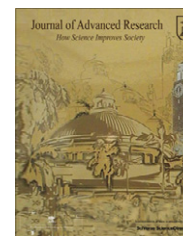Cairo University

Journal of Advanced Research

ORIGINAL ARTICLE

Kinetics of the electropolymerization of aminoanthraquinone from aqueous solutions and analytical applications of the polymer film

Shymaa S. Medany, Khaled M. Ismail, Waheed A. Badawy *

Chemistry Department, Faculty of Science, Cairo University, 12 613 Giza, Egypt

Abstract Poly 1-amino-9,10-anthraquinone (PAAQ) films were prepared by the electropolymerization of 1-amino-9,10-anthraquinone (AAQ) on platinum substrate from aqueous media, where 5.0×10^{-3} mol L^{-1} AAQ and 6.0 mol L^{-1} H_2SO_4 were used. The kinetics of the electropolymerization process was investigated by determining the change of the charge consumed during the polymerization process with time at different concentrations of both monomer and electrolyte. The results have shown that the process follows first order kinetics with respect to the monomer concentration. The order of the reaction with respect to the aqueous solvent i.e. H_2SO_4 was found to be negative. The polymer films were successfully used as sensors for the electroanalytical determination of many hazardous compounds, e.g. phenols, and biologically important materials like dopamine. The electroanalytical determination was based on the measurements of the oxidation current peak of the material in the cyclic voltammetric measurements. The cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1} and different analyte concentrations. A calibration curve was constructed for each analyte, from which the determination of low concentrations of catechol and hydroquinone (HQ) as examples of hazardous compounds present in waste water

* Corresponding author. Tel.: +20 2 3567 6558; fax: +20 2 3568 5799.
E-mail addresses: wbadawy@cu.edu.eg, wbadawy50@hotmail.com (W.A. Badawy).

Production and hosting by Elsevier

and also for ascorbic acid and dopamine as examples of valuable biological materials can be achieved.

Introduction

Electropolymerization is a good approach to prepare polymer-modified electrodes by adjusting the electrochemical parameters that control film thickness, permeation and charge transport characteristics. 1-amino-9,10-anthraquinone (AAQ) was electropolymetized in non-aqueous medium (acetonitrile containing $LiClO_4$ as supporting electrolyte) by scanning the potential between -0.5 and $+1.8$ V (vs. Ag/AgCl/3.0 M KCl) [1], and in aqueous electrolyte (H_2SO_4) in the potential range 0.0–1.3 V against the same reference [2]. The poly-aminoanthraquinone films (PAAQ) prepared in non-aqueous solutions were found to be more stable in organic solvents than in aqueous solutions. The PAAQ films prepared in aqueous electrolytes were found to be more stable in aqueous acidic electrolytes and suffer from degradation in non-aqueous media. The presence of quinine units in the polymer chain suggests promising application in rechargeable batteries, electronic display devices, electrocatalytic processes, biosensors and corrosion protection. The elegant integration of selectivity, sensitivity and built-in transduction function in conducting polymers makes them ideal candidates as sensitive layers in chemical and biological sensors. Polymer-modified electrodes have many advantages in the detection of analytes because of high selectivity, sensitivity and homogeneity in electrochemical deposition, strong adherence to the electrode surface and chemical stability of the polymer film [3,4].

Dopamine is an important neurotransmitter in the central nervous system. Low level of dopamine is related to neurological disorders such as Parkinson's disease, schizophrenia and to HIV infection [5,6]. In recent years, the determination of dopamine is carried out using polymer-modified electrodes [7–9]. Ascorbic acid is a vital vitamin in human diet and is very popular for its antioxidant properties. It has been used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS [10]. It is present in many biological fluids, juices, soft drinks, pharmaceutical formulations and many analytical aspects related to ascorbic acid as analyte have attracted a great deal of attention [11]. Electrodes modified with conducting polymers have been used for the determination of the ascorbic acid. Such electrodes are easy to prepare with the desirable film thickness and are stable enough to be used as electroanalytical sensor [8,9,12].

Phenolic compounds are a class of polluting chemicals which when absorbed through the skin and mucous membranes can cause damage to the lungs, liver, kidney and genitor urinary tract in living bodies [13]. They are widely used in wood preservatives, textiles, herbicides and pesticides, and released into the ground and surface water. The identification and quantification of these compounds represent an important issue in environmental monitoring. Hydroquinone (HQ) and catechol (CC) are two phenolic compounds, which present as contaminants in medical, food and environmental matrices. Different methods have been established for their determination, including liquid chromatography [14], synchronous fluorescence [15], chemiluminescence [16], spectrophotometry [17], gas chromatography/mass spectrometry [18] and pH based-flow injection analysis [19]. Some of these methods are time-consuming and of low sensitivity with complicated pretreatments and also expensive. Electrochemical methods provide an easy and fast alternative for the analysis of such materials [20,21].

