Integration of a photoelectrochemical cell in a flow system for quantification of 4-aminophenol with titanium dioxide

Camila D. Mendonça[a,b,1], Vanoushe Rahemi[a,1], Jonas Hereijgers[c], Tom Breugelmans[c,d], Sergio A.S. Machado[b], Karolien De Wael[a,e,*]

[a] *AXES Research Group, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium*
[b] *Institute of Chemistry of São Carlos, University of São Paulo, IQSC – USP, Av. Trabalhador São-carlense 400, São Carlos, SP, Brazil*
[c] *ELCAT Research Group, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium*
[d] *Separation & Conversion Technologies, VITO, Boeretang 200, 2400 Mol, Belgium*
[e] *NANOlab Center of Excellence, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium*

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ABSTRACT

The photoelectrochemical quantification of phenolic compounds such as hydroquinone (HQ) and 4-aminophenol (4-AP) is accomplished by integrating a photoelectrochemical cell into a flow injection analysis (FIA) setup. It is a well-known fact that during the electroanalysis of phenolic compounds, the electrode surface is susceptible to poisoning. However, electrode fouling can be reduced significantly by using the FIA system with periodic washing of the electrode. Reactive oxygen species (ROS), which are generated on the surface of TiO_2 under UV light, can oxidize phenolic compounds such as 4-AP. The oxidized form of 4-AP is reduced back at the electrode surface, generating a measurable signal proportional to its concentration. The factors influencing the performance of the sensor, such as flow rate, applied potential for back reduction and pH, are investigated in detail. In the concentration range 0.0125–1.0 μM, a linear correlation between the photocurrent and the concentration of 4-AP was observed with a sensitivity of 0.6 A M^{-1} cm^{-2} and a limit of detection of 18 nM. A straightforward analytical methodology for the on-site, highly sensitive and low-cost quantification of phenolic compounds is presented, based on the use of TiO_2 in a photoelectrochemical flow cell.

1. Introduction

Flow injection analysis (FIA) is an approach for the automated chemical analysis of organic contaminants [1–5]. This approach ensures high mass transfer and provides clean electrode surfaces after periodic washing steps [6], improving the robustness of the method and allowing rapid analysis [7]. In order to enhance the sensitivity of detection, FIA has been combined with electrodes modified with carbon nanotubes [6], molecularly imprinted polymers [8], graphene [9] and quantum dots [10]. This combination produces valuable systems with sensitivity and selectivity competitive to their chromatographic alternatives with the advantages of being portable and easy to use [11,12], enabling "in situ" and real-time analysis.

Another recent approach that has attracted considerable attention for the detection of organic compounds is photoelectrochemical analysis [13–17]. Among different photoactive materials, titanium dioxide (TiO_2) is considered one of the most effective photocatalysts due to its

high photoactivity and stability. It has been extensively used in water and wastewater treatment studies because it is chemically and biologically inert, cost-effective, non-toxic, and can promote the oxidation of organic compounds under UV illumination [18–21]. The band gap of TiO_2 is ~ 3.2 eV, depending on its crystalline form (anatase, rutile or brookite). Therefore, light with energy values greater than its band gap is required to excite electrons to the conduction band (CB) with the generation of holes in the valence band (VB) [18]. The photogenerated electron-hole pairs may react with adsorbed species available on the surface of TiO_2, such as OH^- and H_2O, producing reactive oxygen species (ROS) which may further oxidize phenolic compounds, allowing their quantification [22].

Inspired by the advantages of FIA and TiO_2-based photoelectrochemical detection, we have designed an analytical photosensing device for the amperometric quantification of 4-AP, an environmentally hazardous and toxic molecule. Commonly, 4-AP is used in the manufacture of pharmaceutical and cosmetic products; furthermore, it is

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used as a plasticizer, petroleum additive or solvent [23,24]. When it is discarded, this molecule reaches the environment, mainly via aqueous systems, generating a series of problems for living organisms, including genotoxic, hepatotoxic and mutagenic effects [24]. Therefore, the development of a sensitive, fast and reproducible method to quantify 4-AP is desirable.

There are a number of different analytical methods to determine 4-AP, including high-performance chromatography [25–27], capillary electrophoresis [28] and chemiluminescence [5,29]. These methods are known to have a low limit of detection (LOD), high sensitivity and accuracy, but, compared to electrochemical methods, they have disadvantages such as requiring sample pre-treatments, as well as being more time-consuming and costly.

