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Voltammetric determination of 4-nitrophenol at a lithium tetracyanoethylenide (LiTCNE) modified glassy carbon electrode

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Abstract

The reduction of 4-nitrophenol (4-NP) has been carried out on a modified glassy carbon electrode using cyclic and differential pulse voltammetry (DPV). The sensor was prepared by modifying the electrode with lithium tetracyanoethylenide (LiTCNE) and poly-L-lysine (PLL) film. With this modified electrode 4-NP was reduced at −0.7 V versus SCE. The sensor presented better performance in 0.1 mol l^{-1} acetate buffer at pH 4.0. The other experimental parameters, such as concentration of LiTCNE and PLL, pulse amplitude and scan rate were optimized. Under optimized operational conditions, a linear response range from 27 up to 23200 nmol l^{-1} was obtained with a sensitivity of 3.057 nA l $nmol^{-1}$ cm^{-2}. The detection limit for 4-NP determination was 7.5 nmol l^{-1}. The proposed sensor presented good repeatability, evaluated in term of relative standard deviation (R.S.D. = 4.4%) for $n = 10$ and was applied for 4-NP determination in water samples. The average recovery for these samples was 103.0 (± 0.7)%.

Keywords: Lithium tetracyanoethylenide; 4-Nitrophenol; Differential pulse voltammetry; Modified electrode

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1. Introduction

The determinations of phenol compounds in environmental samples have been of high interest due to their toxic effect on human, animals and plants. In this sense, many of these compounds were included in the US Environmental Protection Agency List of Priority Pollutants [1]. Phenols are generated by a number of pollutants processes including those in the petroleum, paper industries and the synthesis of plastics and pharmaceutics [2,3]. 4-Nitrophenol (4-NP) is one of the nitrophenols highly hazardous and toxic which can cause significantive damages to the health and the environment.

The interest in the phenols determination in the environmental samples has proportionated the development of a several methods for their quantification. In this way, different analytical methods have been developed such as: chromatography with mass spectrometry [4–6], spectrophotometry [7–11] and electrochemical methods [12–15].

The use of DPV has proved to be very sensitive for detection of organic molecules [16–20]. The use of modified electrodes also improves the sensitivity in the oxidation or reduction processes of the compound [21].

The chemical modification of the electrodes is a field of growing interest in analytical chemistry. In electrochemistry, it has been demonstrated that chemically modified electrodes (CMEs) possess distinct advantages over conventional electrodes in many application areas including electrocatalysis and electrochemical sensors [22–26].

One of the most important properties of the CMEs, which have been a subject of considerable study, is their ability to catalyze the oxidation or reduction of some compounds.

The main goal of this modification is the establishment and the control of the physico-chemical properties of the electrode-solution interface. In this sense the modification of the electrode surface can be used to promote a better reactivity and selectivity to the base sensor, leading to the development of electrodes for some specific applications,

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such as the catalysis of organic and inorganics reactions [27].

A variety of efficient catalysts have been developed to induce the reduction of some organics compounds [28,29] because these catalysts promote a better electron transfer between the electrode surface and electroactive species in solution.

In this context, was recently reported that a catalytic effect of tetracyanoethylene (TCNE) [30], it is an electron acceptor because the presence of the four cyano groups on the molecule and the relatively large π conjugation system (reduction to the radical anion occurs very easily between three oxidation states: 0, −1, and −2) [31], accelerates reactions of some organics compounds.

Electron-donor and electron-acceptor molecules have become key compounds in molecular materials chemistry, where they are used as electroactive building blocks. Tetracyanoethylene (TCNE) [32] compound is one of the most powerful organic electron acceptors, and it can be considered as the prototype of cyano-based acceptors exhibiting similar properties to the 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) [33], which are able to adsorb electroactive species. In the attempt to combine the advantages of CMEs with the catalytic properties of TCNE, the construction of the TCNE modified electrode was proposed. However, several redox catalysts have leached out from the electrode surfaces, when directly adsorbed on the electrode [20]. In this sense, polyelectrolytes have received particular attention as one way of attaching charged catalysts to the electrode surfaces in an extremely simple, efficient and rapid procedure [34,35]. In addition to the ability in preparing modified electrodes with thin films of ion-exchanger polymers, it has proportionate an excellent method to examine the kinetics of self-exchange redox reactions [36]. In this way, poly-L-lysine has been used due to the ability to form films containing electrostatically bound complexes [37].

