Electrochemical determination of *para*-nitrophenol at apatite-modified carbon paste electrode: Application in river water samples

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ABSTRACT

The behavior of a modified carbon paste electrode (CPE) for *para*-nitrophenol detection by cyclic and square wave voltammetry (SWV) was studied. The electrode was built by incorporating the hydroxyapatite (HAP) to carbon paste. The overall analysis involved a two-step procedure: an accumulation step at open circuit, followed by medium exchange to a pure electrolyte solution for the voltammetric quantification. During the preconcentration step, *para*-nitrophenol was adsorbed onto hydroxyapatite surface. The influence of various experimental parameters on the HAP–CPE response was investigated (i.e. pH, carbon paste composition, accumulation time). Under the optimized conditions, the reduction peak shows that the peak height was found to be directly proportional to the *para*-nitrophenol concentration in the range comprised between 2×10^{-7} mol L^{-1} and 1×10^{-4} mol L^{-1}. With this, it was possible to determine detection limit (DL), which resulted in 8×10^{-9} mol L^{-1} for peak 1. The proposed electrode (HAP–CPE) presented good repeatability, evaluated in term of relative standard deviation (R.S.D. = 2.87%) for $n = 7$ and was applied for *para*-nitrophenol determination in water samples. The average recovery for these samples was 86.2%.

1. Introduction

Aromatic nitrocompounds are among the most toxic substances and are thus commonly used in the manufacture of explosives, pesticides, dyes, plasticizers and pharmaceuticals [1–4]. These compounds have been detected not only in industrial wastewaters but also in freshwater and marine environments [5], and are considered by the United States Environmental Protection Agency (USEPA) as priority pollutants, owing to the fact that they are toxic to humans [6]. In particular, *para*-nitrophenol (*p*-NPh) is a toxic derivative of the parathion insecticide and is also present in wastewaters from industries such as refineries. Detoxification of water contaminated with nitroaromatic compounds is usually a very difficult process since the presence of a nitro-group confers to the aromatic compound a strong chemical stability and resistance to microbial degradation [7]. Early detection of *para*-nitrophenol is important for protecting water resources and food supplies, in the defense against terrorist activity, and for monitoring detoxification processes [8]. Accordingly, there are growing demands for field-deployable devices for reliable on-site monitoring of

para-nitrophenol compounds. Common laboratory-based analytical methods for determining *para*-nitrophenol compounds such as primarily gas and liquid chromatography (HPLC) [9–13], UV–vis spectrophotometry [14,15] and spectrofluorimetry [16] have been reported. The use of enzyme-linked immunosorbent assay (ELISA) has been studied [17]. However, some sample pretreatment involving separation, extraction and/or adsorption is generally necessary, and this can also be time-consuming and complex. Electrochemical methods, such as differential pulse polarography (DPP), anodic stripping voltammetry (ASV) and differential pulse voltammetry (DPV), have been widely applied for the determination of pharmaceuticals, dyes, insecticides and pesticides [18–20].

In recent years, chemically modified electrodes (CMEs) were used for the voltammetric quantification of various organic and inorganic species after their open circuit accumulation [21,22]. Much of the work in this field was directed to exploit the chemical reactivity of the modifier towards a target analyte for electroanalytical purpose. Multitudes of modifying agents were used either as coatings on solid electrode surfaces or dispersed within a conductive matrix. It is noteworthy that this last approach is well suited when using electronically insulating modifiers requiring a direct contact to an electronically conducting substrate as used in connection with electrochemistry. The application of silicates and related mineral materials in electrochemistry is rather recent

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and was directed to combine their intrinsic properties to selected electrochemical reactions in order to improve the response of the electrode. Modified electrodes are being used frequently in the voltammetric determination of organic compounds because of their efficiency, the selectivity that can be obtained by varying the modifier and the sensitivity which is equivalent to that reached in anodic and cathodic stripping. In doing so, clay, zeolite and silica-modified electrodes were prepared, characterized and applied (sometimes tentatively) in various fields including for example electroanalysis and sensors, electrocatalysis, photochemistry, thin-film technology, fuel cells, molecular recognition. Kauffmann [23] has reported that a carbon paste electrode (CPE) modified with lipids and proteins (enzymes) has potential application in environmental analysis. In addition, clay (such as bentonite and zeolite) modified electrodes have been applied widely for the determination of organic compounds. Na-montmorillonite (SWy-2) exhibits similar properties to those of other clays, which are able to adsorb electroactive species for their direct determination.