In the field of electropolymerization two subjects seem to be of great importance. The first is the study of the electropolymerization kinetics [8–13], which provides information about the nature of the reactions taking place at the electrode surface and the chemical structure of the polymer film beside the ways to improve its physical properties. The second is the potential use of these modified electrodes as sensors for qualitative and quantitative analyses of hazardous and biologically active compounds [7–10,13,22]. In this paper we are reporting on the kinetics of electropolymerization of AAQ from aqueous electrolytes. It is also aimed at the use of the prepared PAAQ films as sensors for the quantitative determination of some hazardous compounds like catechol and hydroquinone and also some biologically important compounds like ascorbic acid and dopamine. In this respect chronoamperometry and cyclic voltammetry are mainly used.

Experimental

AAQ (Merck) was used as monomer without further purification. Ascorbic acid, catechol, dopamine, hydroquinone, sulfuric acid and other chemicals were analytical grade reagents and the solutions were prepared using triply distilled water.

A standard three electrode all-glass cell was used as the electrochemical cell. The working electrode is a platinum rotating disk of a constant geometrical area of 0.071 cm^2. Gold and glassy carbon disks with the same area were also investigated and no significant difference was recorded. A silver/silver chloride (Ag/AgCl/3.0 mol L^{-1} KCl) was used as reference electrode and a platinum wire as the counter electrode. Before each experiment the working electrode was polished mechanically with alumina powder down to 1.0 μm diameter, washed with triply distilled water and then rubbed against a smooth cloth. All electrochemical measurements were carried out using the Zahn Elektrik electrochemical work station (Kronach–Germany). The experiments were carried out at room temperature (25 ± 1 °C) and the potentials were measured against and referred to the silver/silver chloride reference electrode ($E° = 0.2225$ V vs. nhe). To achieve acceptable reproducibility, each experiment was carried out at least three times. Details of experimental procedures are as described elsewhere [2].

Results and discussion

Kinetics of the electropolymerization process

The study of the reaction order with respect to the monomer and the electrolyte in the electropolymerization process is an

important issue where it provides information about the nature of reactions taking place at the electrode/electrolyte interface, the chemical structure of the formed film and the way to improve its physical properties e.g. its electrical conductivity.

Assuming that the polymerization follows the following equation:

$$M + E \rightarrow P$$
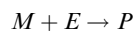
where M is the monomer, E is the electrolyte and P is the polymer, then the kinetic equation can be formulated as:

$$R_p = d[W]/dt = k[E]^a[M]^b \qquad (1)$$

where R_p is the polymerization rate which represents the electrogenerated polymer weight, W, per unit time, per cm^2 of the electrode surface, a and b are the reaction orders with respect to the electrolyte and monomer, respectively, and k is the specific rate constant of the polymerization process.

Electropolymerization data provide kinetic parameters on the assumption that only charge transfer reaction is taking place at the electrode surface. From the synthesis of the I–t transients the polymerization charge density (Q, mC cm^{-2}) can be evaluated by the integration of the corresponding chronoamperograms, when the electrolyte or the monomer concentration was varied [23–26]. If the electrogenerated polymer is the only species produced, the charge consumed during the electropolymerization process (Q) should be proportional to the weight of the electrogenerated polymer, W, i.e.

$$Q = kW \qquad (2)$$

The charge consumed, the electrolyte concentration and the monomer concentration can be correlated together by the following equation:

$$dQ/dt = d[W]/dt = R_p = [E]^a[M]^b \qquad (3)$$

or expressed in logarithmic form as

$$\log dQ/dt = \log k + a \log[E] + b \log[M] \qquad (4)$$

For the electropolymerization of AAQ in aqueous solutions, the kinetic equation can be represented by:

$$R_p = k[\text{AAQ}]^a[\text{H}_2\text{SO}_4\,aq]^b$$

AAQ and sulfuric acid concentrations were varied keeping one of them constant to evaluate their respective reaction orders. The AAQ concentration was varied from 3.5 to 5.0×10^{-3} mol L^{-1} at a constant 6.0 mol L^{-1} H$_2$SO$_4$ concentration. Then, the H$_2$SO$_4$ concentration was varied from 5.5 to 6.5 mol L^{-1} at a constant AAQ concentration of 5.0×10^{-3} mol L^{-1}. The applied potential was $+1.1$ V and the polymerization time was varied between 2 and 780 s.

