





# Flow-through chronoamperometric sensor based on pillar[3]arene[2]quinone derivative for nitrophenol determination and its application in a model effluent

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## Abstract

Electrochemical flow-through sensor based on pillar[3]arene[2]quinone (P[3]A[2]Q) derivative was developed. Nitrophenol determination was based on P[3]A[2]Q redox current changes. Also, the shift of cathodic potential was observed compared to nitrophenol reduction current registration directly. Using carbon black (CB) as a matrix for macrocycle implementation provided the sensor stability in the flow when it was applied with a 3D printed flow-through cell. CB and macrocycle were drop casted from the same aliquot providing one-step modifying layer production by the principle of “one-pot synthesis”. The flow-through chronoamperometric sensor designed allowed determining mononitrophenols in the concentration range of 1 nM – 0.1 mM with the limit of detection (LOD) of 0.5 nM. The linear concentration range of 10 nM – 0.1 mM with LOD of 2 nM was obtained for 2,4-dinitrophenol, 2,6-dinitrophenol and 2,4,6-trinitrophenol. The sensor proposed was tested with a model effluent sample, and sufficient recovery about 98±1% was obtained.

## Key findings

- Electrochemical sensor based on carbon black and pillar[3]arene[2]quinone for nitrophenol determination was developed.
- Pillar[3]arene[2]quinone engages with nitrophenols on the “host-guest” interaction principle, which allowed to shift the cathodic potential of nitrophenol determination.
- Low limits of detection allow using the sensor for eco-monitoring of nitrophenols in a real sample.

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## 1. Introduction

Electrochemical sensors are powerful analytical equipment due to their portability, mobility and affordable cost. Their high sensitivity and selectivity account for their wide usage in environment monitoring and clinical diagnostics, whereas there is a possibility to use them both in laboratory and in point-of-care testing [1].

Electrochemical sensors response is a result of electrochemical conversion of analyte or a redox mediator on the transducer interface into a readable electric signal.

Analytical characteristics such as selectivity and sensitivity are strongly dependent on microstructure and properties of the electrode modifying coating [2], so the nanostructured materials are commonly used to improve

the analytical characteristics of the sensors developed [3]. The inclusion of macrocyclic compounds such as cyclodextrin, calix[n]arene, curcubituril, etc., into modifying layer is a promising approach in the field of electrochemical sensor development. These compounds have the unique size of macrocycle cavities and some specific properties that allow creating novel kinds of selective sensors. Outstanding features of macrocycles found their application in various supramolecular systems such as liquid crystals [4], mechanically interlocked molecules [5], metallorganic backbone structures [6], supramolecular polymers [7–9], drug delivery systems [10, 11], cell bioimaging agents [12], transmembrane ion channels [13], and molecular glue [14]. Supramolecular “bottom-up” assembly provides an efficient tool for multifunctional hybrid system design by including the

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### Keywords

Flow-through analysis; Pillar[3]arene[2]quinone; Nitrophenol determination; Electrochemical sensor; Macrocyces

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### Supplementary information

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### Sustainable Development Goals



individual functional components through the non-covalent interactions. Among them “host-guest” molecular recognition becomes more attractive for the researchers. The reason is the opportunity to bind two or more molecules in a simple and reversible way, which allows to design some new supramolecular structures [15–17]. It confirms the great promise of using macrocycles for sensor devices development.

Pillar[n]arenes are among the most interesting compounds to include into electrochemical sensors assembly. First obtained by T. Ogoshi et al. [18], they represent a novel class of supramolecular compounds [19]. They combine some characteristics of other “host-guest” systems such as highly symmetrical column structure as in cucurbiturils, rich  $\pi$ -electron density in aromatic cavity as in calix[n]arenes and a lot of hydroxyl groups at the rims typical for highly functionalized cyclodextrins [20]. Previously, the functionalized pillar[n]arenes were used as a part of solubilizers [21], gelatinization agents [22], sorbents [23], target drug delivery systems [24], OLED-devices [25] and transmembrane ion channels [26].

Nowadays, the number of studies using pillar[n]arenes as the sensor modifiers is limited, but the idea of their application is an essential and promising one due to the unique properties of their structure [20]. In particular, pillar[5]arene and its derivatives exhibit sufficient electrochemical activity. These compounds were used for a selective determination of organic phosphorus and carbamate pesticides [27], neuromediators [28, 29], paraquat [30], hemoglobine [3], metal ions [31], chiral substances [32], caffeic acid [33], aflatoxine M1 [34], hydrogen peroxide, uric acid [35] and DNA damage discrimination [36]. Thus, pillar[5]arenes (especially those functionalized with different groups) are promising agents which can be used in the development of devices for determining a wide range of compounds.

Nitrophenols represent one of the most important groups of environment pollutants. They are widely used in such industrial areas as production of plastics, paints, insecticides and explosives [37]. They tend to accumulate in water and soil, so they are high priority pollutants of the environment endangering people health [38]. At the moment there are different approaches of chemical analysis used for nitrophenol determination: high-performance liquid chromatography [39], UV-vis spectroscopy [40], fluorescence spectroscopy [41], capillary electrophoresis [42] and electrochemical devices [43]. The latter are the most convenient and exhibit high sensitivity and reproducibility [38] along with an opportunity to carry out the “on-site” analysis [44]. All of these advantages together provide an accurate determination of nitrophenols for ecomonitoring aims.