Recent works, reported in the literature, have shown several applications and electroanalytical methodologies employing glassy carbon electrode as working electrodes [24,25]. Luz et al. [25] constructed a glassy carbon electrode impregnated with a lithium tetracyanoethylenide (LiTCNE) for the determination of *para*-nitrophenol. The reduction of this compound has been carried out on a modified glassy carbon electrode using cyclic and DPV.

This study proposed a new modified carbon paste electrode which has been prepared by the hydroxyapatite (HAP) for *para*-nitrophenol detection. It has shown a selective preconcentration and quantization of *para*-nitrophenol by cyclic and square wave voltammetry (SWV). This study has led to the development of a new modified electrode for the determination of *para*-nitrophenol with improved qualities such as simplicity of electrode preparation, wider linear range, low detection limit (DL), high selectivity and very good stability of modifier. The procedure is based on the reduction of *para*-nitrophenol after it was preconcentrated on a carbon paste electrode modified with the HAP, under open circuit conditions.

2. Experimental

2.1. Reagents

Suprapur grade *para*-nitrophenol was purchased from Fluka. Water purified by means of a Milli Q–Milli RO system was used throughout the preparation of the solutions. Carbon paste was supplied from (Carbone, Lorraine, ref 9900, France). All chemicals were of analytical grade and used without further purification. The hydroxyapatite used in this manuscript was synthesized with the doubly decomposition method [26].

2.2. Electrodes

Modified electrodes were prepared by mixing a carbon powder and the desired weight of hydroxyapatite with potassium sulphate. The body of the working electrode for voltammetric experiments was a PTFE cylinder that was tightly packed with carbon paste. The geometric area of this electrode was $0.1256\,cm^2$. Electrical contact was made at the back by means of a bare carbon.

2.3. Apparatus and software

Voltammetric experiments were performed using a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software) run
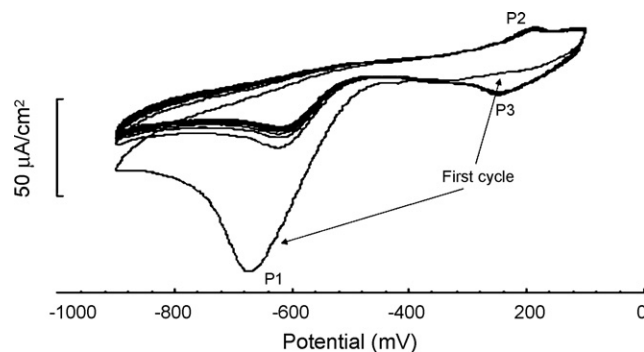
Fig. 1. Voltammetric curve for HAP–CPE preconcentrated for 15 min in $5 \times 10^{-4}\,mol\,L^{-1}$ *para*-nitrophenol (pH 8.0), scan rate: $20\,mV\,s^{-1}$, 12.5% (w/w) of HAP/CP ratio, supporting electrolyte is CH_3CO_2H (1:1).

under windows 98. The three-electrode system consisted of a chemically modified carbon paste electrode as the working electrode a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode.

2.4. Procedure

The modified carbon paste electrode was immersed in a cell containing 20 ml of the *para*-nitrophenol sample solution adjusted to a pH value, to get the chemical deposition. Meanwhile the solution was stirred by a 1.6-cm magnetic stirrer bar (rotating about 600 rpm) at open circuit. After a preconcentration step, the electrode was removed from the preconcentration cell, rinsed with water and placed in the measurement cell containing the supporting electrolyte (buffer CH_3CO_2H (1:1)). The square wave voltammogram was recorded from $-100\,mV$ to $-900\,mV$ vs. SCE. Results were obtained by using a step potential of 25 mV; amplitude 5 mV and duration 5 s at scan rate $1\,mV\,s^{-1}$. Impedance measurements were obtained with the same three electrode–cell setup described before. The complete frequency spectrum from 100 kHz to 10 MHz can be measured with AC amplitude of 5–10 mV. In order to insure the inert effect of HAP electrode during the experiment, the potential of 0 mV was chosen in presence or in absence of accumulated *para*-nitrophenol.