Fig. 1a presents the polymerization charge versus time plots corresponding to the PAAQ formation from a constant 6.0 mol L^{-1} H$_2$SO$_4$ concentration and varying AAQ monomer concentrations. The log dQ/dt versus log [AAQ] relation is presented as insert in this figure. The slope of the linear relation was found to be 1.01 which means that the polymerization reaction is first order with respect to AAQ. Fig. 1b shows the effect of the change of H$_2$SO$_4$ concentration on the polymerization charge at a constant concentration AAQ. The plot of log dQ/dt against log [H$_2$SO$_4$] is presented as insert in this figure. The linear relation has a negative slope of -0.66. Such a negative order implies that sulfuric acid inhibits the polymerization reaction [27–29]. Such inhibition of the polymerization process has reflected itself on the activity of the formed polymer film. The kinetic equation of the polymerization process is therefore,

$$R_p = k[\text{AAQ}]^{1.01}[\text{H}_2\text{SO}_4\,aq]^{-0.66}$$

Electroanalytical applications

The cyclic voltammograms of the electrochemical oxidation of 1.0×10^{-2} mol L^{-1} ascorbic acid in a background solution of 0.1 mol L^{-1} sodium citrate/0.1 mol L^{-1} NaH$_2$PO$_4$ and dopamine in 0.1 mol L^{-1} H$_2$SO$_4$ on both the bare Pt electrode and the PAAQ modified electrode prepared from aqueous media in the potential range $+0.3$ to $+0.9$ V are presented in Figs. 2 and 3, respectively. It is clear that the modified electrode has remarkable response to the oxidation
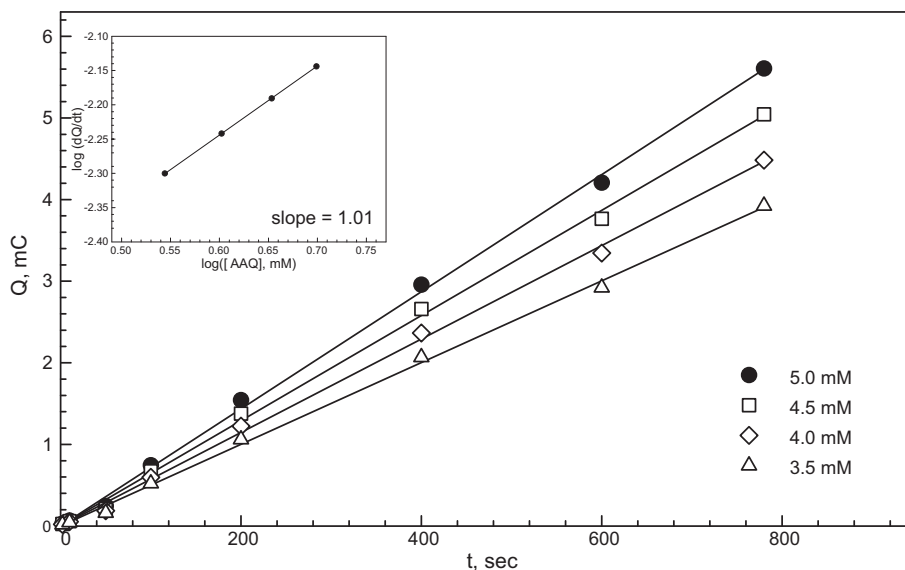

Fig. 1a Polymerization charge vs. time as a function of AAQ concentration at 1.1 V and 25 °C. The inset presents log dQ/dt vs. log [AAQ] linear relation.
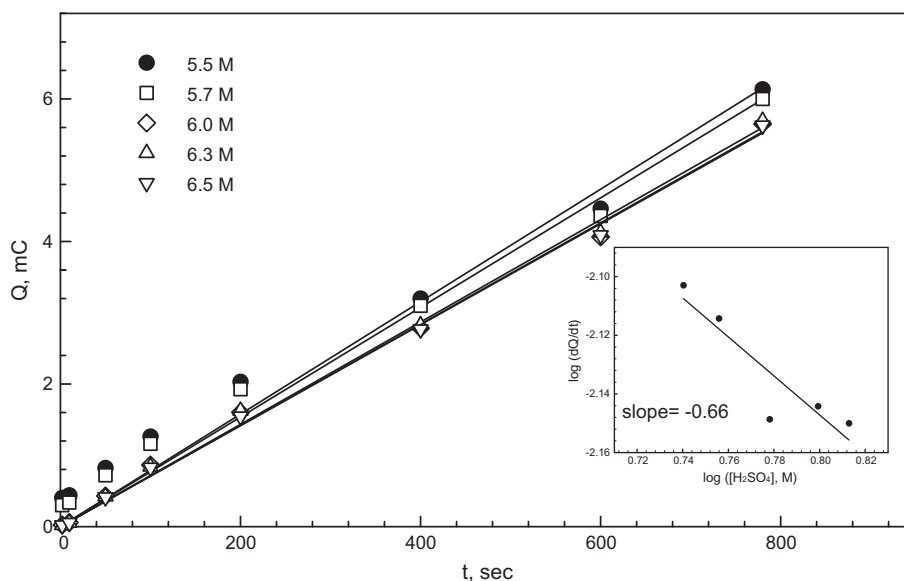
Fig. 1b Polymerization charge vs. time as a function of H_2SO_4 concentration at 1.1 V and 25 °C. The inset presents log dQ/dt vs. log $[H_2SO_4]$ linear relation.
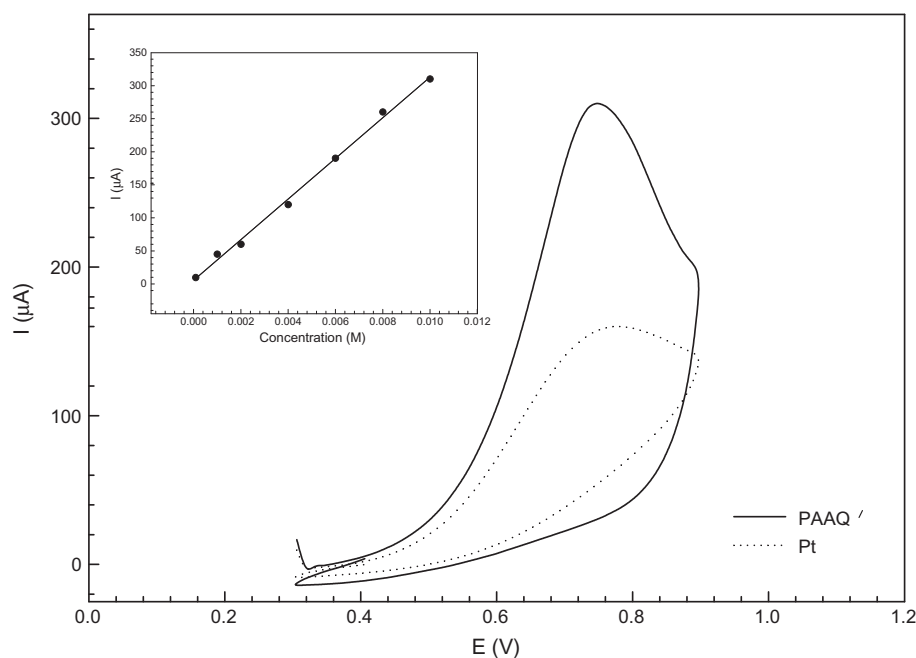