Film coating of PLL is quite stable and they provide a surface coating that remains polycationic at pH values as high as 10. This characteristic has been exploited to the incorporation of stable redox couples in PLL polyelectrolyte coatings [38–41].

Protonated PLL undergoes a very extensive swelling in aqueous electrolytes to produce films with relatively large separations between the polymer chains. This feature accentuates the role of the reactants that are dissolved in the solution occupying the empty spaces within the swollen film. However, the presence of two phases in the PLL film assure a minor contact between the supporting electrolyte in the film and the electroactive compound present in the “Donnan domain” [42].

Based on these aspects, the development of a sensor for 4-nitrophenol determinations incorporating LiTCNE at glassy carbon electrode using a poly-L-lysine film is discussed. The performance of the modified electrode for practical purpose was also investigated.

2. Experimental

2.1. Chemical and solutions

All used chemical were analytical grade reagent. Lithium tetracyanoethylenide (LiTCNE) was obtained by synthesis of TCNE (Aldrich, Steinheim, Germany) and LiI (Merck, Darmstadt, Germany), according to literature [43].

Poly-L-lysine hydrochloride (PLL) and citric acid were acquired from Sigma, St. Louis, USA. 4-Nitrophenol was purchased from Merck, Darmstadt-Germany. Monopotassium phosphate (KH_2PO_4) and disodium phosphate (Na_2HPO_4) were acquired from Synth, São Paulo, Brazil and sodium acetate and acetic acid were supplied from Nuclear, São Paulo, Brazil.

The solutions were prepared with water purified in Milli-Q Millipore system and the actual pH of the buffer solutions were determined with a Corning pH/Ion Analyser model 350.

2.2. Construction of the sensor

A glassy carbon (GC) electrode acquired from Metrohm-Switzerland, with geometrical area of 0.071 cm^2 (3 mm diam) was used for sensor construction. Prior to the modification, the electrode surface was treated, according to the procedure described by Zhu and Na-Qiang [44].

After cleaning the electrode, 20 μl of an acetonitrile solution LiTCNE of a determined concentration was put onto a surface of the GC electrode and after drying at room temperature, 20 μl of a PLL solution in a determined concentration was added. The addition of PLL gave film with good adherence to the surface.

In order to evaluate the influence of LiTCNE concentration on the sensor response, seven different concentrations were investigated: 0.95, 1.20, 1.45, 1.95, 2.90, 3.86 and 4.85 $mmol\,l^{-1}$, using a fixed PLL solution 24.50 $\mu mol\,l^{-1}$. Finally, to verify the influence of PLL concentration on the sensor response, seven solutions containing the poly-L-lysine in concentration of 20.40, 24.60, 28.60, 34.70, 40.80, 51.00 and 61.20 $\mu mol\,l^{-1}$ were tested in the presence of 1.95 $mmol\,l^{-1}$ of LiTCNE.

2.3. Voltammetric measurements

The voltammetric measurements using differential pulse voltammetry were carried out with a potentiostat PGSTAT10 Model from Autolab Echo Chemie (Utrecht, Netherlands), using an electrochemical cell with three electrodes: a saturated calomel electrode (SCE) as reference, a Pt wire as auxiliary and the modified GC with 3 mm diam as working electrode. The measurements were carried out without stirring, using 5.0 ml of buffer solution. Oxygen in the system was removed by bubbling nitrogen through the solution. The optimized parameters in DPV were set up as follow: scan rate: 0.1 $V\,s^{-1}$; pulse amplitude: 0.05 V and for all measurements were used, a pulse period of 0.5 s, except for the scan rate study.

3. Results and discussion

3.1. Imobilization of LiTCNE on the electrode surface

Initially, LiTCNE was adsorbed on the electrode surface. After this step, successive cyclic voltammograms were performed in a potential range between 0 and −1 V. After twenty cycles, a decrease of about 50% in the peak current was observed, indicating that LiTCNE leaches out from the electrode surface. In this sense, in order to graft LiTCNE on the electrode surface in a stable way, a PLL polyelectrolyte was used.