3. Results and discussion

3.1. Preliminary voltammetric characterization

The performance of the newly developed hydroxyapatite-modified carbon paste electrode is based on the preconcentration of *para*-nitrophenol from aqueous solution onto the surface of the modified electrode by adsorption onto the modifier surfaces. Fig. 1 shows a cyclic voltammogram between $-0.1\,V$ and $-0.9\,V$ for a 12.5% modified carbon paste electrode at $20\,mV\,s^{-1}$, obtained after exposure to a $5 \times 10^{-4}\,mol\,L^{-1}$ solution of *para*-nitrophenol in a stirred solution. During the first cycle, one peak (P_1) appears at $-0.568\,V$ on the cathodic sweep, and another one appears at $-0.19\,V$ (P_2) on the anodic sweep. In the successive cycles, in addition to P_1, one new reductive peak (P_3) also appears at $-0.48\,V$ on the cathodic sweep. It is interesting that the reversible redox couple (P_2:P_3) increases at the expense of the irreversible peak (P_1), which indicated that the product of *para*-nitrophenol by irreversible reduction remained on or near the modified electrode surface and was oxidized on the anodic sweep. When the scan potential was changed in the range of $-0.1\,V$ to $-0.4\,V$, the redox couple disappeared gradually. These interesting phenomena indicated that the development of P_1 peak is responsible for the
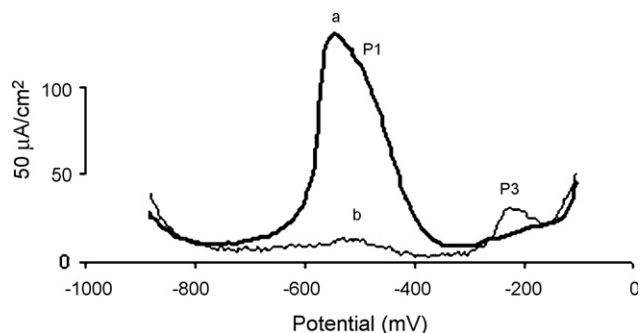
Fig. 2. Square wave voltammograms of 5×10^{-4} mol L^{-1} *para*-nitrophenol (pH 8.0) in tampon acetic acid (1:1) at HAP–CPE (12.5% HAP), accumulation time (t_p): 10 min, (a) first cycle (b) second cycle.

Fig. 3. Current density vs. time of 5×10^{-4} mol L^{-1} *para*-nitrophenol (pH 8.0) at HAP–CPE (12.5%) in tampon acetic acid (1:1) under 0.14 mV.

formation of P$_2$ and P$_3$ peaks. Heineman and Kissinger [27] reported that parathion at hanging mercury drop electrode gave the same behavior as that of *para*-nitrophenol in our studies. Nicholson and Shain [28] also reported that *para*-nitrosophenol (ØNO) could be transferred easily to *para*-hydroxylaminophenol (ØNHOH) by the reversible two-electron oxidation/reduction by using stationary electrode polarography. Nevertheless, it is believed that the same electron transfer mechanism can be applied in this study:

$$\varnothing NO_2 + 4H^+ + 4e^- \rightarrow \varnothing NHOH \tag{1}$$

$$\varnothing NHOH - 2H^+ - 2e^- \rightarrow \varnothing NO \tag{2}$$

The same behavior is recorded by square wave voltammetry, for the *p*-nitrophenol compound (Fig. 2). We clearly observe the decrease of the intensity of the peak P$_1$ recorded in the first cathodic cyclic sweep, on the other hand we note the apparition of the peak P$_3$ in the second cathodic cyclic sweep.