Fig. 2 Cyclic voltammograms of the electrochemical oxidation of 1.0×10^{-2} mol L^{-1} ascorbic acid in a background solution of 0.1 mol L^{-1} sodium citrate/0.1 mol L^{-1} NaH_2PO_4 at pH 7 on both the bare Pt electrode and PAAQ modified electrode prepared from aqueous medium in the potential range between $+0.3$ and $+0.9$ V at a scan rate of 100 mV s^{-1} and 25 °C. (insert) Calibration curve for the electroanalytical determination of ascorbic acid on the PAAQ modified electrode prepared from aqueous media (the concentration was varied between 1.0×10^{-5} and 1.0×10^{-2} mol L^{-1} at pH 7 and 25 °C.

of ascorbic acid and dopamine compared to the bare Pt electrode. Definite anodic peaks with a peak current of 310.1 and 413.4 μA were recorded for ascorbic acid and dopamine, respectively. Beside the decrease in the overpotential of the oxidation process which is reflected in a lower value of the peak potential, a large increase in the peak current corresponding to the oxidation reaction was

recorded. The electrode was found to be sensitive for the change in the concentration of the analyte, and the anodic peak current increases with the increase of the concentration of the material. A linear relation was obtained on plotting the value of anodic peak current as a function of the analyte concentration, where the concentration was varied between 1.0×10^{-5} and 1.0×10^{-2} mol L^{-1}. This linear relation
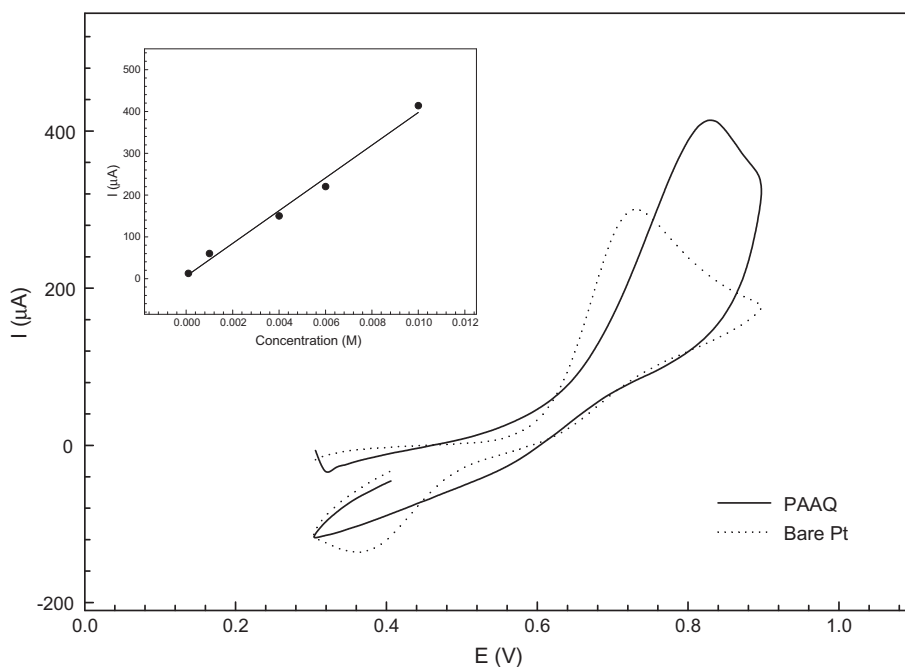