Therefore, an experiment was also performed in order to test the response of the GC electrode modified with LiTCNE/PLL film and PLL only (Fig. 1). As can be observed, for a PLL modified electrode, only a charging current always flows, since the potential is continuously changing. This result is attributed to the electrical double layer present in electrode-solution interface. On the other hand, when the PLL film was doped with LiTCNE compound an irreversible wave was observed in a cathodic sweep. This irreversible wave show a beginning around the same potential that the 4-NP reduction on the bare electrode.

3.2. Stability of LiTCNE/PLL modified electrode

LiTCNE/PLL modified electrode stability was checked performing successive cyclic voltamograms. The variation of the peak current was evaluated as the relative standard deviation (R.S.D.). After twenty cycles was observed an R.S.D. lower than 2%, suggesting a good stability, probably due to the ability of PLL in fixing LiTCNE on the electrode surface. On the other hand, have been related in the literature that metal tetracyanoethylenide anion-radical ($TCNE^-$) is quite sensitive to oxygen and, in a much lesser degree, to water [43]. Based on these aspects, it can be affirmed that the PLL act as a protective membrane to LiTCNE. In this sense, the reaction of LiTCNE with the water in the modified electrode is extremely low, and it is possible to use this electrode for long time, i.e., at least three months.

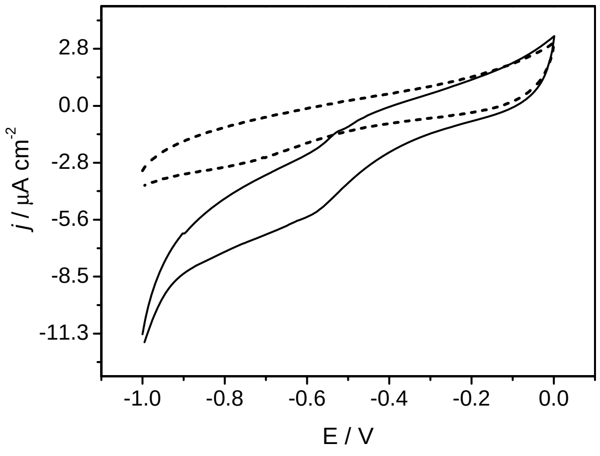

Fig. 1. Cyclic voltammograms of the LiTCNE/PLL modified electrode (—) and bare GC (. . .) in 0.1 mol l^{-1} MackIlvaine buffer pH 4.5. Scan rate: 0.05 V s^{-1}; [LiTCNE] = 1.20 mmol l^{-1} and [PLL] = 24.50 μmol l^{-1}.

Table 1
Influence of the [LiTCNE] used on the preparation film on the peak current density obtained with the sensor for 5 μmol l^{-1} 4-NP in Mackllvaine buffer solution (pH 4.5) and 24.5 μmol l^{-1} PLL

[LiTCNE]/(mmol l^{-1})	j_p/(μA cm^{-2})
0.95	1.042
1.20	1.268
1.45	1.479
1.95	1.521
2.90	1.479
3.86	1.465
4.85	1.451

Scan rate: 0.02 V s^{-1}.

3.3. Influence of the amount of LiTCNE and PLL in the sensor response

As far as the electrode conditions are concerned, the amount of LiTCNE and PLL is a control factor of great importance. In Table 1, are listed the response for 4-NP obtained for different concentration of the LiTCNE used in the sensor preparation. The results shown in Table 1 indicate that the best response was obtained using 1.95 mmol l^{-1} of lithium tetracyanoethylenide concentration solution. The membrane with a LiTCNE concentration lower than 1.95 mmol l^{-1} presented a lower response, probably due to the lower amount of lithium tetracyanoethylenide compound on the electrode surface. On the other hand, for concentration higher than 1.95 mmol l^{-1} of the compound, the sensor response was diminished due to a poor adherence of the poly-L-lysine film on the electrode surface. Additionally, the membrane obtained was not uniform and the response was not stable. Based on these aspects, the membrane prepared with concentration of 1.95 μmol l^{-1} was chosen as giving the best sensor performance, assuring that the compound is homogeneously dispersed on the film.

