Desalination and Water Treatment
www.deswater.com
doi:10.5004/dwt.2017.20740

83 (2017) 321–326
July

Direct ultra-trace detection of alkylphenols in water using a cavity carbon-paste microelectrode sensor

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Received 2 March 2017; Accepted 20 March 2017

ABSTRACT

In this work, a new electrochemical method has been developed using a cavity carbon-paste microelectrode sensor (CP-CME) in cyclic voltammetry in order to detect alkylphenol micropollutants in water, especially 4-nonylphenol, 4-octylphenol and 4-*tert*-octylphenol. CP-CME sensor is characterized by small quantities of materials in the cavity and by a significant reduction of the electrochemical interface in comparison to the usual carbon paste electrode. Especially with the CME, the ohmic drop and the double layer capacitance are notably reduced in cyclic voltammetry allowing measurements of alkylphenol concentrations in water without any electrolyte addition. First, the electrochemical sensor was used for the detection of alkylphenols in a classical cell. Anodic oxidation of alkylphenols appears as an irreversible electrochemical process and experiments at different scan rates demonstrate that alkylphenol oxidation at the CME is not limited by diffusion but by a limited quantity of electroactive species (adsorption of alkylphenols). Also a surface activation step is required prior to a new measurement so as to liberate the adsorption sites occupied by oxidized alkylphenols and to subsequently adsorb alkylphenols. The developed method was validated by examining the linearity ranges, the repeatability, the accuracy, as well as the detection limits for each alkylphenol which are very low and ranged between 20 and 35 nM. The established calibration curves cover a large concentration range allowing alkylphenols quantification. The calculated accuracy accounts to 92 % and 99 % for the different alkylphenols, indicating that the developed method shows a good repeatability and very high accuracy. Furthermore, the electrochemical sensor was used in a special flow cell and alkylphenols could be also detected continuously by the CP-CME in adapted conditions. Flow rate and adsorption time were optimized in order to obtain good and repeatable signals. In conclusion, the CP-CME sensor has demonstrated its capability to detect alkylphenols continuously and directly in water.

Keywords: Cavity microelectrode sensor; Carbon paste; Cyclic voltammetry; Alkylphenols

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1. Introduction

Alkylphenols (APs), like 4-nonylphenol (4-NP), 4-octylphenol (4-OP) and 4-*tert*-octylphenol (4-*tert*-OP) are classified as phenolic endocrine disruptors [1,2]. They are especially used as raw material in the manufacturing of alkylphenols ethoxylates by reacting with ethylene oxide. However, alkylphenols ethoxylates (APEs) are classified as one of the most non-ionic surfactants widely used due to their structures that make it easily soluble in water and helps disperse dirt and grease from soiled surfaces into water. Octylphenol ethoxylates (OPEs) and nonylphenol ethoxylates (NPEs) are two of the most common non-ionic surfactants in the marketplace and represent both for more than 80% of the total used alkylphenols [3]. Moreover, they are used as intermediates in the preparation of phenolics resins and formaldehyde. However, phenolic resins are

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Presented at the First International Symposium on Materials, Electrochemistry and Environment (CIMEE 2016), 22–24 September 2016, Tripoli, Lebanon

used in the varnishes for electrical isolation, in the printing inks, in the foundry industry as emulsifiers and in the off-shore platforms [4,5].

Although, alkylphenols are frequently identified in the aquatic environment, especially wastewater but also in surface water and tap water at low concentration levels. It has been reported that APOs enter the environment primarily via industrial and municipal wastewater treatment plant effluents (liquid and sludge), but also due to direct discharge such as through pesticide application [5]. Thus, it seems that the sources of octylphenol released into the environment are linked to non-industrial use of octylphenol derivatives (paints, inks, pesticides etc). In all cases, whatever the source of contamination it's very important to have available monitoring techniques and rapid screening methods that are able to detect alkylphenol micro-pollutants directly in water.

Several analytical techniques are available for alkylphenol detection in water, such as high performance liquid chromatography and gas chromatography-mass spectrometry [6–8]. However, despite their analytical performances (sensitivity and detection limits), many of these techniques require complicated pretreatment procedures like pre-concentration or derivation steps and are very expensive and time consuming.

In the literature, electrochemical sensors are reported as alternative solution for AP detection. Many electrochemical methods have been developed and studied for this purpose [9–12]. Nonetheless, all these sensors are unable to perform electrochemical measurements directly in water without any electrolyte addition and to detect APs continuously.