In this work we suggested mononitrophenols, 2,4-dinitrophenol, 2,6-dinitrophenol and 2,4,6-trinitrophenol determination through redox peak currents of pillar[5]arene quinone derivative. This derivative engages with nitrophenols on the principle “host-guest” interaction which allows shifting the cathodic potential of nitrophenol determination compared to their own reduction peaks registration. The

electrochemical sensor based on pillar[5]arene quinone derivative demonstrates a high level of sensitivity towards all the nitrophenols studied. Both cyclic voltammetry and chronoamperometry were applied for the evaluation of analyte determination parameters. The flow-through chronoamperometric determination was carried out with a 3D printed electrochemical cell made of polylactic acid. This material meets all the requirements of three-dimension printing. In addition, biodegradability of this substance, its compatibility with biopolymers, low cost, and sufficient treatment accuracy make polylactic acid an appropriate material for flow-through cell production.

## 2. Materials and methods

### 2.1. Reagents

4,8,14,18,23,26,28,31,32,34-decakis(2'-bromethoxy)-pillar[5]arene (pillar[3]arene[2]quinone, P[3]A[2]Q) (Figure 1) was synthesized according to ref [45].

Carbon black (CB) N220 was purchased from Cabot (Ravenna, Italy). Prior to its use, 1.0 mg of CB was mixed with 0.25 mL of concentrated nitric acid and 0.75 mL of concentrated sulphuric acid followed by ultrasonication for 60 min. The sediment was spinned off, rinsed and dried at 60 °C. The oxidized CB was ultrasonicated in 1.5 mL of propylene carbonate for 2 h to obtain 0.66 mg/mL working solution. The P[3]A[2]Q exact mass was dissolved in CB 0.66 mg/mL suspension up to 10 mM concentration followed by ultrasonication for 2 h in the case of modifier “one-pot synthesis”.

All the other reagents were of analytical grade and did not require any additional purification. The working solutions were prepared using deionized water Millipore-Q (Simplicity®, Merck-Millipore, Mosheim, France).

All the measurements were carried out in the Britton-Robinson buffer (BRB) consisting of 40 mM acetic acid, 40 mM phosphoric acid, 40 mM boric acid and 50 mM potassium sulphate.

The model solution of effluents contained 0.04 M  $H_3PO_4$ , 0.04 M  $H_3BO_3$ , 0.04 M  $CH_3COOH$ , 0.05 M  $NaSO_4$ , 0.41 mM  $CaCl_2$ , 0.26 mM  $MgCl_2$ , 93  $\mu$ M  $NH_4Cl$ , 0.27 mM  $KOH$  [46] spiked with *m*-nitrophenol was used for sensor aprobatation in a real sample.

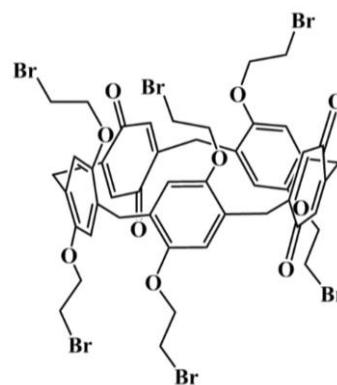


Figure 1 Chemical structure of P[3]A[2]Q.

## 2.2. Screen-printed carbon electrodes (SPCEs) modification

SPCEs were produced utilizing a printer DEC 248 (Dec, London, England) on Lomond PE DS Laser Film (thickness 125  $\mu\text{m}$ , Lomond Trading Ltd., Douglas, Isle of Man) through step-by-step coating of 4 layers. They were: the conductive polymeric PSP-2 silver tracks (Delta-Paste, Moscow, Russia), silver paste layer for pseudo-reference electrode fabrication (polymeric paste Ag/AgCl PSCP-1, Delta-Paste, Moscow, Russia), tracks of carbon/graphite paste C2030519P4 as a counter and a working electrode (Gwent group, Pontypool, the UK) and an isolating layer (paste D21440114D5 Gwent group, Pontypool, the UK). Every layer was hardened at 80  $^{\circ}\text{C}$ . The geometric area of working electrode was equal to 3.8  $\text{mm}^2$ .

The working electrode modification was carried out by drop casting of 1  $\mu\text{L}$  suspension consisted of 0.66  $\text{mg/mL}$  CB and 10  $\text{mM}$  P[3]A[2]Q in propylene carbonate followed by drying in the oven at 100  $^{\circ}\text{C}$ .

## 2.3. Flow-through cells fabrication

The flow-through cell was designed using Wanhao Duplicator 9/300 (Jinhua Wanhao Spare Parts, Wanhao, China) with one extruder (nozzle diameter 0.3  $\text{mm}$ ) from the poly(lactic acid) filaments. The layer thickness was 0.1  $\text{mm}$  with a printing rate 700  $\text{mm}$  per second at 220  $^{\circ}\text{C}$ . The 3D model of the flow-through cell designed is presented at Figure S1. The dimensions of the cells were 2.4x4.4x2.7  $\text{cm}$ . The volume of a replaceable inner camera of the flow-through cell was 10  $\mu\text{L}$ .

Multi-mode potentiostat BioStat (ESA Bioscience Inc., Chelmsford, Massachusetts, USA) was used for chronoamperometric experiments. Voltammetric investigations were carried out with potentiostat-galvanostat CHI 660E (CH Instruments, Austin, Texas, the USA).