The influence of the PLL concentration on the sensor response was also investigated (Table 2). The results clearly show that the best response is obtained with the electrode modified with a 28.6 μmol l^{-1} PLL solution. The peak current values increase with the PLL solution from 20.4 up to 28.6 μmol l^{-1}. This behavior was attributed to the leach out of the LiTCNE compound of the electrode surface due to the PLL concentration used is insufficient to complex immobilization. However, the use of PLL concentration larger than 28.6 μmol l^{-1} result in a lower response, probably due to the barrier generated by the polymer film between the LiTCNE in the electrode surface and 4-NP in a bulk solution.

Table 2
Influence of the PLL concentration used on the preparation film on the peak current density. [LiTCNE] = 1.95 mmol l^{-1} in the same conditions of Table 1

[PLL]/(μmol l^{-1})	j_p/(μA cm^{-2})
20.40	0.958
24.50	1.535
28.60	2.085
34.70	1.958
40.80	1.338
51.00	1.197
61.20	1.225

The sensors prepared in this way allowed to obtain uniform films, good signals, repeatability and stability.

3.4. Voltammetric behavior of 4-Nitrophenol

As can be seen in the Fig. 2, a significant increasing in of the cathodic current peak was observed at the modified electrode due to the modifier film act as promoter to enhance the electrochemical reaction. The increasing peak current was about four times as the peak current measured at bare GC electrode. This result can be explained that when R–NHOH is formed on the modified electrode it remains fixed in LITCNE/PLL film, whereas it diffuse away from the bare GC [21]. A well-defined differential cathodic peak placed at −0.7 V versus SCE, corresponding to the reduction process of 4-nitrophenol on the LITCNE/PLL modified electrode. This behavior suggests that the LiTCNE compound is working as catalyst to reduce 4-NP on the sensor surface.

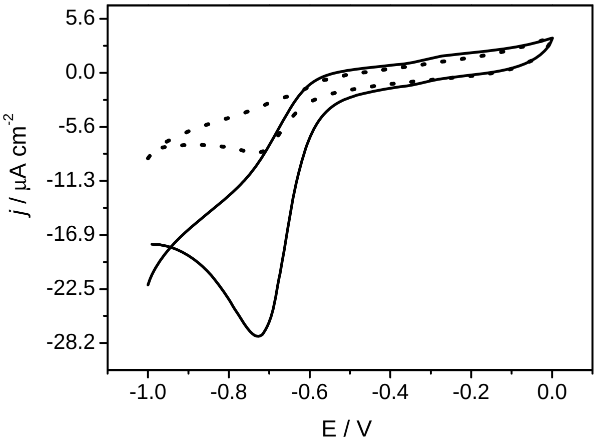

Fig. 2. Cyclic voltammetry response of 13 μmol l^{-1} 4-NP at modified electrode (—) and bare GC (. . .) in 0.1 mol l^{-1} MackIlvaine buffer at pH 4.5. Scan rate: 0.1 V s^{-1}; [4-NP] = 13 μmol l^{-1}, [LiTCNE] = 1.20 mmol l^{-1}, and [PLL] = 24.50 μmol l^{-1}.

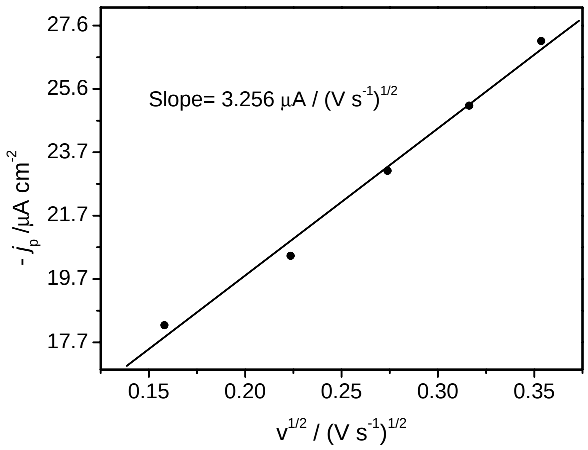

Fig. 3. Relation between peak current density and scan rate for 13 μmol l^{-1} 4-NP obtained by cyclic voltammetry at modified electrode in 0.1 mol l^{-1} MackIlvaine buffer pH 4.5. Scan rate: 0.025, 0.05, 0.075, 0.100, and 0.125 V s^{-1}; [LiTCNE] = 1.20 mmol l^{-1} and [PLL] = 24.50 μmol l^{-1}.