In this paper, we report the development of a new electrochemical method using a cavity carbon-paste microelectrode sensor (CP-CME) for alkylphenol detection directly in water. This method allows especially the direct detection of ultra-trace of APs without any electrolyte addition. The method is characterized by its simple implementation, low-cost, relatively short response time and its high efficiency.

2. Experimental details

2.1. Apparatus and electrodes

Voltamperometric measurements have been carried out with Potensiostat/Galvanostat Autolab (PGSTAT 101) purchased from Metrohm. A cavity carbon-paste microelectrode was used as working electrode (WE). The cavity has a characteristic diameter (D) of 50 µm, a characteristic depth (H) of 17 µm (Fig. 1) and a cavity volume of 3.34×10^{-8} cm^3. A platinum electrode of 1 mm diameter (XM 100, Radiometer Analytical) was used as auxiliary electrode (CE). An Ag/AgCl electrode (XR 300, Radiometer Analytical) was used as reference electrode (RE). A classic electrochemical cell with three electrodes system obtained from Metrohm was used in this study. An electrochemical flow cell (homemade) was connected to a peristaltic pump (0.1 < flow rate < 3.0 mL/s) and the measurements were performed continuously with a three electrodes system, in which WE was placed between CE and RE (Fig. 2). A cylindrical cell chamber provides the flow of solution in parallel to the electrode surfaces.

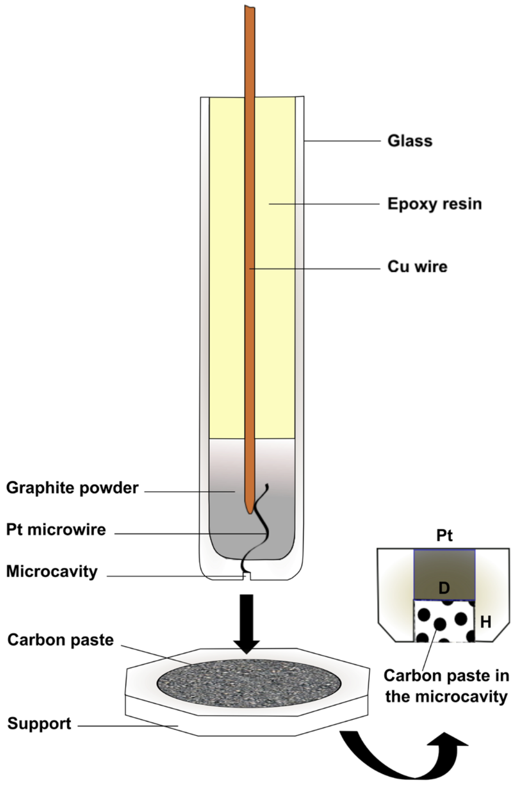

Fig. 1. Descriptive scheme of the cavity microelectrode (CME) and zoom on the apex of its filling with the carbon paste material.

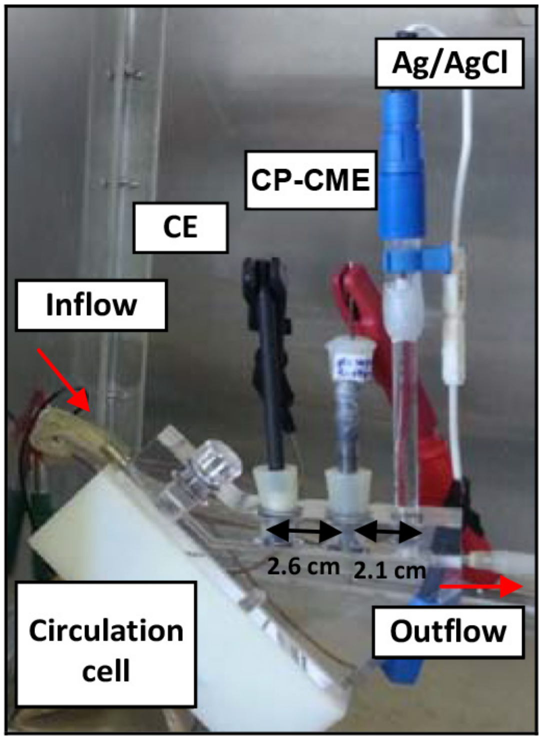

Fig. 2. The CP-CME sensor insert in the electrochemical flow cell.