## 3. Results and Discussion

### 3.1. Electrochemical behaviour of coating based on CB and P[3]A[2]Q

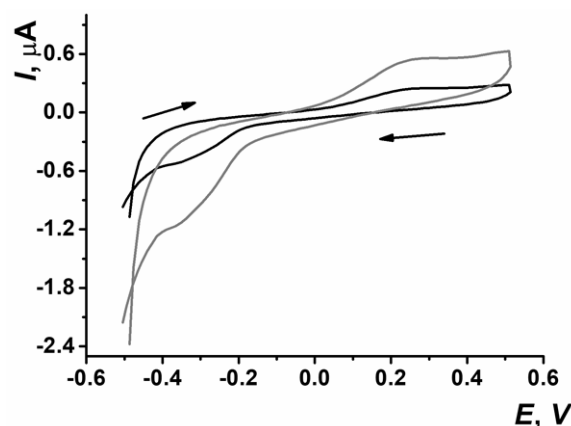
Pillar[5]arenes [47] and their derivatives [48] were successfully used as electron transfer mediators in electrochemical sensor and biosensor development. However, these compounds have some disadvantages, for example, electrode coating based on pillar[5]arene can lose its electrochemical activity over time due to intramolecular bounds formation [49]. Pillarquinones are devoid of this disadvantage and demonstrate the tendency to quasi-reversible redox conversion that is not complicated by intramolecular bounds appearance [45].

Pillar[5]arenes as a modifying electrode coating are often used together with carbon nanomaterials to prevent surface inactivation caused by chemisorption of intermediate oxidation products [50]. In this work P[3]A[2]Q was applied simultaneously with CB from a single aliquot in one-

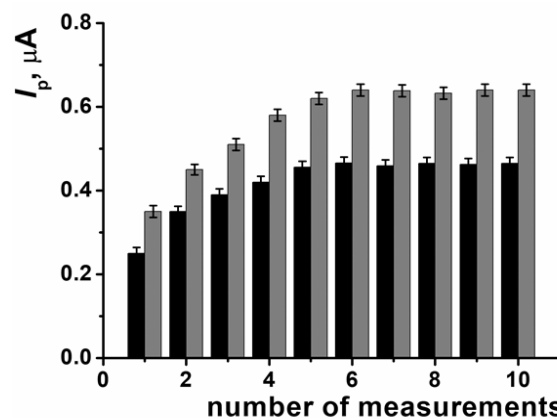
step protocol that was possible because propylene carbonate was used as a solvent. Implementation of CB into the coating content led to 2.5 times increase in the P[3]A[2]Q redox peak height (Figure 2).

The surface activation after the modifier deposition on the electrode was carried out by tenfold scanning of the potential. Redox peak currents grew during five consecutive cycles of potential scanning followed by the stabilization of the peak currents (Figure 3).

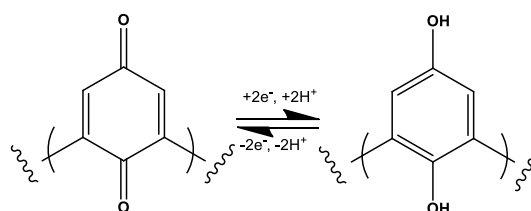
The nature of the redox signals and P[3]A[2]Q electrochemical conversion was discussed in details in the previous studies [45]. The proposed mechanism of reversible reduction and oxidation of quinone fragments in P[3]A[2]Q molecules is presented in Scheme 1.



**Figure 2** Voltammograms recorded on SPCEs modified with P[3]A[2]Q only (black) and CB with P[3]A[2]Q (grey). Cyclic voltammetry, BRB, pH 7.0, 0.1  $\text{V/s}$ .



**Figure 3** Anodic (black) and cathodic (grey) peak currents recorded on SPCEs modified with CB and P[3]A[2]Q depending on number of measurements. Average  $\pm$  S.D. for five individual sensors prepared from the set of equal reagents. Cyclic voltammetry, BRB, pH 7.0, 0.1  $\text{V/s}$ .

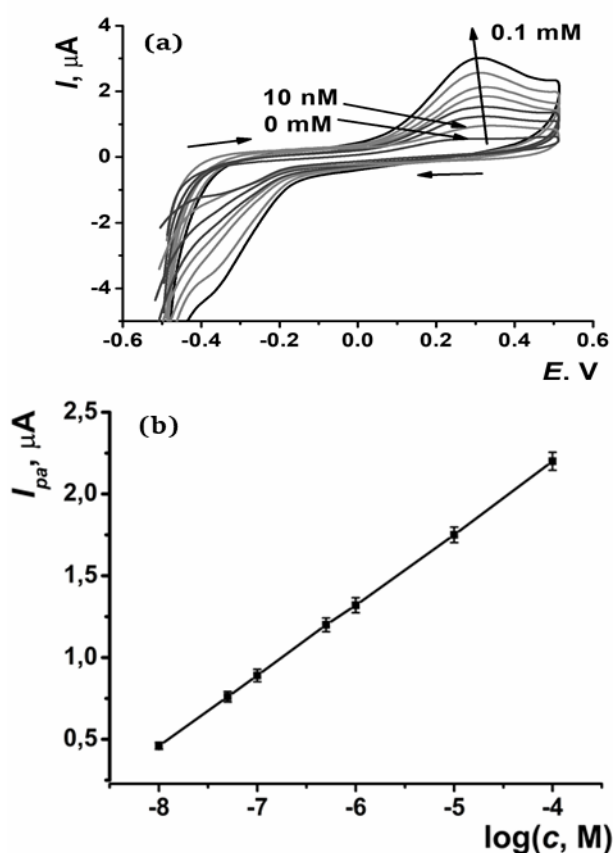


**Scheme 1** The proposed mechanism of reversible reduction and oxidation of quinone fragments in P[3]A[2]Q molecules.

### 3.2. Voltammetric determination of nitrophenols

The response changes of the coating based on P[3]A[2]Q in presence of *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, 2,4,6-trinitrophenol were investigated. Redox peak currents of P[3]A[2]Q increased with nitrophenol concentration. Probably, the interaction between P[3]A[2]Q and nitrophenols occurs through the “host-guest” mechanism [51]. Electrochemical determination of nitrophenols by P[3]A[2]Q peak currents has the advantage compared to the other common methods. This advantage is based on intrinsic nitrophenol reduction currents. Here, the redox peaks were observed at much lower potentials in the range from  $-0.8$  to  $-0.6$  V [38, 52, 53] compared to P[3]A[2]Q oxidation peak potential in the area close to 0.25 V. For all mononitrophenols the morphology and the peak current values were quite similar. The typical cyclic voltammograms for *m*-nitrophenol determination are presented in Figure 4a.