From both figures it became evident that adsorption of *para*-nitrophenol with hydroxyapatite took place on the electrode surface. The well-defined irreversible cathodic peak (P$_1$), higher than the peaks P$_2$ and P$_3$, was suitable for quantification of *para*-nitrophenol at very low concentrations.

In order to ascertain the number of electrons involved in the oxidation of *para*-nitrophenol at modified electrode, we determined the *n* value from cyclic voltammograms by using the following equation [29]:

$$n = \frac{0.0565}{E_p - E_{p/2}} \tag{3}$$

The *n* was 1.871 at modified electrode in 5×10^{-4} mol L^{-1} *para*-nitrophenol, which suggests that the number of the electrons corresponding to the redox process (P$_2$:P$_3$) is two. This process involves the loss of 2e$^-$ and 2H$^+$, which is consistent with the electron transfer mechanism applied in this study.

The scan rate was varied from 10 mV s^{-1} to 150 mV s^{-1}. The variation of the peak intensity with the scan rate was studied. An approximately linear relationship was found between the peak intensity and the square root of the scan rate ($R^2 = 0.9856$); indicating that the HAP–CPE reaction is controlled by diffusion process. The scan rate of 20 mV s^{-1} was used for further studies.

The method of chronoamperometry was used to characterize the electrochemical reactivity of *para*-nitrophenol on the HAP–CPE in tampon acetic acid (1:1) (Fig. 3). This curve has been obtained after the first cyclic sweep by applying a stationary potential $E = 0.14$ mV during 10 min. During the two hundred first second, the current intensity is inversely proportional to $1/\sqrt{t}$; this variation is controlled by a diffusional step. From 300 s the variation of the current intensity vs. time is a sinusoïdale curve expressed by Eq. (4). This result confirms the réversibility of the couple NHOH/NO
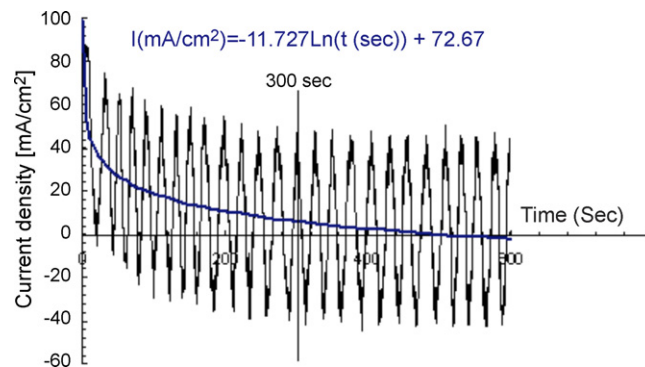
observed by the cyclic voltammetry.

$$I \, (\mu A/cm^2) = 44.64 \sin \left(\frac{2\pi}{Tt} + \frac{\pi}{2} \right) \text{ with } T = 27.4 \text{ s.} \tag{4}$$

### 3.2. Optimization of experimental conditions

Optimum conditions for the electrochemical response were established by measuring the peak current in dependence on all parameters.

3.2.1. Influence of accumulation time

The effect of the accumulation time is investigated (Fig. 4); this significantly affects the reduction peak current of *para*-nitrophenol. The peak current of 4×10^{-4} mol L^{-1} *para*-nitrophenol increases greatly within the first 10-min and then enhances slowly. Further increase in accumulation time does not increase the amount of *para*-nitrophenol at the electrode surface owing to surface saturation, and the peak current remains constant. This phenomenon is due to the cavity structure of hydroxyapatite that improves the ability of the electrode to adsorb electroactive *para*-nitrophenol. Maybe this is attributed to the saturated adsorption of *para*-nitrophenol on the hydroxyapatite–CPE surface. Taking account of sensitivity and efficiency, accumulation time was 10 min in the following experiments.