2.2. Reagents and solutions

Graphite powder of 99% purity was obtained from Sigma Aldrich (mesh < 20 µm; density = 2.2 g·cm^{-3}). 4-nonylphenol, 4-octylphenol and 4-*tert*-octylphenol were also purchased from Sigma-Aldrich with high purity grade. Hydrogen peroxide 10% used for microcavity cleaning was obtained from Fisher Scientific. Paraffin oil was purchased from Fluka and used as binder for carbon paste (CP) preparation. The stock solutions of 4-OP and 4-*tert*-OP were prepared in demineralized water (conductivity < 5 µS/cm) at 48.4 ± 0.2 µM and at 27.5 ± 0.2 µM for the stock solution of 4-NP. All the prepared solutions were stored in the dark at 4°C when not used. All measurements were carried out at room temperature.

2.3. Preparation of the carbon-paste cavity microelectrode

The carbon paste was prepared as described in the literature [12,13]. Briefly, 100 mg of graphite powder was mixed with 16 µl of paraffin oil until obtaining a homogeneous paste. A sufficient quantity of this paste was deposed on a glass plate and the CME was pressed in order to compact the paste into the microcavity (Fig. 1). The total mass of the paste introduced in the microcavity was approximately 0.5 ng (for more details see references [14,15]).

Prior to a new filling, the cavity microelectrode was unloaded and cleaned by ultrasonic cleaner with successive baths of HNO_3 (1 mol·L^{-1}), H_2O_2 (30%) and demineralized water for 5 min each. However, a check should be performed to ensure a clean cavity using a classic three-electrode electrochemical cell. For this purpose, a cyclic voltammogram was recorded in a sulfuric acid solution (0.5 M) vs. Ag/AgCl reference electrode and compared with typical platinum electrode voltammogram response showing the adsorption and the desorption peak systems of hydrogen (–0.4 ; –0.3 V) and the oxidation and the reduction peaks of platinum oxide system (1.1 ; 1.5 V).

3. Results and discussion

3.1. Cyclic voltammetry of alkylphenols in water at CP-CME

In order to study the electrochemical properties of alkylphenols in water at the CP-CME, the electrochemical redox system has been investigated by cyclic voltammetry at scan rate of 0.05 V/s. The voltammograms obtained in water without supporting electrolyte addition exhibit a well-defined oxidation peak at 0.85 V (4-NP), 0.88 V (4-OP) and 0.90 V (4-*tert*-OP) (Fig. 3). These peaks shift slightly to higher potential depending on AP concentration in water as well as the scan rate measurement. Nevertheless, no reduction peak was observed during the reverse scan suggesting that APs oxidation is an irreversible electrochemical process. These electrochemical behaviors of APs were also reported in the literature [16,17]. However, it is well-known that the direct oxidation of phenolic compounds via one- and two electron transfers cause the generation of the phenoxy radical and quinone, respectively [18]. To investigate the adsorption behavior of alkylphenols on the CP-CME surface, the cyclic voltammograms of 10 µM of APs with various scan rates in the range of 0.01–0.30 V/s were recorded (Fig. 4). The increase of υ was accompanied by a peak broadening and a peak shifting towards more anodic potentials. This phenomenon is largely greater than the potential shift predicted theoretically by E. Laviron ($Ep = k + (RT/\alpha nF)Ln\,\upsilon$) [19]. It is probably due to a contribution of the ohmic potential drop which becomes important as the scan rates increases. However, the peak currents (i_p) for the oxidation of APs were directly proportional to the scan rate ($r^2 > 0.99$) (Fig. 5). It means that the oxidation electrode process of APs is not limited by diffusion but by an adsorption controlled electrochemical process. This phenomenon was also reported in the literature by Zeng and his collaborators [20]. They suggest that the oxidation behavior of nonylphenol at a modified glassy carbon electrode was typical adsorption controlled electrode process [20]. However, an adsorption time was required to maintain APs adsorption/desorption on the CP-CME surface