Fig. 3 Cyclic voltammograms of the electrochemical oxidation of 1.0×10^{-2} mol L^{-1} dopamine at pH = 1.0, adjusted by H$_2$SO$_4$ additions, on both the bare Pt electrode and PAAQ modified electrode prepared from aqueous medium in the potential range between $+0.3$ and $+0.9$ V at a scan rate of 100 mV s^{-1} at 25 °C. (insert) Calibration curve for the electroanalytical determination dopamine on the PAAQ modified electrode prepared from aqueous media (the concentration was varied between 1.0×10^{-5} and 1.0×10^{-2} mol L^{-1} at pH = 1.0, adjusted by H$_2$SO$_4$ additions, and 25 °C.
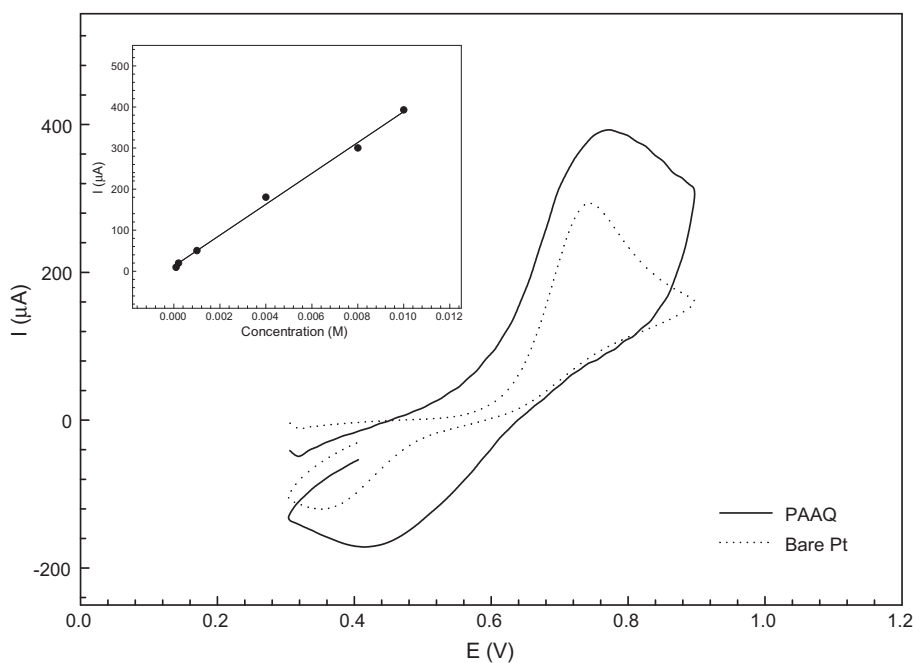

Fig. 4 Cyclic voltammograms of the electrochemical oxidation of 1.0×10^{-2} mol L^{-1} catechol at pH = 1.0, adjusted by H$_2$SO$_4$ additions, on both the bare Pt electrode and PAAQ modified electrode prepared from aqueous medium in the potential range between $+0.3$ and $+0.9$ V at a scan rate of 100 mV s^{-1} at 25 °C. (insert) Calibration curve for the electroanalytical determination of catechol on the PAAQ modified electrode prepared from aqueous media (the concentration was varied between 1.0×10^{-5} and 1.0×10^{-2} mol L^{-1} at pH = 1.0, adjusted by H$_2$SO$_4$ additions, and 25 °C.
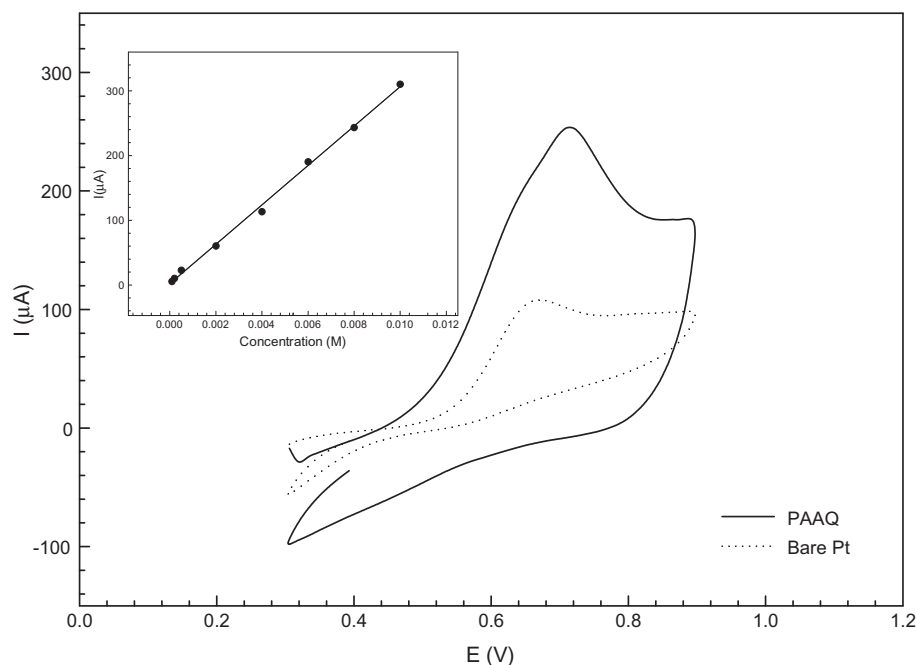
Fig. 5 Cyclic voltammograms of the electrochemical oxidation of 1.0×10^{-2} mol L^{-1} hydroquinone at pH = 1.0, adjusted by H$_2$SO$_4$ additions, on both the bare Pt electrode and PAAQ modified electrode prepared from aqueous medium in the potential range between $+0.3$ and $+0.9$ V at a scan rate of 100 mV s^{-1} and 25 °C. (insert) Calibration curve for the electroanalytical determination hydroquinone on the PAAQ modified electrode prepared from aqueous media (the concentration was varied between 1.0×10^{-5} and 1.0×10^{-2} mol L^{-1} at pH = 1.0, adjusted by H$_2$SO$_4$ additions, and 25 °C.