3.2.2. Influence of initial pH

The response of the HAP–CPE during the accumulation step was strongly pH dependent. As the pH increased from pH 3.0 to 7.0, the peak current increased at first because HAP can slowly dissolve in acidic solution and lose its ability of immobilizing *para*-nitrophenol. The optimum pH range was found between 6.0
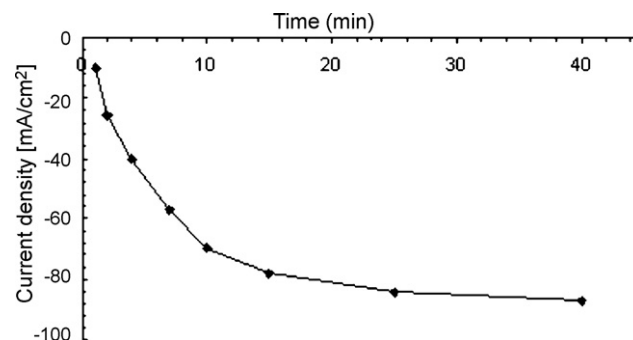
Fig. 4. Effects of accumulation time on peak currents (P$_1$) of 4×10^{-4} mol L^{-1} *para*-nitrophenol (pH 7.4) at HAP–CPE (%HAP = 12.5), supporting electrolyte is CH$_3$CO$_2$H (1:1).
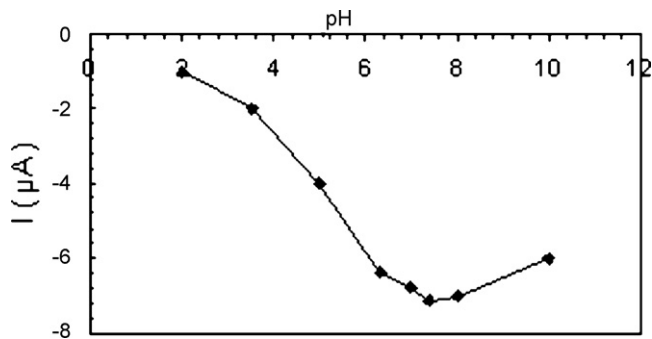
Fig. 5. Effects of solution pH on the peak current (P_1) for 2×10^{-5} mol L^{-1} *para*-nitrophenol at HAP–CPE (%HAP = 12.5), t_p = 10 min, supporting electrolyte is CH$_3$CO$_2$H (1:1).

Fig. 7. Calibration curve of *para*-nitrophenol at HAP–CPE under the optimized conditions, in tampon acetic acid (1:1).

and 10.0, showing a maximum response at pH 7.0 (Fig. 5). It was reported that the decrease in proton concentration as pH increasing from 3.0 to 10 exert a pronounced effect on the SWV response of *para*-nitrophenol.

3.2.3. Influence of amount of modifier

The effect of apatite incorporated within the carbon paste electrode was evaluated (Fig. 6). The use of apatite as modifier of the chemically modified carbon paste electrode can greatly increase the sensitivity of determination, which is due to the adsorption of *para*-nitrophenol. The peak intensity increases with the increasing of amount of modifier because the concentration of HAP on the surface of the modified electrode increases correspondingly. At 12.5% HAP, relative to the mass of graphite powder, the largest peak current was obtained. However, the continuous increase of amount of modifier causes a decrease of peak current, due to the decrease of conductivity of the modified electrode.

3.3. Calibration graph

Under the optimized experiment conditions, the calibration curve for *para*-nitrophenol in tampon acetic acid solution (1:1) at HAP–CPE was investigated, and the linear dynamic range was comprised between 2×10^{-7} mol L^{-1} and 1×10^{-4} mol L^{-1} (Fig. 7) in terms of the relationship between *para*-nitrophenol concentration and the reduction peak current height (P_1). The relationship can be described with the following linear regression equation in the mentioned concentration range:

$$I_p = -0.3023c - 0.3862 \quad (R = 0.9835) \tag{5}$$

According to Miller and Miller [30] the standard deviation of the mean current (S.D.) measured at reduction potential of *para*-nitrophenol for 10 voltammograms of the blank solution in pure
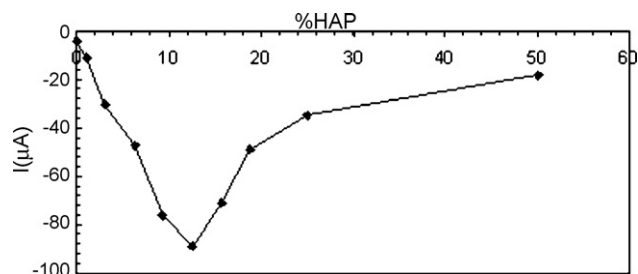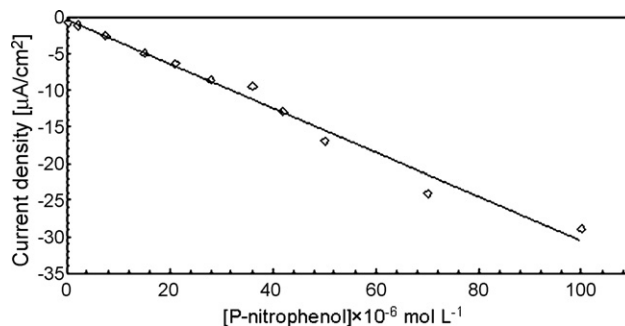
electrolytes was calculated from:

$$S.D. = \frac{1}{(n-2)} \sum_{j=0}^{n} (i_j - I_j)^2 \tag{6}$$

where i_j is the experimental value of the experiment number j and I_j is the corresponding recalculated value, at the same concentration using the regression line equation. The calculated S.D. was used in the determination of the detection limit ($3 \times$ S.D./slope) and the quantification limit (QL, $10 \times$ S.D./slope). From these values, a detection and quantification limits for peak 1 respectively of 8×10^{-9} mol L^{-1} and 1.5×10^{-8} mol L^{-1} *para*-nitrophenol were obtained. From the results, it can be observed that the values of DL and QL obtained are comparable to those published in literature [25]. Such results are shown to be very appropriate for the determination of traces of *para*-nitrophenol in natural water.

After each measurement the modified electrode was refreshed by successive cyclic voltammetric sweeps in blank solution to get a reproducible electrode surface. The relative standard deviation (R.S.D.) of 2.87% for seven times parallel detections of 4.0×10^{-5} mol L^{-1} *para*-nitrophenol, suggesting a good reproducibility of HAP–CPE.

Table 1
Electrical parameters calculated from the impedance spectra in CH$_3$CO$_2$H tampon (1:1), for the HAP–CPE and HAP–CPE/*para*-nitrophenol solution interfaces

	R_e (kΩ cm^2)	R_{ct} (kΩ cm^2)	C_{dl} (pF cm^{-2})
HAP–CPE	2.93	28.44	176.8
HAP–CPE/*para*-nitrophenol	3.79	19.83	224.6

Fig. 6. Effects of the content of HAP in carbon paste mixture % (w/w) on peak currents (P_1) of 5.5×10^{-4} mol L^{-1} *para*-nitrophenol (pH 7.4) at HAP–CPE, t_p = 10 min, supporting electrolyte is CH$_3$CO$_2$H (1:1).
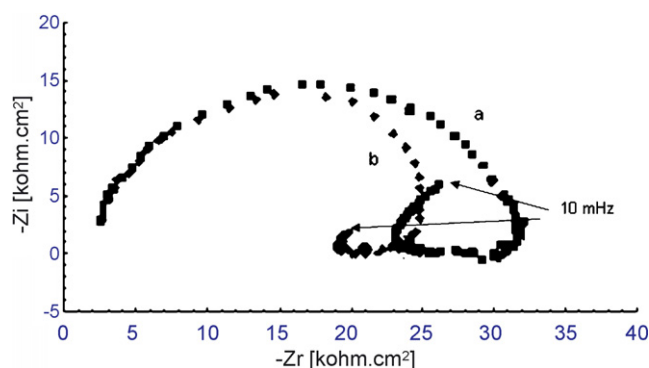

Fig. 8. Impedance spectra at 0 V (vs. SCE) in CH$_3$COOH tampon (1:1), (a) HAP–CPE (b) HAP–CPE/*para*-nitrophenol under the optimized conditions.