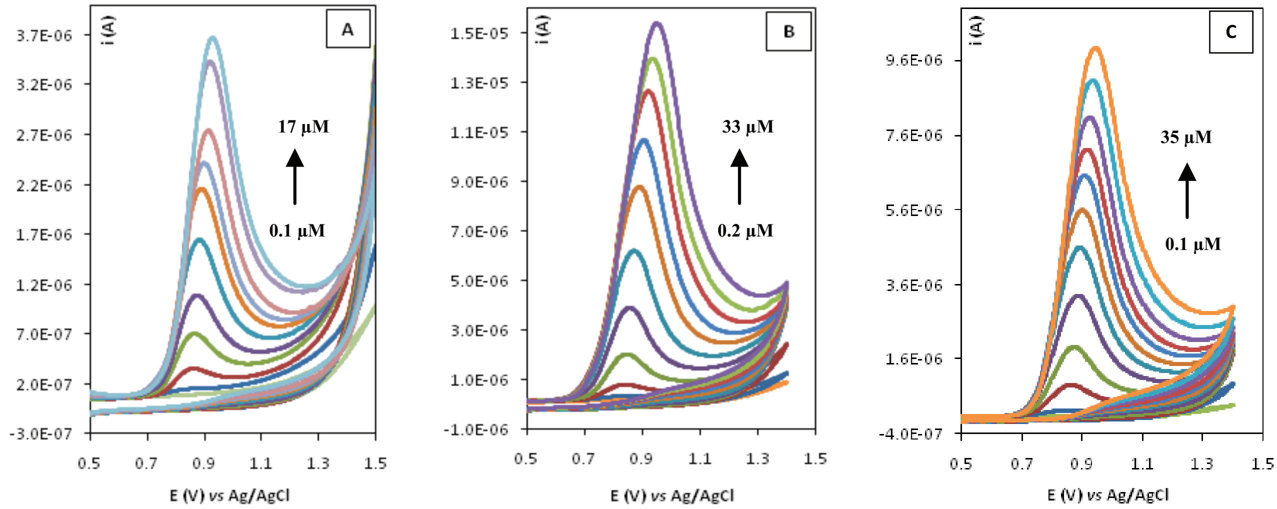

Fig. 3. Cyclic voltammograms at CP-MEC in water at υ = 0.05 V/s in the presence of increasing amounts of (A) 4-nonylphenol, (B) 4-octylphenol and (C) 4-tert-octylphenol.

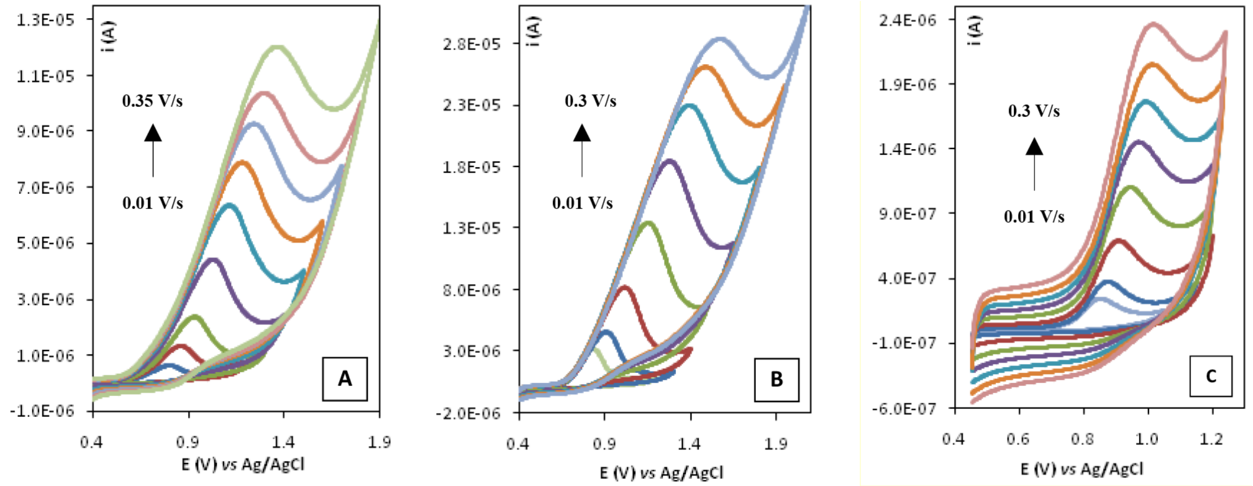

Fig. 4. Cyclic voltammograms at CP-MEC in water for 10 µM of APs at various scan rates (A) 4-nonylphenol, (B) 4-octylphenol and (C) 4-*tert*-octylphenol.