Although various electrochemical sensors have been developed to detect 4-AP [30–35], most of them have a long procedure for modification of the electrodes and quite a high LOD. In our work, commercial TiO_2, illuminated with UV light, is combined with a FIA system for nM-range detection of phenols in a more straightforward and low-cost procedure. In addition, compared to a steady-state batch system, the integration of flow systems into a photoelectrochemical cell provides high sensitivity and, consequently low LOD and high reproducibility, due to periodic washing sequences preventing the poisoning of the electrode surface.

2. Experimental

2.1. Materials

Nafion® 117 (5% in a mixture of lower aliphatic alcohols and water), potassium chloride (KCl), 2-aminophenol (2-AP), 3-aminophenol (3-AP), 4-aminophenol (4-AP), bisphenol A (BPA), 2-chlorophenol (2-ClP), 3-nitrophenol (3-NP), phenol, and potassium phosphate monobasic (KH_2PO_4) were purchased from Sigma-Aldrich. Hydroquinone (HQ) was obtained from Acros, TiO_2 (Millennium PC500, mesoporous) from Crystal Global (prior to use, the TiO_2 was calcined to 450 °C to enlarge its pore size) and 2-[4-(2-hydroxyethyl)-piperazinyl] ethane sulfonic acid (HEPES) was purchased from VWR®. The graphite screen-printed electrode DS 110 was obtained from Metrohm DropSens. 10 mM KH_2PO_4 phosphate buffer and 0.1 M KCl solution (pH 7.0) was used as supporting electrolyte. The phosphate buffer solution was set to pH 7.0 using a NaOH solution. All reagents were used without further purification and all solutions were prepared with deionized water.

2.2. Apparatus

A homemade flow cell, made of poly(methyl methacrylate) (PMMA) with dimensions 22.75 × 8 mm (internal) and 36.75 × 25.55 mm (external) and with an internal volume of 0.15 mL, was used for the amperometric measurements of 4-AP and HQ (Fig. S1). A peristaltic pump (Perkin-Elmer, France) propelled the buffer into the flow line with a flow rate of 1 mL/min using Tygon tubing and omnifit labware (Diba). A manual sample injection valve was used to inject 50 μL of the sample solution into the carrier stream. Electrochemical measurements were carried out using a PalmSens potentiostat (Utrecht, The Netherlands) controlled by PSTrace software (version 5.6).

A UV LED (blue light, λ_{peak} = 400 nm, 10 mW) was used for excitation of the titania material (purchased from Kingbright, Germany). The distance between the LED and the surface of the electrode in the flow cell was 1.2 cm.

2.3. Electrode modification

The screen-printed graphite electrode (SPE) was modified with 10 g L^{-1} of TiO_2 dispersed in a solution of Nafion® (76:24, v/v HEPES 25 mM and Nafion®). Nafion® was used as an adhesive binder in order

to provide better stability to TiO_2 at the surface of the electrode. A volume of 5 μL of the suspension was dropped on the surface of the electrode and dried at room temperature in the dark for approximately 2 h, obtaining the modified electrode described as SPE|TiO_2.

2.4. Analytical procedure

The flow rate, working potential, and pH were optimized in order to improve the amperometric response. All the electrochemical measurements were conducted using chronoamperometry and four measurements were performed for each experiment (n = 4).

The proposed photosensor and the optimized setup were used to detect HQ as a model molecule and 4-AP. The photocatalytic mechanism of 4-AP oxidation is expected to be the same as for HQ. Therefore, HQ was selected as a model molecule for optimization of the experimental conditions. The LOD was calculated using the equation: LOD = $3s_b/a$, where s_b is the standard deviation of the blank and a is the slope of the calibration curve.

The river water was collected from Scheldt river at Lillo, Antwerp district, Belgium (coordinates: 51° 18′ 8.0676″N 4° 17′ 11.3604″E). The river water sample was previously filtered using 0.2 μm polyethersulfone (PES) purchased from VWR®. The two stream flow tubes were separated and one of the tubes was used for Milli-Q water as a carrier solution for the sample and the other one was used for twice-concentrated buffer solution (20 mM KH_2PO_4 containing 0.2 M KCl). Subsequently, the double concentrated buffer will be mixed with the MQ water (line E, Fig. S1) and the final concentration of buffer will be 10 mM KH_2PO_4 containing 0.1 M KCl.