Table 2
Physico-chemical parameters of used natural water

pH	MES $(mg\,L^{-1})$	O_2 (dissolved) $(mg\,L^{-1})$	NH_4^+ $(mg\,L^{-1})$	Mn^{2+} $(mg\,L^{-1})$	NO_2^- $(mg\,L^{-1})$	NO_3^- $(mg\,L^{-1})$	Nitrogen total $(mg\,L^{-1})$
8.85	9.5	11	0.26	0.03	0.18	5.6	0.7

3.4. Impedance measurements of HAP–CPE

The current study focuses on using electrochemical impedance spectroscopy (EIS) to investigate the adsorption behaviors of the *para*-nitrophenol on the HAP–CPE. The EIS experiments were carried out in tampon acetic acid (1:1) in order to confirm the mechanisms suggested in the voltammetric part of this work regarding the HAP–CPE/*para*-nitrophenol interaction (Fig. 8). The electrical parameters were calculated using Voltamaster 4.0 software. The results are regrouped in Table 1. The HAP–CPE has the highest R_{ct} and lowest C_{dl}. R_{ct} equals to the semicircle diameter in the Niquist plot, presenting the interfacial electron transfer rate of redox between the electrolyte and the electrode. Furthermore, the double layer capacitance of HAP–CPE is usually lower than that of organic layers, such as *para*-nitrophenol. After *para*-nitrophenol immobilization, R_{ct} decreases and C_{dl} increases due to the presence of *para*-nitrophenol onto HAP–CPE surfaces.

3.5. Practical application

In order to evaluate the performance of HAP-modified carbon paste electrode by practical analytical applications, the determination of *para*-nitrophenol was carried out in natural waters (Alhansali Dam, Tadla-Azilal region) without any pretreatment. The *para*-nitrophenol concentration was determined by the standard addition technique. It should be mentioned at this point that the reason for using the standard addition technique is to compensate the matrix effect from natural water samples that contain high concentrations of nitrate ions and other foreign ions (Table 2). Hence, for determination of *para*-nitrophenol in these samples by calibration method the interferences of these ions impose errors on *para*-nitrophenol determination. Moreover, it is clear that there are not such difficulties in determining *para*-nitrophenol in pure water because of the simplicity of matrix in these samples. No *para*-nitrophenol traces were found when the proposed procedure was used. However, it was observed that peak current vs. *para*-nitrophenol added into the real sample solution increased linearly (Eq. (7)), hence the proposed method is suitable for the determination of *para*-nitrophenol in these waters.

$$i\mathrm{P}_1\ (\mu A) = -0.2654c\,(\mu mol\,L^{-1}) + 0.5675, \quad R = 0.98 \tag{7}$$

The statistical calculations for the assay results showed suitable precision of the proposed method (Table 3). However, the analytical sensitivity of the methodology proposed was decreased. This illustration was probably due to the presence of organic/inorganic matter, which can inhibit the adsorption process of *para*-nitrophenol onto the modifier surfaces.

Table 3
Results obtained from the linear regression curves (Eq. (7)) for the determination of *p*-nitrophenol at HAP–CPE in natural waters. The recovery was obtained for water spiked by 1×10^{-4} mol L^{-1} *para*-nitrophenol

Parameters	Peak 1
R^2	0.984
|Slope| $(A\,L\,mol^{-1})$	0.265
Standard deviation $\times 10^{-10}$ (A)	0.672
Relative standard deviation (%)	3.20
Recovery (%)	86.2

4. Conclusion

We have demonstrated the use of apatite-modified carbon paste electrode for a greatly enhanced voltammetric sensing of *para*-nitrophenol compounds. The reduction of this compound on the modified electrode occurs in an irreversible manner. Optimization of the experimental conditions yielded a detection limit for *para*-nitrophenol of 8×10^{-9} mol L^{-1} much better than that described in the literature and this electrode showed a wide linear response range, good sensitivity and repeatability. The modified electrode was successfully applied in water samples. The method could be improved in a simple way without introducing additional procedures and without increasing the time required for *para*-nitrophenol quantification. The electrode construction was extremely simple and with low cost. No unstable or toxic reagents were used.

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