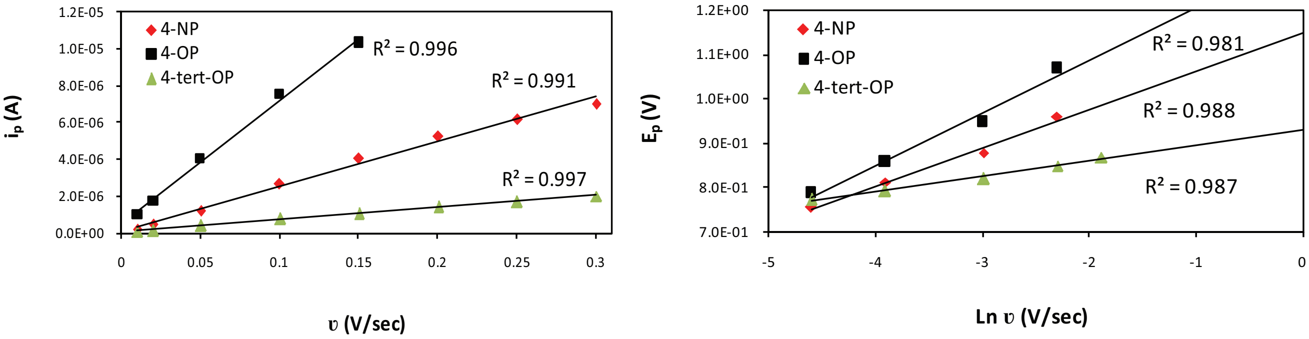

Fig. 5. Influence of the scan rate (υ) on the oxidation peak current (i_p) of 10 µM of APs in water and the evolution of the plotted Ep versus to Ln υ.

before new measurement in order to liberate the occupied adsorption sites by the oxidized alkylphenols and once again adsorb the APs on the electrode surface. This activation step of the electrode surface was maintained by means of a stirring bar agitation and optimized to 6 min before every new measurement. In these conditions stable electrochemical responses were observed indicating that the adsorption equilibrium of APs was reached. Thus, an optimized accumulation time of 6 min was employed in further experiments and is comparable to this obtained by Lu et al. [12].

3.2. Validation of the developed method

3.2.1. Limit of detection

A series of APs samples with different concentrations were directly detected in water without any electrolyte addition by the CP-CME. 4-*tert*-OP was found to present the lowest detection limit among the three APs tested (20 nM). For the two other APs, the estimated detection limit was 35 nM and 25 nM for 4-NP and 4-OP, respectively. These values of detection limit were obtained with successive micro-additions of APs in water and determinate when an oxidation peak was detectable. The ability of the CP-CME sensor to detect ultra-trace of APs directly in water is related to the small size of the sensor and the high surface area of the carbon-paste. This permits the detection of lower faradic currents than with the conventional electrode, allowing the recording of voltammograms without pronounced distortions. Moreover, the detection limits of APs with the use of the CP-CME sensor in water are quite similar to the value obtained by Lu et al. by using a carbon past electrode modified by CTAB (0.01 µM) for the analysis of 4-NP in buffered solution [12]. We can conclude that the CP-CME sensor represents a real competitive, facile and rapid method for APs detection in water in comparison of chromatographic techniques [6–8].

3.2.2. Linearity range

The cyclic voltammograms obtained with the CP-CME as function to the APs concentration are presented in Fig. 3. It can be seen that the oxidation peak current (peaks high) increases significantly with the APs concentration in water. From peak current measurements, the calibration curves showed a linear response for 4-NP, 4-OP and 4-*tert*-OP in a sufficient large concentrations range

(2 decades) which proves the electroanalytical performance of the developed method (Table 1). These allow using the developed CP-CME sensor to quantify a real sample contaminated by traces of AP.

3.2.3. Repeatability and accuracy

The repeatability of the CP-CME response has been investigated in the same laboratory, by the same analyst and with the same sensor (CME with the same filling of CP) but at different times. It was calculated as the relative standard deviation from ten replicates ($n = 10$) for a given concentration of 9.7 ± 0.1 µM of 4-NP, 8.3 ± 0.1 µM of 4-OP and 4-*tert*-OP. The repeatability of APs were respectively: 5.7%, 3.1% and 3.7%. In the other hand, accuracy of the developed method has been studied for a given concentration level by comparing the expected value (calculated value) with the average of the experimental values (10 replicas) obtained from the calibration curve of each AP. The calculated accuracy was between 92% and 99% for the different APs, indicating that developed method for APs detection by the CP-CME sensor has a good repeatability and very high accuracy.