More detailed studies of peak current were made by cyclic voltammetry to obtain new insights to the 4-NP reduction on the sensor surface. In a first step, the plot of peak current density (j_p) versus square root of the potential scan rate ($\nu^{1/2}$) (Fig. 3), results in a straight line, suggesting that the process is similar to those controlled by diffusion in the studied range. Using the slope of this plot was possible to determine the number of electrons (n) involved in the reduction of 4-NP at the modified electrode. As can be seen in Fig. 2 cyclic voltammetry of 4-NP presents only cathodic peak in the investigated potential range. This behavior is typical of totally irreversible systems [43]. Assuming an irreversible reduction of 4-NP on the modified electrode the following equation was used [45]:

$$j_p = (2.99 \times 10^5)\, n\, (\alpha n_a)^{1/2} C_o^* D_o^{1/2} \nu^{1/2} \qquad (1)$$

where j_p is the peak current density, n the number of total electrons involved in the reaction, α is the electron transfer coefficient, n_a the number of electrons involved in the rate-determining step, "D_o" is the diffusion coefficient of the electroactive species ($cm^2\,s^{-1}$), C_o* ($mol\,cm^{-3}$) is the concentration of the electroactive species ν is the potential scan rate.

Values of αn_a were calculated for the irreversible reduction of 4-NP, according to Eq. (2) $\alpha n_a = 47.7/(E_p - E_{p/2})$ [45]. The value of αn_a at the modified electrode was obtained as 0.95, utilizing a concentration of 4-NP of 13 μmol l^{-1} and diffusion coefficient of 9.19×10^{-6} $cm^2\,s^{-1}$ [46]. The number of total electrons calculated was about 3.93, suggesting an electron transfer mechanism of four electrons for the electrocatalytic reduction of 4-NP. This value is according to these determined by others researchs [47–49].

After that, in order to verify the chemical order of protons of the electro-reduction of 4-NP an analysis of the dependence of E_p (peak potential) versus pH was performed (Fig. 4).

This applied method is based on previous studies on the electrochemical proprieties of nitro-substituted compounds and it demonstrated that in moderately acidic media, the nitro-aromatic compounds are reduced in a four electron and four proton process to the hydroxylamine [49].

$$R\text{–}NO_2 + e^- \rightarrow R\text{–}NO_2^- \ \text{(slow)} \qquad (2)$$

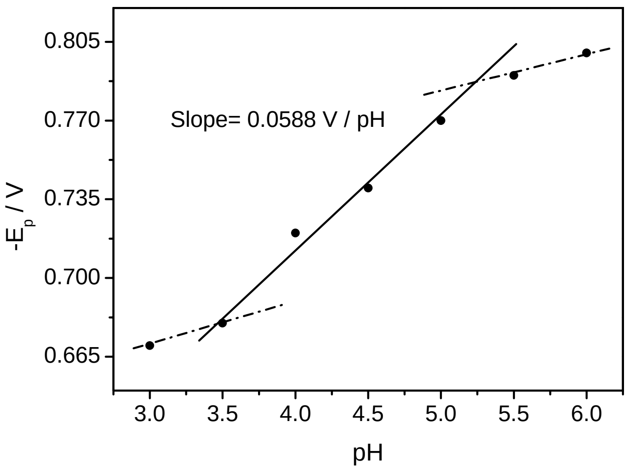

Fig. 4. Influence of pH on the peak potentials for 5 μmol l^{-1} 4-NP obtained by DPV in Mackllvaine buffer solution 0.1 mol l^{-1}. Scan rate: 0.02 V s^{-1}; [LiTCNE] = 1.20 mmol l^{-1} and [PLL] = 24.50 μmol l^{-1}.