Voltammetric determination of nitrophenols through redox peak currents of P[3]A[2]Q allows the quantification of mononitrophenols in the range from 10 nM to 0.1 mM with the limit of detection (LOD) of 5 nM. The LOD value was calculated for  $S/N = 3$  criteria. The example of calibration curve for *m*-nitrophenol is presented in Figure 4b, the calibration curves for all *mono*-nitrophenols are presented in Figure S2.



**Figure 4** Voltammograms of SPCEs modified with CB and P[3]A[2]Q in the presence of different concentrations of *m*-nitrophenol (a); calibration curve of *m*-nitrophenol determination. Average  $\pm$  S.D. for five individual sensors prepared from the set of equal reagents (b). BRB, pH 7.0, 0.1 V/s.

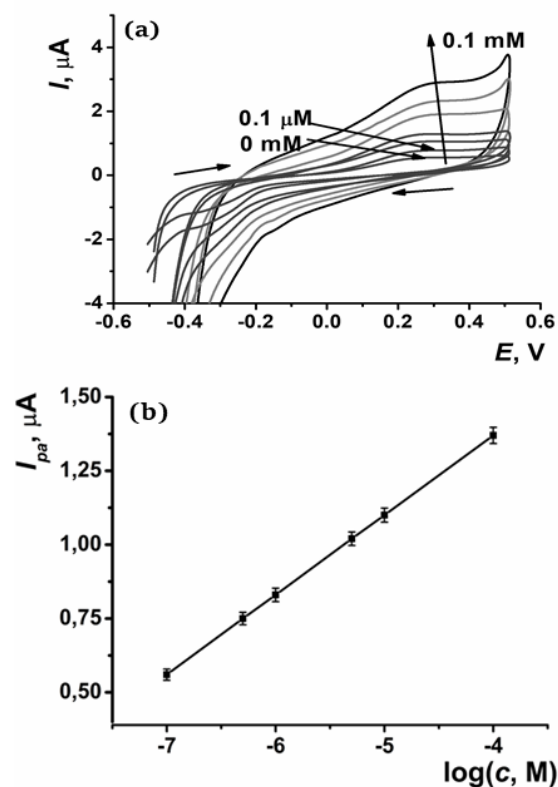
The voltammograms of 2,4-dinitrophenols, 2,6-dinitrophenols and 2,4,6-trinitrophenols were recorded in the same way. The current peak morphology and the values were very similar for these three compounds. But compared to voltammograms recorded for *m*-nitrophenols, the oxidation peak for di- and trinitrophenols was less pronounced. The difference in the sensor response and shape of the peaks for mono-, di-, and trinitrophenols is likely due to steric constraints within di- and tri-nitro compound incorporation into the cavity of P[3]A[2]Q. It is attributed to the number of substituents and, consequently, size. The typical cyclic voltammograms for 2,4-dinitrophenol determination are presented in Figure 5a.

The P[3]A[2]Q redox peak currents allow determining 2,4-dinitrophenol, 2,6-dinitrophenol and 2,4,6-trinitrophenols in the range from 0.1 μM to 0.1 mM using the voltammetric approach. The LOD was equal to 50 nM calculated for  $S/N = 3$  criteria. The example of calibration curve for 2,4-dinitrophenol is presented in Figure 5b; the calibration curves for di- and trinitrophenols are presented in Figure S3.

The linear regression equation parameters for each type of the compounds studied are presented in Table 1.

### 3.3. Chronoamperometric nitrophenol detection

The approach introduced was further used for chronoamperometric sensor development based on 3D printed flow-through system and SPCE modified with CB and P[3]A[2]Q.



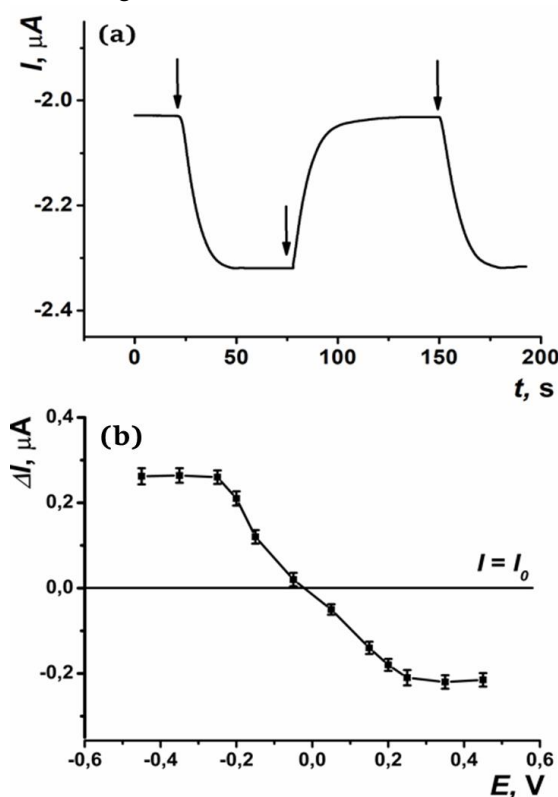
**Figure 5** Voltammograms recorded on SPCEs modified with CB and P[3]A[2]Q in the presence of different concentrations of 2,4-dinitrophenol (a); calibration curve of 2,4-dinitrophenol determination (b). Average  $\pm$  S.D. for five individual sensors prepared from the set of equal reagents. BRB, pH 7.0, 0.1 V/s.