3.3. Integration of the CP-CME in an electrochemical flow cell

In order to implement the CP-CME sensor in a process treatment monitoring system, the developed sensor has been investigated in an electrochemical flow cell supporting the three electrodes system (Fig. 2). A peristaltic pump was used to ensure a constant flow rate of contaminated APs solution. The flow rate was parallel to the electrode surfaces. The distance separating between electrodes was approximately 2.6 and 2.1 cm. The results obtained in these conditions show that APs can be also detected by the CP-CME sensor. The adsorption step was maintained by a constant flow rate of the APs solution in the flow cell. However, the flow rate and the adsorption time must be optimized; Fig. 6A and 6B respectively. As shown, 2 mL·s^{-1} was the optimum flow rate for APs detection and 2 min was normally sufficient to re-activate the surface of the CP-CME sensor between successive recordings. Also, APs can be also detected semi-continuously with the CP-CME sensor incorporated in an electrochemical flow cell. However, it will be important to note that the semi-continuously detection of APs depends directly on circulation velocity and indirectly on the flow cell geometry and the electrode position inside the cell.

4. Conclusion

In this paper, a novel electrochemical method was established to detect and quantify alkylphenols (APs) in water by a cavity carbon-paste microelectrode sensor (CP-CME) without any electrolyte addition. The proposed sensor demonstrated a rapid and sensitive detection of APs as well as a good repeatability and high accuracy. The detection limits were very low for all the investigated APs (20–35 nM). The oxidation process was studied and showed an adsorption step that justifies the sensitivity of the method. The calibration curves cover large concentration range for all studied APs. CP-CME has been employed and tested in a special flow cell and showed an ability to detect APs semi-continuously suggesting the use of the CP-CME sensor to monitor APs in a real treatment process. It's essentially characterized by its simple operation, low-cost, relatively short response time and its high efficiency. All these advantages make it an ideal tool for qualitative and quantitative measurement of APs during monitoring or water treatment processes.

Table 1
Calibration curves for oxidation peak current in presence of increasing amount of alkylphenols in water

Alkylphenol	Concentration range (mol·L^{-1})	Calibration curve equation	R^2
4-NP	1.10^{-7}–1.7×10^{-5}	$i_p = 1.86 \times 10^{-7}$ x C + 3.02×10^{-8}	0.995
4-OP	2.10^{-7}–3.5×10^{-5}	$i_p = 4.26 \times 10^{-7}$ x C – 1.66×10^{-7}	0.996
4-*tert*-OP	1.10^{-7}–3.3×10^{-5}	$i_p = 2.59 \times 10^{-7}$ x C + 5.28×10^{-7}	0.990

* i_p represent the peak current in A and C is the concentration in mol·L^{-1}

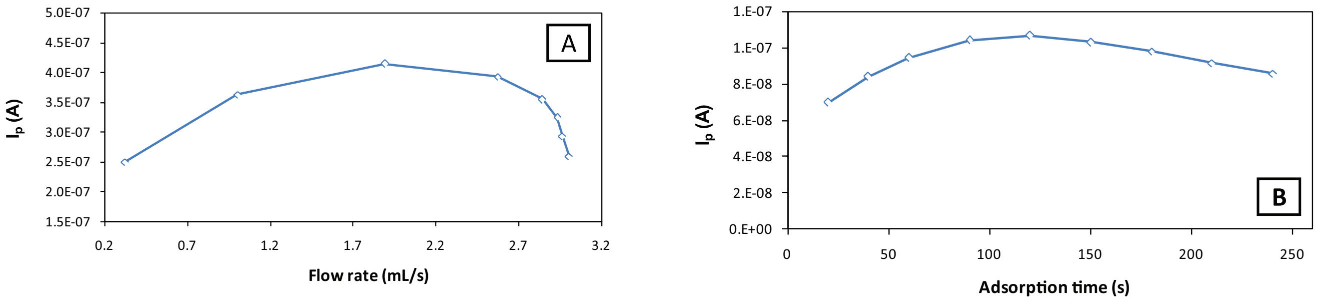

Fig. 6. Influence of the flow rate (A) and the adsorption time (B) on the oxidation peak current (i_p) of 1 µM of 4-tert-OP in water at the CP-CME.

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