic media implemented in the reactor that may be added in a slurry free form or immobilized on an adapted support (Plantard and Goetz, 2014).

Sensitive and cost-effective detection techniques are fundamental in order to accurately determine the level of waters contamination before, during and after treatment process. Conventional methods involve HPLC, GC/MS and 2D ^{1}H ^{13}C ^{15}N NMR analysis (Vogna et al., 2002; Espinosa Bosch et al., 2006). These methods are highly sensitive and allow the determination of a large number of compounds, but they are costly, long and/or require time-consuming pre-treatment procedures that may cause a partial loss or transformation of the target, thereby leading to underestimated results (Espinosa Bosch et al., 2006). Moreover, these methods are not suitable for on-line and real-time analysis.

Alternative methods are mainly based on the biosensor technology, they have already been developed for the detection of several pharmaceutical compounds in water (Adrian et al., 2009) including paracetamol (Odaci et al., 2006; González-Sánchez et al., 2011). However, enzymatic biosensors, one of the most promising advanced monitoring methods (Istamboulie et al., 2010a), have not been reported yet for the control of pharmaceuticals degradation processes. Valero et al. showed that paracetamol can be oxidized by the monophenolase activity of tyrosinase to its corresponding o-quinone (Valero et al., 2002, 2003a). This group has also studied the use of tyrosinase for paracetamol quantification, mentioning the possibility to immobilize this enzyme for designing a specific biosensor (Valero et al., 2003b). Based on this idea, a biosensor including avocado tissue as a source of tyrosinase has been developed (Vieira et al., 2013), and applied to the chronoamperometric determination of paracetamol in pharmaceutical formulations (Fatibello-Filho, 2001).

In the current study, an enzymatic biosensor was developed by immobilizing tyrosinase on specially-tailored screen-printed electrodes allowing the fast and accurate determination of paracetamol. The biosensor was incorporated in a flow-cell system that was associated to the photocatalytic process, thus allowing the real-time monitoring of paracetamol photodegradation. The validation of the monitoring system was performed using conventional chromatographic analysis (HPLC-UV).

2. Materials and methods

2.1. Chemicals and materials

Tyrosinase (Tyr, EC.1.14.18.1 from mushroom) having 4276 U mg^{-1} and paracetamol (4-acetaminophen) were obtained from Sigma–Aldrich (France). Poly (vinyl alcohol) azide-unit water pendant photo-crosslinkable polymer (PVA-AWP) was provided by Toyo Gosei Kogyo Co (Chiba, Japan). The enzyme was dissolved in distilled water containing 0.1% albumin at 50 U mL^{-1}, and the stock solution was dispensed into several aliquots that were stored frozen at −20 °C. The pastes used for screen-printing, Electrodag 423SS and 6037SS, were obtained from Acheson (Plymouth, UK), cobalt phthalocyanine (CoPC)-modified carbon paste was purchased from Gwent Electronic Materials, Ltd (Gwent, UK). A glycerophthalic paint (Astral, France) was used as insulating layer. Transparent PVC sheets (200 mm × 100 mm × 0.5 mm) (SKK, Germany) were used as screen-printing supports.

2.2. Photocatalytic reactor

The photo-reactor was a cylindrical borosilicate glass tube (internal diameter 1.2 cm, length 80 cm) operating in a closed recirculation circuit with a stirred reservoir tank, with a total working volume of 1 L (Goetz et al., 2009). The solution flowed through the reactor inside the annular space formed between the inner tube and the reactor inside wall and was mixed in the recirculation tank. The solution was continuously re-introduced by means of a volumetric pump. Temperature inside the chamber containing the system was kept almost constant by means of a fan blowing the warm air out. The radiation source was a UV lamp (VL-330) with emission centred at 365 nm and the radiation flux density at the reactor axis was fixed at 10 W m^{-2}. To illuminate the total surface of the reactor, an aluminium parabolic collector was positioned just behind the reactor.

Two TiO_2 catalyst materials with different properties were investigated: a powder supplied by Degussa and a cellulose support impregnated with TiO_2 provided by Alhstrom. Degussa P-25 is the most widely used photocatalyst, it is considered as the reference material according to its photocatalytic behavior. Its specific surface area (BET) was 54 m^2 g^{-1} and the particles of TiO_2 had an average diameter of about 20 nm. The catalyst in a powder form was dispersed in solution to obtain a suspension. As described in a previous work, an optimum concentration of 0.7 g L^1 was used, allowing the total absorption of the radiation entering the tubular reactor (Plantard and Goetz, 2014). The Ahlstrom photocatalytic material consisted of TiO_2 (Millenium PC-500) immobilized on a flat and flexible non-woven support of cellulose fibers (paper grade 1048). Its specific surface area referenced with the total photocatalytic material mass was equal to 98 m^2 g^{-1}. More precisely, this photocatalytic material consisted of cellulosic fibers (38 g m^{-2}), TiO_2 (16.7 g m^{-2}), zeolite (2 g m^{-2}) and SiO_2 (13.3 g m^{-2}). The photocatalytic media was wrapped around a tube (diameter 5 mm) at the axial center of the reactor. The useful surface of the photocatalytic media in the reactor was 0.02 m^2.

2.3. Tyrosinase-based sensors and flow system

Screen-printed electrodes (SPE) were prepared using a semi-automatic DEK 248 screen-printing system (Weymouth, UK) according to a procedure previously described (Istamboulie et al., 2010b). The working electrode was a 4 mm diameter disk, the counter electrode was a 16 mm × 1.5 mm curved line and the Ag/AgCl