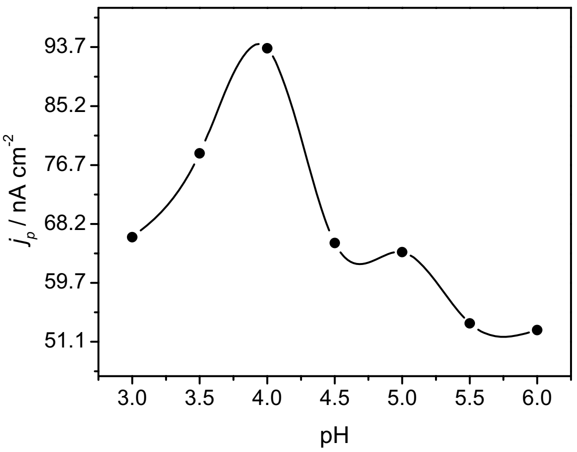

Fig. 5. Influence of pH on the sensor response for 5 μmol l^{-1} 4-NP obtained by DPV measurements carried out in 0.1 mol l^{-1} MackIlvaine buffer (pH 4.5). Scan rate: 0.02 V s^{-1}; [LiTCNE] = 1.20 mmol l^{-1} and [PLL] = 24.50 μmol l^{-1}.

$$\text{R–NO}_2 + 3e^- + 4\text{H}^+ \rightarrow \text{R–NHOH} + \text{H}_2\text{O (fast)} \qquad (3)$$

According to the second step, the concentration of the hydrogen ion (proton) will affect the rate of the reaction. The hydroxyl group gradually dissociates and shifts the peak potential to ward more negative value increasing pH [49].

Usually in water the transference of proton from or toward organic molecule is considered fast, meaning that protons are in equilibrium in solution near to the electrode [50] justifying this investigation. The linear correlation obtained in the pH 3,5 up to 5,0 showed a slope of 0.0588 V/pH (Fig. 4). This slope is close to that expected for a monoelectronic/monoprotonic electrode reaction which is 0.0592 V/pH at 25 °C. On the other hand the number of electrons determined in the reduction of 4-nitrophenol in this work was four electrons. In this sense, there is only one possibility for pH between 3.5 and 5.0. The number of proton involved in this process should be four, or 0.0592 (n_p/n_e) V/pH where n_p and n_e involved in the electrode process ($n_p = n_e = 4$) [51,52]. In order to use the modified electrode to 4-NP determination the optimization of the analytical procedure a systematic study of the experimental parameters that affect the DPV response, namely, the pH of the medium, type of buffer, the concentration of the buffer solution, scan rate (ν) and amplitude (a) was made.

3.5. Influences of pH, buffer solution and buffer concentration

In a first step, the effect of pH on electrode response was investigated. Fig. 5 shows the influence of the solution pH in the electrochemical response of 4-NP using the MackIlvaine buffer. The current and potential of the peak depend on the solution pH. The peak current density increased with pH in the range from 3.0 up to 4.0. and in pH 4.0, the peak current density gives a maximum peak. A decrease in the current is observed when the solution pH is higher than 4.0. Thus, the optimum pH for further studies was fix in 4.0.

The influence of the buffer solution on the sensor response was tested in four different buffer solutions (MackIlvaine, acetate, citrate and succinate) with concentrations of 0.1 mol l^{-1} and indicated that acetate buffer solutions gives the best responses, according to the results showed in Table 3.

Finally, Table 4 shows the results obtained for the measurements carried out in different concentrations of acetate. Acetate buffer concentrations of 0.10, 0.25 and 0.50 mol l^{-1} presented almost constant current density. In this sense, was chosen the concentration of 0.1 mol l^{-1}.

Table 3
Influence of the 0.1 mol^{-1} buffer solution in the sensor current density obtained by DPV for 5 μmol l^{-1} 4-NP

Buffer	j_p/(μA cm^{-2})
Succinate	1.015
Acetate	1.389
Citrate	1.179
Mackllvaine	1.282

Scan rate: 0.02 V s^{-1}. [LiTCNE] = 1.20 mmol l^{-1}; [PLL] = 24.50 μmol l^{-1}.