**Table 1** Linear regression equation parameters for the nitrophenols studied with voltametric approach on SPCE covered with CB and P[3]A[2]Q.

| Analyte               | $y = a + bx$   |  | $R^2$  |
|-----------------------|--|--|--------|
|                       | $\Delta(I, \mu\text{A}) = a + b \cdot \log(c, \text{M})$                       |  |        |
| <i>p</i> -nitrophenol | $I, \mu\text{A} = (3.87 \pm 0.02) + (0.429 \pm 0.002) \cdot \log(c, \text{M})$ |  | 0.9998 |
| <i>m</i> -nitrophenol | $I, \mu\text{A} = (3.92 \pm 0.01) + (0.433 \pm 0.002) \cdot \log(c, \text{M})$ |  | 0.9999 |
| <i>o</i> -nitrophenol | $I, \mu\text{A} = (3.96 \pm 0.02) + (0.437 \pm 0.003) \cdot \log(c, \text{M})$ |  | 0.9997 |
| 2,4-dinitrophenol     | $I, \mu\text{A} = (2.45 \pm 0.01) + (0.264 \pm 0.002) \cdot \log(c, \text{M})$ |  | 0.9998 |
| 2,6-dinitrophenol     | $I, \mu\text{A} = (2.40 \pm 0.02) + (0.269 \pm 0.002) \cdot \log(c, \text{M})$ |  | 0.9998 |
| 2,4,6-trinitrophenol  | $I, \mu\text{A} = (2.49 \pm 0.03) + (0.275 \pm 0.004) \cdot \log(c, \text{M})$ |  | 0.9997 |

The flow of buffer or analyte solution was sequentially passed through the electrochemical cell, and the current shift was recorded. The chronoamperometric signal was quite similar for such mononitrophenols as *o*-nitrophenol, *m*-nitrophenol, and *p*-nitrophenol. Another group of compounds with similar signal was formed from di- and trinitrophenols: 2,4-dinitrophenol, 2,6-dinitrophenol, and 2,4,6-trinitrophenol.

The sensor signal ( $\Delta I$ ) for all nitrophenols studied was defined as a difference between the currents measured in absence ( $I_0$ ) and in presence ( $I$ ) of nitrophenol in the flow. Dynamic sensor response for *m*-nitrophenol as an example is shown in Figure 6a.



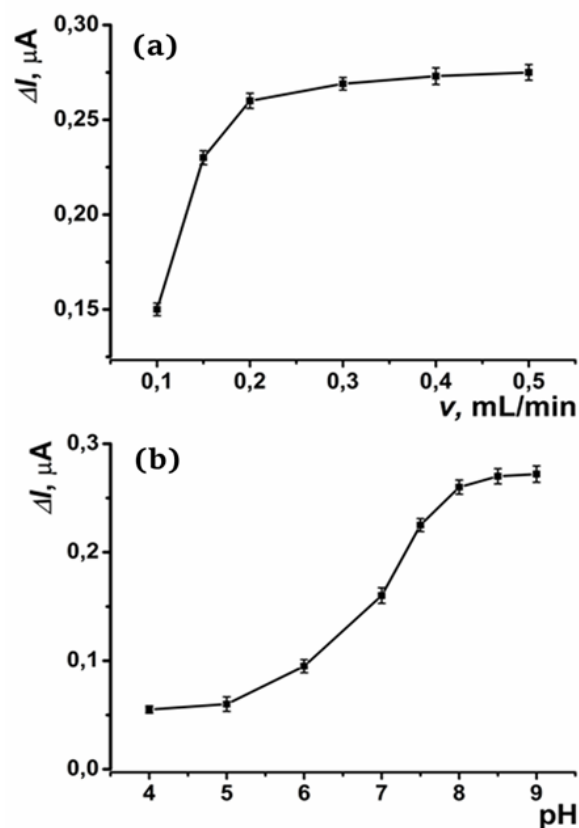
**Figure 6** Chronoamperometric sensor response at  $-0.25$  V (a) and current shift dependence on polarization potential on SPCE modified with CB and P[3]A[2]Q in presence of  $10 \mu\text{M}$  of *m*-nitrophenol (b). Arrows indicate the flow switching from buffer solution to *m*-nitrophenol solution and back. Average  $\pm$  S.D. for five individual sensors prepared from the set of equal reagents. Chronoamperometry, BRB, pH 8.0, flow rate 0.2 mL/min.

The chronoamperometric response was observed both at negative and positive potentials; however, the maximal response was achieved at  $-0.25$  V. The typical current shift dependence on the polarization potential for *m*-nitrophenol is presented in Figure 6b.