represents a calibration curve that can be used for the determination of unknown analyte concentration in the specified concentration range. The calibration curves for ascorbic acid and dopamine are presented as inserts in Figs. 2 and 3, respectively.

The two phenolic compounds, catechol and hydroquinone, are also detected and determined using the PAAQ modified electrode. Typical cyclic voltammograms of the electrochemical oxidation of 1.0×10^{-2} mol L^{-1} catechol and hydroquinone on bare Pt and the PAAQ modified electrodes are presented in Figs. 4 and 5, respectively. The values of the oxidation peak currents and the peak potential of the four different analytes on bare Pt and PAAQ modified electrode are presented in Table 1. The calibration curves for the determination of both catechol and hydroquinone in the concentration range 1.0×10^{-5} to 1.0×10^{-2} mol L^{-1} are constructed and presented as inserts in Figs. 4 and 5, respectively.

The lower limits of detection (LOD) and lower limits of quantization (LOQ) were calculated according to the following equations [30]:

$$LOD = 3 \times SD/slope$$
$$LOQ = 10 \times SD/slope$$

where SD is the standard deviation obtained from at least four different runs. The calculated values for each material at PAAQ modified electrode prepared in aqueous medium are presented in Table 2.

Table 1 Oxidation potentials and anodic peak current values for bare Pt and PAAQ modified electrode prepared in aqueous media for 1.0×10^{-2} mol L^{-1} of each of the tested compounds dissolved in 0.1 mol L^{-1} H$_2$SO$_4$ except for ascorbic acid in a background of 0.1 mol L^{-1} sodium citrate/0.1 mol L^{-1} NaH$_2$PO$_4$, scan rate = 100 mV s^{-1}, potential range between $+0.3$ and $+0.9$ V vs. Ag/AgCl/Cl$^-$, at (25 ± 1) °C.

Analyte	Bare Pt electrode		PAAQ modified electrode	
	E_{pa} (V)	I_{pa} (µA)	E_{pa} (V)	I_{pa} (µA)
Ascorbic acid	+0.774	160.1	+0.748	310.1
Catechol	+0.748	292.8	+0.774	392.7
Dopamine	+0.735	299.7	+0.826	413.4
Hydroquinone	+0.644	368.6	+0.683	406.9

Table 2 Regression data of the calibration lines for the quantitative determination of ascorbic acid, catechol, dopamine and hydroquinone at PAAQ prepared from aqueous medium using cyclic voltammetry technique.

Analyte	N	RSD	LOD (mol L^{-1})	LOQ (mol L^{-1})
Ascorbic acid	4	5.2×10^{-3}	4.88×10^{-8}	1.6×10^{-7}
Catechol	4	0.5	3.7×10^{-6}	1.2×10^{-5}
Dopamine	4	4×10^{-3}	3.8×10^{-8}	1.3×10^{-7}
Hydroquinone	4	9.4×10^{-3}	4.93×10^{-8}	1.6×10^{-7}

RSD = Relative SD, LOD = Lower limit of detection, LOQ = Lower limit of quantization. The number of experiments (N) = 4 and the regression factor (R) of the data is equal to 0.998. The standard deviation (SD) = 5×10^{-4} except for catechol it is equal to 0.048.

Validation of the method

Specificity

Catechol and hydroquinone can be determined specifically with high sensitivity using PAAQ prepared from aqueous medium. In this case, where other phenolic compounds interfere during the determination, the difference in oxidation peak potential height is used to differentiate between each analyte if they found in the same sample.