3. Results and discussion

3.1. Electrochemical behavior of HQ at SPE|TiO_2 under UV illumination

The photocatalytic efficiency of TiO_2 under UV illumination in the presence of HQ using the FIA system is studied. Photocatalyzed reactions are facilitated through the presence of ROS on the surface of TiO_2 [36,37]. In a previous publication [37], the authors showed using the EPR method that TiO_2 can generate ROS under illumination by light. These species, with a free unpaired electron, are formed by reaction of photo-generated electron-hole pairs with an adsorbed molecule (such as O_2 or H_2O) on the surface of TiO_2. The resulting ROS may further oxidize phenolic compounds such as HQ. When a negative potential is applied, the oxidized form of HQ, benzoquinone (BQ), is reduced back to its original form and the reduction current is recorded. The SPE|TiO_2 electrode showed intense responses to HQ in the range 0.0125–2.5 μM (Fig. 1, Fig. S2).

As can be seen from the calibration curve (Fig. 1 inset red), the responses at the SPE|TiO_2 electrode upon the addition of HQ in the dark are very low (Fig. S3). Similar behaviour was observed when a bare graphite electrode was used instead of TiO_2 (Fig. S4). Indeed, in the absence of a light source (Fig. 1 inset) and in the absence of TiO_2 (Fig. S4), ROS formation is not expected, meaning that the detection of HQ is only possible when TiO_2 is illuminated with UV.

The LOD and the sensitivity obtained for HQ on SPE|TiO_2 under UV light were 31.2 nM and 0.2 A M^{-1} cm^{-2}, respectively, with a repeatability of 4.5% RSD (n = 10 per electrode for five different electrodes in the presence of 2.5 μM HQ). The reproducibility was 8.5% RSD, which is calculated from the sensitivity of an electrode during measurements over several days (n = 5) in the concentration range 0.0125–2.5 μM HQ (Fig. S5). The stability was evaluated by following the changes in the photocurrent of 2.5 μM HQ after 50 injections during 100 min of uninterrupted measurement. A decrease of only 5.4% in the amperometric response was observed. This exceptional stability can be explained by the chemical stability of TiO_2 and the properties of a typical FIA setup that allow accurate results even after a considerable measuring time [38–40].
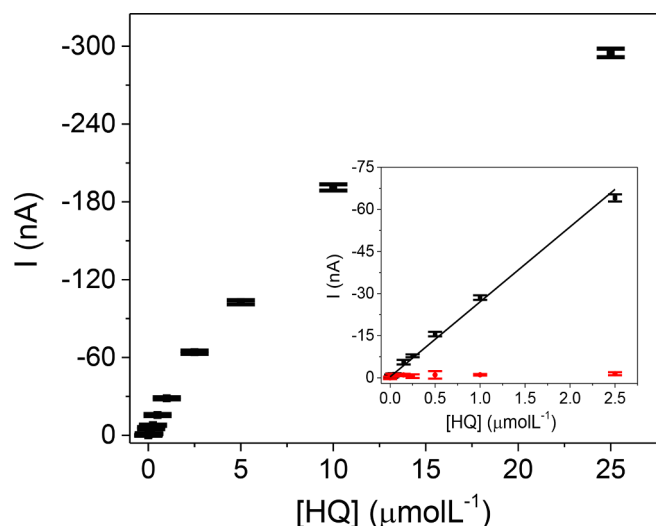
Fig. 1. Calibration curve for 0.0125–25 μM HQ at SPE|TiO$_2$ under UV illumination in 10 mM KH$_2$PO$_4$ containing 0.1 M KCl (pH 7.0), applied potential −0.14 V vs Ag pseudo reference electrode ($n = 4$). Flow rate: 1 mL/min. Inset: Linear curve 0.0125–2.5 μM HQ under UV illumination (black) and in the absence of a light source (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Effect of flow rate

One of the main advantages of FIA, which improves the LOD, is higher mass transport to the working electrode surface in comparison to a stagnant electrochemical cell. This characteristic can be affected by the flow rate [41]. The latter is a crucial parameter to be optimized in FIA because it defines the contact time of the sample with the surface of the electrode. The flow rate optimization was conducted in the range 0.25–1.5 mL min^{-1} (Fig. S6) by measuring the photocurrents of 2.5 μM HQ. According to the obtained photocurrents, there is no significant difference between the different flow rates. Therefore, a flow of 1.0 mL min^{-1} was selected as it ensures a rapid analysis and prevents the waste of a large amount of buffer solution.