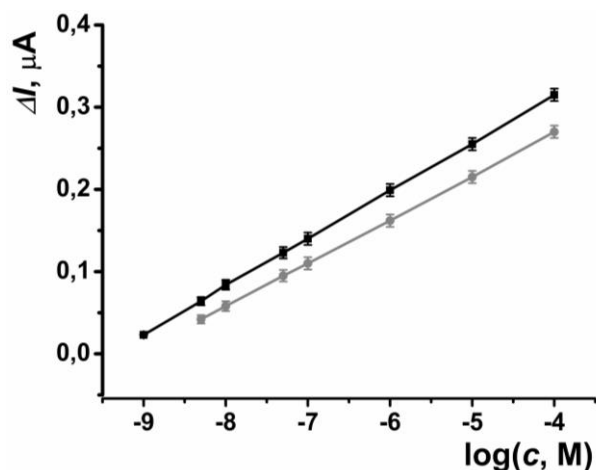
To get the highest response value, the flow rate of 0.2 mL/min and the pH value of 8.0 should have been used for all nitrophenols. The current shift dependences on flow rate and pH value for *m*-nitrophenol are presented in Figure 7. This type of regularity was observed for all of nitrophenols investigated.

The signal increased with pH value in the range from 2.0 to 6.0 with a sharp increase in the area of 6.0–8.0. After the pH value reached 8.0, the signal stabilization was observed. This behavior can be explained by alternative oxidation of quinone groups by dissolved oxygen. The oxygen reactivity is higher in alkaline medium.

The sensors developed allowed determining various mononitrophenols at concentrations from 1 nM to 0.1 mM with LOD of 0.5 nM, according to the  $S/N = 3$  criteria. As for 2,4-dinitrophenol, 2,6-dinitrophenol, and 2,4,6-trinitrophenol, the linear range was from 10 nM to 0.1 mM with LOD equal to 2 nM, calculated for  $S/N = 3$  criteria. Calibration curves for *m*-nitrophenol and 2,4-dinitrophenol as the examples are shown in Figure 8, calibration curves for all the compounds are presented in Figure S4 and Figure S5.



**Figure 7** Current shift dependences on flow rate (a) and pH value (b) for SPCEs modified with CB and P[3]A[2]Q in presence of  $10 \mu\text{M}$  of *m*-nitrophenol at  $-0.25$  V. Average  $\pm$  S.D. for five individual sensors prepared from the set of equal reagents. Chronoamperometry, BRB, (a) pH 8.0, (b) flow rate 0.2 mL/min.



**Figure 8** Calibration curves of *m*-nitrophenol (black) and 2,4-dinitrophenol (grey) on SPCEs modified with CB and P[3]A[2]Q. Average ± S.D. for five individual sensors prepared from the set of equal reagents. Chronoamperometry, BRB, pH 8.0, flow rate 0.2 mL/min, -0.25 V.

Analytical characteristics of the mono-, di-, and trinitrophenols with the flow-through system are presented in Table 2.

The 3D printed flow-through system using SPCE modified with CB and P[3]A[2]Q allows performing up to 40 measurements per hour on the same electrode.

In spite of the durable effect of the flow in the flow-through system, there were no significant changes in the properties of modifying layer on SPCEs. This can be explained by the high stability of the coating based on CB combined with P[3]A[2]Q.

Analytical characteristics of the nitrophenol determination on the sensors developed are presented in Table 3 and are comparable or better than ones for the other electrochemical sensors previously reported in the literature.

The interfering effect of the components of model effluent solution on *m*-nitrophenol chronoamperometric determination parameters was assessed (Table 4).

**Table 2** Analytical characteristics of the various nitrophenols determination using the flow-through system and SPCEs modified with CB and P[3]A[2]Q.

| Analyte              | $y = a + bx$  |                            | $R^2$  |
|----------------------|---|----------------------------|--------|
|                      | $\Delta(I, \mu A)$  | $= a + b \cdot \log(c, M)$ |        |
| p-nitrophenol        | $\Delta(I, \mu A) = (0.557 \pm 0.004) + (0.0579 \pm 0.0003) \cdot \log(c, M)$ |                            | 0.9998 |
| m-nitrophenol        | $\Delta(I, \mu A) = (0.549 \pm 0.02) + (0.0584 \pm 0.0003) \cdot \log(c, M)$  |                            | 0.9999 |
| o-nitrophenol        | $\Delta(I, \mu A) = (0.534 \pm 0.03) + (0.0592 \pm 0.0004) \cdot \log(c, M)$  |                            | 0.9998 |
| 2,4-dinitrophenol    | $\Delta(I, \mu A) = (0.479 \pm 0.002) + (0.0527 \pm 0.0003) \cdot \log(c, M)$ |                            | 0.9998 |
| 2,6-dinitrophenol    | $\Delta(I, \mu A) = (0.482 \pm 0.002) + (0.0534 \pm 0.0004) \cdot \log(c, M)$ |                            | 0.9997 |
| 2,4,6-trinitrophenol | $\Delta(I, \mu A) = (0.475 \pm 0.003) + (0.0519 \pm 0.002) \cdot \log(c, M)$  |                            | 0.9997 |

The model sample of effluent contained 0.04 M H<sub>3</sub>PO<sub>4</sub>, 0.04 M H<sub>3</sub>BO<sub>3</sub>, 0.04 M CH<sub>3</sub>COOH, 0.05 M Na<sub>2</sub>SO<sub>4</sub>, 0.41 mM CaCl<sub>2</sub>, 0.26 mM MgCl<sub>2</sub>, 93 μM NH<sub>4</sub>Cl and 0.27 mM KOH. After 100-fold dilution of the sample with working buffer solution the recovery obtained was 98 %. Since the maximum permissible concentration level of nitrophenols in the effluents was in micromolar range [72], the sensor developed can provide a reliable determination of the ecotoxicant in natural reservoirs.

#### 4. Limitations

There are no special limitations in our study.