Accuracy

The accuracy of the method for the determination of the different compounds under investigation was performed by the addition of standard concentration of each compound to 10 mL tap water and recording the oxidation peak current. For example, 5.0×10^{-3} mol L^{-1} catechol was added to 10 mL tap water then the current response was recorded using the PAAQ modified electrode. The current recorded by PAAQ modified electrode prepared from aqueous medium was found to be 200 μA which corresponds to 4.98×10^{-3} mol L^{-1} catechol. The percent of error did not exceed 1%. The measurements have indicated the accuracy of the method.

Precision and repeatability

Each determination for the four different compounds has been carried out at least four times. The relative standard deviation was found to be less than 1% indicating the high precision of the method and the confidence in its repeatability.

The detection limits obtained by the use of PAAQ modified electrodes were compared with those obtained by other methods, especially for the determination of dopamine. The data are presented in Table 3, which shows clearly that the PAAQ modified electrodes can detect concentrations down to 10^{-8} mol L^{-1}, a range lower with an order of magnitude than the other standard methods.

Robustness

The method was found to be fast where the preparation of the modified electrode does not exceed 15 min. The method of preparation is easy and does not require special pretreatments or sophisticated designs. The process of determination of the analyte is very fast and is taking place in less than 1 min.

The PAAQ modified electrode is stable and can be used several times over two weeks. The current response recorded using the previously prepared PAAQ modified electrode was always the same within a range of ± 0.01 μA.

Conclusions

PAAQ thin films are prepared conveniently and reproducibly by the electropolymerization of AAQ on Pt substrates from aqueous medium. The process is fast and economic. The electropolymerization reaction was found to be first order with respect to the monomer concentration. H_2SO_4 had a negative order of -0.66 but it is essential for the dissolution of the monomer. The PAAQ films are stable and show good performance as electroanalytical sensors for the quantitative determination of ascorbic acid, catechol, dopamine and hydroquinone.

Acknowledgments

Table 3 The lower limit of detection (LOD) of the different methods used for the determination of dopamine and the references of these methods.

Analytical method	LOD (mol L^{-1})
Spectrophotometry [31]	1.6×10^{-7}
Fluorimetry [32]	4.3×10^{-7}
Capillary electrophoresis–Ultraviolet [33]	0.7×10^{-6}
Capillary electrophoresis–mass spectroscopy [33]	1.2×10^{-6}
Flow injection fluorescence using photoinduced electron transfer boronic acid derivatives [34]	3.7×10^{-6}
Spectrophotometric determination using microfluidic system based on polymeric technology [35]	6.3×10^{-6}
PAAQ modified electrode prepared from aqueous medium	3.8×10^{-8}

References

[1] Ismail KM, Khalifa ZM, Abdel Azzem M, Badawy WA. Electrochemical preparation and characterization of poly (1-amino-9,10-anthraquinone) films. Electrochim Acta 2002;47(12):1867–73.

[2] Badawy WA, Ismail KM, Medany SS. Optimization of the electropolymerization of 1-amino-9,10-anthraquinone conducting films from aqueous media. Electrochim Acta 2006;51(28):6353–560.

[3] Huang PF, Wang L, Bai JY, Wang HJ, Zhao YQ, Fan SD. Simultaneous electrochemical detection of dopamine and ascorbic acid at a poly(p-toluene sulfonic acid) modified electrode. Microchim Acta 2007;157(1–2):41–7.

[4] Kumar SA, Tang CF, Chen SM. Poly (4-amino-1-1′-azobenzene-3, 4′-disulfonic acid) coated electrode for selective detection of dopamine from its interferences. Talanta 2008;74(4):860–6.

[5] Heinz H, Przuntek G, Winterer A, Pietzeker A. Clinical aspects and follow-up of dopamine-induced psychoses in continuous dopaminergic therapy and their implications for the dopamine hypothesis of schizophrenic symptoms. Nervenarzt 1995;66(9):662–9.

[6] Holloway RG, Biglan KM. A review of pramipexole and its clinical utility in Parkinson's disease. Expert Opin Pharmacother 2002;3(2):197–210.

[7] Li J, Zhao J, Wei X. A sensitive and selective sensor for dopamine determination based on a molecularly imprinted electropolymer of o-aminophenol. Sensors Actuators B 2009;140(2):663–9.

[8] Kalimuthu P, John SA. Electropolymerized film of functionalized thiadiazole on glassy carbon electrode for the simultaneous determination of ascorbic acid, dopamine and uric acid. Bioelectrochem 2009;77(1):13–8.

[9] Zhang R, Jin G-D, Chen D, Hu X-Y. Simultaneous electrochemical determination of dopamine, ascorbic acid and uric acid using poly (acid chrome blue K) modified glassy carbon electrode. Sensors Actuators B 2009;138(1):174–81.