3.3. Effect of working potential and pH on the photocurrent of HQ

As the sensitivity of the electrode is influenced by the applied working potential, the effect of the working potential is investigated over a potential range from 0.1 to −0.3 V in a solution containing 2.5 μM HQ. The photocurrent and the background current (baseline) increase as the applied potential shifts towards more negative values (Fig. 2, Fig. S7), due to the presence of other reactions, such as the reduction of oxygen [37,42]. To prevent the influence of other possible reactions and also to achieve a low background current, −0.14 V vs Ag pseudo reference electrode of the SPE was chosen as the optimal working potential.

The performance of SPE|TiO$_2$ in the presence of 2.5 μM HQ was evaluated in the pH range 5.0–8.0 (Fig. 3). It is noticeable that the photocurrent increases with an increase in pH value until it reaches pH 7.0, and at pH > 7.0 the photocurrent response decreases. This trend is due to the fact that protons participate in the electrochemical reaction of HQ [43].

At a low pH range (pH < 7.0), the hydroxyl group in the HQ structure can be protonated to R-OH$_2^+$ [44]. When the pH is slowly increased from pH 5.1 to 7.0, gradual deprotonation occurs and non-protonated hydroxyl groups at pH 7.0 contribute to the photocurrent response. HQ is a protic aromatic molecule and can easily be deprotonated at higher pH values [45]. The shortage of protons at high pH (pH > 7.0) could be one of the reasons leading to a decrease in the photocurrent response [43]. Additionally, the isoelectric point of the
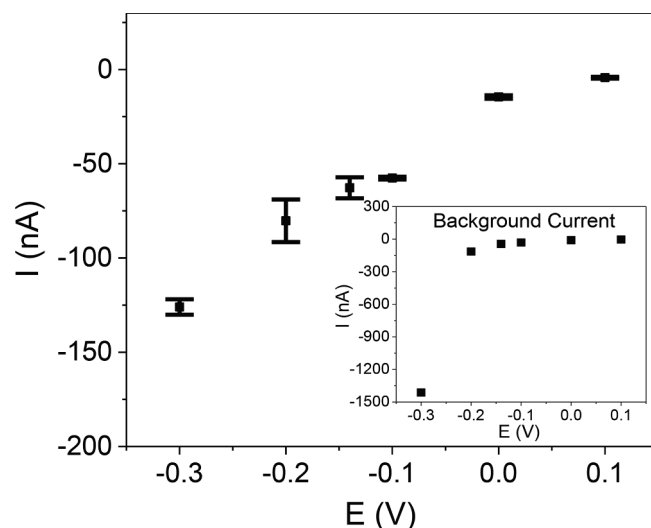

Fig. 2. Effect of working potential on the amperometric response of 2.5 μM HQ in 10 mM KH$_2$PO$_4$ containing 0.1 M KCl (pH 7.0) ($n = 4$). Flow rate: 1 mL/min. Inset: Changes in the background current upon applying different potentials.
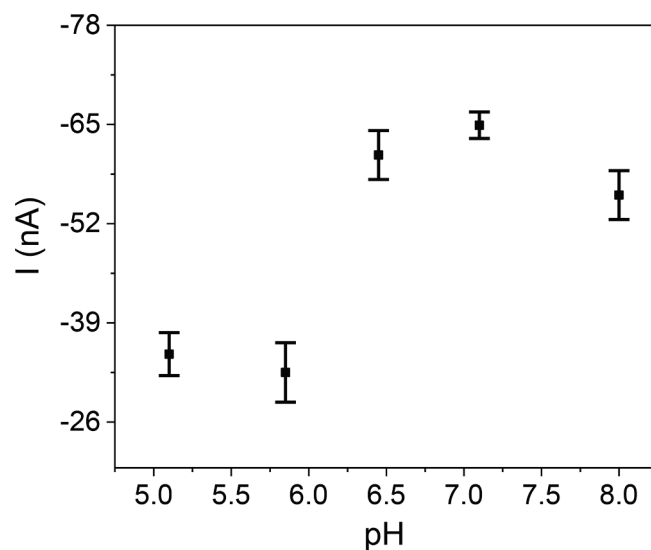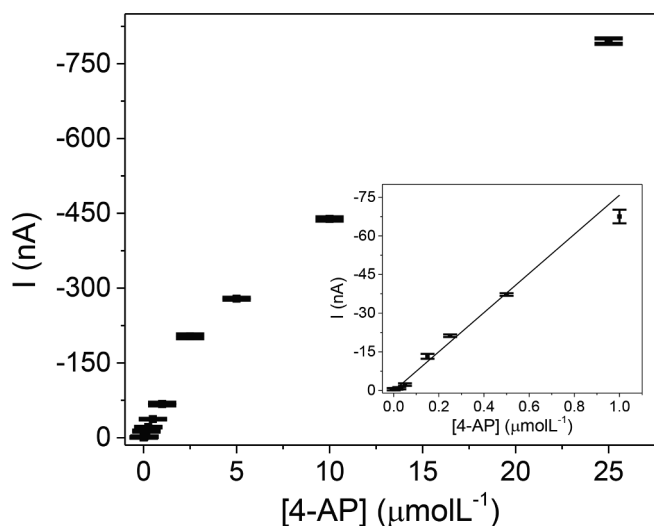