#### 5. Conclusion

The electrochemical sensor based on SPCE modified with CB and P[3]A[2]Q was developed. The device demonstrated high sensitivity towards a group of nitrophenols. Voltammetric measurements allowed observing the increase of P[3]A[2]Q own redox peaks in presence of nitrophenols, which can be attributed to their possible “host-guest” interaction. This fact helped to carry out the chronoamperometric measurements at the potential of -0.25 V which is much higher than the cathodic potential of nitrophenols direct reduction recorded at the range -0.8...-0.6 V. The flow-through chronoamperometric approach provided the possibility of mononitrophenols and 2,4-dinitrophenol, 2,6-dinitrophenol and 2,4,6-trinitrophenol determination in the concentration ranges from 1.0 nM to 0.1 mM with LOD of 0.5 nM and from 10 nM to 0.1 mM with LOD of 2 nM, respectively.

The electrochemical sensor suggested has a low cost and a simple assembly. Thus, all the modifying components were casted from a single aliquot that allowed us to produce the modifying coating in one step using “one-pot synthesis” principle. Beside this, using CB as a matrix for P[3]A[2]Q implementation into the electrode coating helped to maintain its mechanical stability during the flow-through measurements. This feature provides multiple (up to 40 per hour) measurements on a single sensor.

The recovery value of 100-fold diluted sample of model effluent was 98 ± 1% for *m*-nitrophenol. In addition, low limits of detections and micromolar permissible concentration levels allow using the sensor developed for eco-monitoring of nitrophenols in natural water. The advantage of flow-through analysis methods is primarily provided by the large number of analyzed samples over a period of time. Additionally, the use of 3D printed flow-through cell has such advantages as easy replacement of individual components, extremely low manufacturing cost, biocompatibility and biodegradability.

**Table 3** Comparison of the electrochemical characteristics of the sensors developed with other electrochemical sensors for nitrophenol determination described in literature.