Table 4
Influence of the acetate buffer concentration on the peak current density obtained by DPV with the sensor for 5 μmol l^{-1} 4-NP

Buffer/(mol l^{-1})	j_p/(μA cm^{-2})
0.025	1.111
0.05	1.303
0.10	1.384
0.25	1.389
0.50	1.423

Scan rate: 0.02 V s^{-1}. [LiTCNE] = 1.20 mmol l^{-1}; [PLL] = 24.50 μmol l^{-1}.

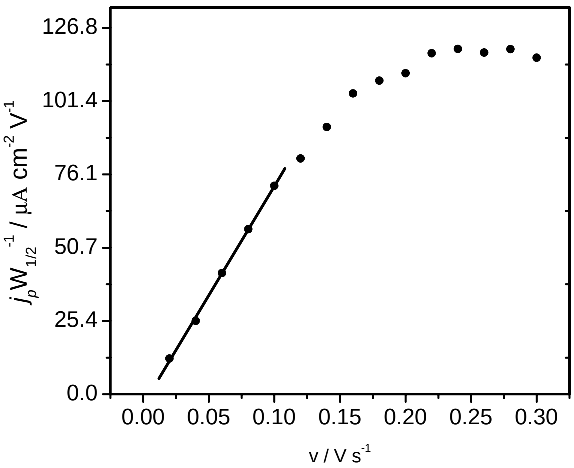

Fig. 6. Dependence of the peak current density/peak half width ratio with the DPV scan rate for experiments carried out under the following conditions: [4-NP]= 2.5 μmol l^{-1} in acetate buffer (pH 4.0); [LiTCNE] = 1.95 mmol l^{-1}, [PLL] = 28.60 μmol l^{-1}.

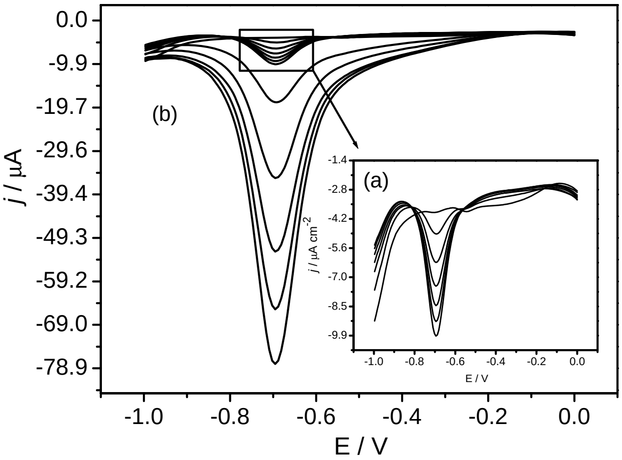

Fig. 7. DPV for the electro-reduction of 4-NP obtained in optimized conditions for concentration range between 27 and 2170 nmol l^{-1} (a) and 4490–23200 nmol l^{-1}(b). Scan rate 0.1 V and potential amplitude 0.05 V.

3.6. Influence of the potential scan rate (v) and potential pulse amplitude (a)

The effect of the scan rate on the differential pulse voltammetric response of the glassy carbon electrode modified with LiTCNE and PLL in acetate buffer solution is shown in Fig. 6. The peak current/peak half width ratios (j_p $W_{1/2}^{-1}$/μA cm^{-2} V^{-1}) values presented a linear increase with the scan rate from 0.02 up to 0.1 V s^{-1} as observed in this figure. On the other hand, when the scan rate is higher than 0.1 V s^{-1}, the increase of the peak current value was accompanied by broadening and distortion of the peaks. From these results, scan rate of 0.1 V s^{-1} was chosen, as it led to the best voltammetric profile with higher sensitivity and subsequently used throughout the present study. The current values of peak was also found to vary with pulse amplitude (0.01–0.15 V) applied in the DPV voltammetry at a scan rate of 0.1 V s^{-1} for a glassy carbon electrode modified with LITCNE/PLL. However, the use of potential pulse amplitude larger than 0.05 V led to an increase in the values of capacitive current. In this sense, the better voltammetric sensitivity was obtained for a potential pulse amplitude of 0.05 V and, therefore, this value was chosen for furthers studies.