Fig. 3. Effect of pH on the amperometric response of 2.5 μM HQ in 10 mM KH$_2$PO$_4$ containing 0.1 M KCl, applied potential −0.14 V vs Ag pseudo reference electrode ($n = 4$). Flow rate: 1 mL/min.

TiO$_2$ batch is ~6.8 and the surface of TiO$_2$ will be negative at a basic pH. Therefore, the electrostatic repulsion between HQ and the TiO$_2$ surface increases with an increase in pH, which leads to lower photocurrents. In this sense, the reaction rate is favored at a neutral pH. Thus, pH 7.0 was selected as the optimum pH for further experiments.

3.4. Photoelectrochemical response of the sensor for 4-AP

To explore the applicability of the electrode, 4-AP was measured at SPE|TiO$_2$ under UV light illumination. The calibration plot exhibits the typical current response of the electrode with increasing 4-AP concentration (Fig. 4). The reduction peaks of 4-AP (Fig. S8) increased linearly with its concentration in the range 0.0125–1.0 μM. The LOD and the sensitivity calculated for 4-AP were 18 nM and 0.6 A M^{-1} cm^{-2}, respectively.

The LOD for 4-AP in this work is at least five times lower than the reported LOD values in the literature (Table 1), which demonstrates the favorable analytical performance of the proposed photosensor.

Fig. 4. Calibration curve for 4-AP at SPE|TiO_2 under UV illumination in 10 mM KH_2PO_4 containing 0.1 M KCl (pH 7.0), applied potential -0.14 V vs Ag pseudo reference electrode ($n = 4$). Flow rate: 1 mL/min. Inset: Calibration curve for lower 4-AP concentration range 0.0125–1.0 μM.

Table 1
Comparison of the limit of detection for 4-aminophenol using flow injection analysis.

Method	Limit of detection (μM)	Reference
FIA combined with a glucose oxidase-mutarotase reactor	0.1 ± 0.01	[1]
FIA	0.39	[2]
FIA combined with MIP column	0.21	[8]
FIA with spectrophotometric detection	10.0	[46]
FIA with chemiluminescence detection	17.6	[47]
HPLC	3.00	[25]
FIA with PEC	0.018	This work

Key: FIA, flow injection analysis; PEC, photoelectrochemical; HPLC, high performance liquid chromatography.

An interference study is included in the supplementary information and the results in Fig. S9 show that there is no significant interference from other common phenolic compounds in the quantification of 4-AP.

3.5. Real sample analysis

The proposed setup was used for the determination of HQ and 4-AP in tap water and river water. Standard addition was performed with three different concentration levels of HQ (0.75, 1.5 and 2.0 μM) and 4-AP (0.1, 0.4 and 0.75 μM) and the results were evaluated by the percentage of recovery, as shown in Table S1. The average recovery values were found to be in the range 90–108.9% for HQ and 93.5–106.9% for 4-AP, confirming the potential of the sensor for the determination of HQ and 4-AP in complex samples such as river water.

4. Conclusions

For the first time, we show that commercial TiO_2 without any modification can be used under UV light illumination in combination with a flow system to detect phenolic compounds at nM level. The nanomolar detection capability of this sensor was illustrated by monitoring HQ and 4-AP in river water. The detection mechanism is related to the generation of ROS on TiO_2 under UV light illumination, evidenced by the control experiment in the dark. Overall, the results obtained with this photosensor confirm its usefulness and represent a valuable starting point for monitoring the quality of water in situ and in real time.

CRediT authorship contribution statement

Camila D. Mendonça: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Vanoushe Rahemi:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Jonas Hereijgers:** Methodology, Resources, Writing - review & editing. **Tom Breugelmans:** Methodology, Resources, Writing - review & editing. **Sergio A.S. Machado:** Supervision, Conceptualization, Resources, Writing - review & editing. **Karolien De Wael:** Supervision, Conceptualization, Resources, Data curation, Writing - review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2020.106767.

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