| Sensor content  | Detection mode   | Concentration range, M                      | LOD, M               | Ref.      |
|---|------------------|---|----------------------|-----------|
| <i>o</i> -nitrophenol   |                  |   |                      |           |
| GCE <sup>a</sup> /graphene nanosheets, functionalized with $\beta$ -cyclodextrins | DPV <sup>b</sup> | $5.0 \cdot 10^{-6}$ – $4.0 \cdot 10^{-4}$   | $3.0 \cdot 10^{-7}$  | [54]      |
| GCE/GO <sup>c</sup> /poly(ethyleneimine) dendrimer                                | DPV              | $5.0 \cdot 10^{-6}$ – $1.55 \cdot 10^{-4}$  | $1.0 \cdot 10^{-7}$  | [55]      |
| GCE/cyclodextrin/RGO <sup>d</sup> , functionalized with chitosan                  | DPV              | $1.2 \cdot 10^{-7}$ – $4.0 \cdot 10^{-5}$   | $1.8 \cdot 10^{-8}$  | [56]      |
| SPCE/(CB + P[3]A[2]Q)   | CV <sup>e</sup>  | $1.0 \cdot 10^{-8}$ – $1 \cdot 10^{-4}$     | $5.0 \cdot 10^{-9}$  | This work |
| SPCE/(CB + P[3]A[2]Q)   | CA <sup>f</sup>  | $1.0 \cdot 10^{-9}$ – $1 \cdot 10^{-4}$     | $5.0 \cdot 10^{-10}$ | This work |
| <i>m</i> -nitrophenol   |                  |   |                      |           |
| CPE <sup>g</sup> / $\beta$ -cyclodextrin, mesoporous Si                           | CV               | $2.0 \cdot 10^{-7}$ – $1.4 \cdot 10^{-6}$   | $5.0 \cdot 10^{-8}$  | [57]      |
| GCE/macroporous carbon, amino-bridged organic poly-calix[4]arenes                 | DPV              | $1.0 \cdot 10^{-6}$ – $4.0 \cdot 10^{-4}$   | $1.22 \cdot 10^{-7}$ | [58]      |
| GCE/magnetite-PtNPs <sup>h</sup> , stabilized with 3-n-propyl-4-picoline          | DPV              | $1.0 \cdot 10^{-7}$ – $1.5 \cdot 10^{-6}$   | $4.5 \cdot 10^{-8}$  | [59]      |
| SPCE/(CB + P[3]A[2]Q)   | CV               | $1.0 \cdot 10^{-8}$ – $1 \cdot 10^{-4}$     | $5.0 \cdot 10^{-9}$  | This work |
| SPCE/(CB + P[3]A[2]Q)   | CA               | $1.0 \cdot 10^{-9}$ – $1 \cdot 10^{-4}$     | $5.0 \cdot 10^{-10}$ | This work |
| <i>p</i> -nitrophenol   |                  |   |                      |           |
| GCE/Ni/N-doped carbon nanocomposite   | DPV              | $6.0 \cdot 10^{-8}$ – $1.0 \cdot 10^{-4}$   | $4.0 \cdot 10^{-9}$  | [60]      |
| GCE/Cr-MOF <sup>i</sup> NPs   | DPV              | $2.0 \cdot 10^{-6}$ – $5.0 \cdot 10^{-4}$   | $7.0 \cdot 10^{-7}$  | [61]      |
| GCE/GO  | DPV              | $1.0 \cdot 10^{-7}$ – $1.2 \cdot 10^{-4}$   | $2.0 \cdot 10^{-8}$  | [62]      |
| SPCE/(CB + P[3]A[2]Q)   | CV               | $1.0 \cdot 10^{-8}$ – $1 \cdot 10^{-4}$     | $5.0 \cdot 10^{-9}$  | This work |
| SPCE/(CB + P[3]A[2]Q)   | CA               | $1.0 \cdot 10^{-9}$ – $1 \cdot 10^{-4}$     | $5.0 \cdot 10^{-10}$ | This work |
| 2,4-dinitrophenol   |                  |   |                      |           |
| GCE/MIP <sup>j</sup> /GO  | CV               | $1.0 \cdot 10^{-6}$ – $1.5 \cdot 10^{-3}$   | $1.0 \cdot 10^{-6}$  | [63]      |
| GCE/C <sub>3</sub> N <sub>4</sub> /V <sub>2</sub> O <sub>5</sub>                  | CV               | $1.0 \cdot 10^{-8}$ – $1.0 \cdot 10^{-4}$   | $3.3 \cdot 10^{-9}$  | [64]      |
| GCE/RuO <sub>2</sub> NPs-decorated V <sub>2</sub> O <sub>5</sub> nanoflakes       | DPV              | $5.0 \cdot 10^{-9}$ – $3.5 \cdot 10^{-6}$   | $1.07 \cdot 10^{-9}$ | [65]      |
| SPCE/(CB + P[3]A[2]Q)   | CV               | $1.0 \cdot 10^{-7}$ – $1.0 \cdot 10^{-4}$   | $5.0 \cdot 10^{-8}$  | This work |
| SPCE/(CB + P[3]A[2]Q)   | CA               | $1.0 \cdot 10^{-8}$ – $1.0 \cdot 10^{-4}$   | $2.0 \cdot 10^{-9}$  | This work |
| 2,6-dinitrophenol   |                  |   |                      |           |
| PGE/AgNPs/chitosan/SrSnO <sub>3</sub> nanocomposite                               | DPV              | $1.5 \cdot 10^{-6}$ – $1.35 \cdot 10^{-5}$  | $1.8 \cdot 10^{-7}$  | [66]      |
| GCE/poly(Congo red)   | CV               | $5.0 \cdot 10^{-7}$ – $6.5 \cdot 10^{-5}$   | $1.0 \cdot 10^{-7}$  | [67]      |
| GCE/ ZnO-PbO microstructures  | DPV              | $3.23 \cdot 10^{-6}$ – $1.67 \cdot 10^{-5}$ | $2.95 \cdot 10^{-6}$ | [68]      |
| SPCE/(CB + P[3]A[2]Q)   | CV               | $1.0 \cdot 10^{-7}$ – $1.0 \cdot 10^{-4}$   | $5.0 \cdot 10^{-8}$  | This work |
| SPCE/(CB + P[3]A[2]Q)   | CA               | $1.0 \cdot 10^{-8}$ – $1.0 \cdot 10^{-4}$   | $2.0 \cdot 10^{-9}$  | This work |
| 2,4,6-trinitrophenol  |                  |   |                      |           |
| Au electrode/carbon quantum dots  | DPV              | $5.0 \cdot 10^{-10}$ – $5.0 \cdot 10^{-6}$  | $3.5 \cdot 10^{-10}$ | [69]      |
| PGE/MIP/RGO/polypyrrol  | DPV              | $1.0 \cdot 10^{-5}$ – $1.0 \cdot 10^{-3}$   | $1.4 \cdot 10^{-6}$  | [70]      |
| GCE/1,3,5-benzotricarboxylic acid/RGO   | DPV              | $2.0 \cdot 10^{-7}$ – $1.0 \cdot 10^{-5}$   | $1.0 \cdot 10^{-7}$  | [71]      |
| SPCE/(CB + P[3]A[2]Q)   | CV               | $1.0 \cdot 10^{-7}$ – $1.0 \cdot 10^{-4}$   | $5.0 \cdot 10^{-8}$  | This work |
| SPCE/(CB + P[3]A[2]Q)   | CA               | $1.0 \cdot 10^{-8}$ – $1.0 \cdot 10^{-4}$   | $2.0 \cdot 10^{-9}$  | This work |

<sup>a</sup> GCE – glassy carbon electrode;<sup>b</sup> DPV – differential pulse voltammetry;<sup>c</sup> GO – graphene oxide;<sup>d</sup> RGO – reduced graphene oxide;<sup>e</sup> CV – cyclic voltammetry;<sup>f</sup> CA – chronoamperometry;<sup>g</sup> CPE – carbon paste electrode;<sup>h</sup> NPs – nanoparticles;<sup>i</sup> Cr-MOF – chrome metal-organic framework;<sup>j</sup> MIP – molecularly imprinted polymers.

**Table 4** Chronoamperometric recovery of *m*-nitrophenol in a model effluent sample.

| Model effluent sample | <i>m</i> -nitrophenol, $\mu\text{M}$ |               | Sr    | Recovery, % |
|-----------------------|--------------------------------------|---------------|-------|-------------|
|                       | Added                                | Found         |       |             |
| No dilution           |                                      | 3.5 $\pm$ 0.2 | 0.045 | 35 $\pm$ 2  |
| Dilution 1:10         | 10                                   | 6.7 $\pm$ 0.1 | 0.015 | 67 $\pm$ 1  |
| Dilution 1:100        |                                      | 9.8 $\pm$ 0.1 | 0.010 | 98 $\pm$ 1  |

### Supplementary materials

This manuscript contains supplementary materials, which are available on the corresponding online page.

### Data availability statement

The raw/processed data required to reproduce the above findings cannot be shared at this time as the data also forms part of an ongoing study.

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None.

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### Conflict of interest

The authors declare no conflict of interest.

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