3.7. Analytical characterization

In order to obtain an analytical curve for the developed sensor were carried out differential pulse voltammograms for reduction of 4-NP at different concentrations in 0.1 mol l^{-1} acetate buffer at pH 4.0 after the optimization of the experimental parameters (Fig. 7). Under optimized conditions the proposed sensor showed a typical linear response range from 27 up to 23200 nmol l^{-1}, which can be expressed according to the following equation:

$$\frac{j_{\mathrm{p}}}{\mathrm{nA}} = 25(\pm 13) + 3.057(\pm 0.001) \times [4 - \mathrm{Nitrophenol}]\,\mathrm{per}\,(\mathrm{nmol}\,l^{-1}) \quad (4)$$

with a correlation coefficient of 0.999 (for $n = 12$) and better sensitivity than those reported by others researches [21,50,53]. Such good sensitivity can be attributed to the efficiency of electron transfer between the LiTCNE and the phenol compound.

A detection limit of 7.5 nmol l^{-1} was determined using a 3σ/slope ratio and quantification limit was 25.0 nmol l^{-1}, where σ is the standard deviation of the mean value for ten voltammograms of the blank, calculated, according to the IUPAC [53] recommendations. The response range and detection limit presented by this sensor for 4-NP determination was better than those reported in the literature [54–61].

Constructing ten sensors and determining the peak current obtained for each one, the repeatability in the construction of sensor was evaluated. The repeatability expressed as the relative standard deviation (R.S.D.) was 4.4% for $n = 10$. This result indicates a good repeatability in the sensor construction possibly due to strong adsorption of the LiTCNE and PLL in the electrode surface.

3.8. Application to samples

This method was applied for 4-NP determination in three water samples (A, B and C). No signal for 4-NP was observed when the samples B was analyzed, probably the 4-NP level was below of the detection limit, however, for samples A and C was determined a value of 1.27 (± 0.01) × 10^{-7} and 6.86 (± 0.02) × 10^{-8} mol l^{-1}, rescpectively. The concentration of 4-NP were determined using the standard addition method. Results suggest that the method is very effective for the determination of very low levels of 4-NP.

Table 5
Addition and recovery of 4-nitrophenol in three water samples ($n = 3$)

Samples	4-NP added ($mol\,l^{-1}$)	4-NP expected ($mol\,l^{-1}$)	4-NP found ($mol\,l^{-1}$)	Recovery (%)
A	0.0	–	$1.27\ (\pm\ 0.01) \times 10^{-7}$	–
	1.0×10^{-7}	2.27×10^{-7}	$2.23\ (\pm\ 0.03) \times 10^{-7}$	101.1 (± 0.7)
B	0.0	–	nd[a]	–
	$1\ 0 \times 10^{-7}$	1.0×10^{-7}	$1.20\ (\pm\ 0.01) \times 10^{-7}$	103.0 (± 1.0)
C	0.0	–	$6.86\ (\pm\ 0.02) \times 10^{-8}$	–
	1.0×10^{-7}	1.69×10^{-7}	$1.77\ (\pm\ 0.01) \times 10^{-7}$	105.0 (± 0.3)

[a] Non detected.

3.9. Recovery tests

For an additional check on the accuracy of the developed method and the interference of the matrices, analytical recovery experiments were performed by adding known amounts of 4-nitrophenol in three water samples in triplicate. The percentage of the recovery values were calculated by comparing the concentration obtained from the samples with actual and added concentrations. The recoveries for the water samples are shown in Table 5. It can be clearly observed that there is no influence of the matrices on the developed sensor.

4. Conclusions

This work demonstrated that glassy carbon electrode modified with Litcne/PLL is a feasible alternative for the analytical determination of 4-NP. The reduction of this compound on the modified electrode occurs in an irreversible manner. Optimization of the experimental conditions for differential pulse voltammetry yielded a detection limit for 4-NP of $7.5\,nmol\,l^{-1}$ much better than that described in the literature and this sensor showed a wide linear response range, good sensitivity and repeatability. The sensor was successfully applied in water samples from lake and river.

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