[10] Arrigoni O, Tullio MC. Ascorbic acid: much more than just an antioxidant. Biochim Biophys Acta 2002;1569(1–3):1–9.

[11] Arya SP, Mahajan M, Jain P. Non-spectrophotometric methods for the determination of Vitamin C. Anal Chim Acta 2000;417(1):1–14.

[12] Malinauskas A, Garjonyté R, Mažeikiené R, Jurevičiūté I. Electrochemical response of ascorbic acid at conducting and electrogenerated polymer modified electrodes for electroanalytical applications: a review. Talanta 2004;64(1):121–9.

[13] Freire RS, Duran N, Kubota LT. Electrochemical biosensor-based devices for continuous phenols monitoring in environmental matrices. J Braz Chem Soc 2002;13(4):456–62.

[14] Asan A, Isildak I. Determination of major phenolic compounds in water by reversed-phase liquid chromatography after pre-column derivatization with benzoyl chloride. J Chromatogr A 2003;988(1):145–9.

[15] Pistonesi MF, Nezio MSD, Centurin ME, Palomeque ME, Lista AG, Band BSF. Determination of phenol, resorcinol and hydroquinone in air samples by synchronous fluorescence using partial least-squares (PLS). Talanta 2006;69(5):1265–8.

[16] Li S, Li X, Xu J, Wei X. Flow-injection chemiluminescence determination of polyphenols using luminol–NaIO$_4$–gold nanoparticles system. Talanta 2008;75(1):32–7.

[17] Nagaraja P, Vasantha RA, Sunitha KR. A sensitive and selective spectrophotometric estimation of catechol derivatives in pharmaceutical preparations. Talanta 2001;55(6):1039–46.

[18] Moldoveanu SC, Kiser M. Gas chromatography/mass spectrometry versus liquid chromatography/fluorescence detection in the analysis of phenols in mainstream cigarette smoke. J Chromatogr A 2007;1141(1):90–7.

[19] Garcia-Mesa JA, Mateos R. Direct automatic determination of bitterness and total phenolic compounds in virgin olive oil using a pH-based flow-injection analysis system. J Agric Food Chem 2007;55(10):3863–8.

[20] Ghanem MA. Electrocatalytic activity and simultaneous determination of catechol and hydroquinone at mesoporous platinum electrode. Electrochem Commun 2007;9(10):2501–9.

[21] Yu J, Du W, Zhao F, Zeng B. High sensitive simultaneous determination of catechol and hydroquinone at mesoporous carbon CMK-3 electrode in comparison with multi-walled carbon nanotubes and Vulcan XC-72 carbon electrodes. Electrochim Acta 2009;54(3):984–8.

[22] Zhao D-M, Zhang X-H, Feng L-J, Jia L, Wang S-F. Simultaneous determination of hydroquinone and catechol at PASA/MWNTs composite film modified glassy carbon electrode. Colloids Surfaces B: Biointerf 2009;74(1):317–21.

[23] Villarreal I, Morales E, Otero TF, Acosta JL. Electropolymerization kinetics of pyrrole in aqueous solution on graphite felt electrodes. Synth Mets 2001;123(3):487–92.

[24] Cambra A, Redondo MI, González-Tejera MJ. Kinetic study of poly-N-methylpyrrole electrogeneration. Synth Mets 2004;142(1–3):93–100.

[25] Ismail KM. Electrochemical preparation and kinetic study of poly (o-tolidine) in aqueous medium. Electrochim Acta 2007;52(12):3883–8.

[26] Downard AJ, Pletcher D. The influence of water on the electrodeposition of polypyrrole in acetonitrile. J Electroanal Chem 1986;206(1–2):139–45.

[27] Gangwal VR, van der Schaaf J, Kuster BFM, Schouten JC. The effect of mass transport limitation on the estimation of intrinsic kinetic parameters for negative order reactions. Appl. Catal A 2004;274(1–2):275–83.

[28] Han Y-F, Wang J-H, Kumar D, Yan Z, Goodman DW. A kinetic study of vinyl acetate synthesis over Pd-based catalysts: kinetics of vinyl acetate synthesis over Pd–Au/SiO$_2$ and Pd/SiO$_2$ catalysts. J Catal 2005;232(2):467–75.

[29] Rioux RM, Komor R, Song H, Hoefelmeyer JD, Grass M, Niesz K, Yang P, Somorjai GA. Kinetics and mechanism of ethylene hydrogenation poisoned by CO on silica-supported monodisperse Pt nanoparticles. J Catal 2008;254(1):1–11.

[30] Miller JC, Miller JN. Statistics for analytical chemistry. Ellis Hardwood Series. New York, London: PTR Prentice Hall; 1993, p. 119.

[31] Nagaraja P, Vasantha RA, Sunitha KR. A new sensitive and selective spectrophotometric method for the determination of catechol derivatives and its pharmaceutical preparations. J Pharm Biomed Anal 2001;25(3–4):417–24.

[32] Wang HY, SunY, Tang B. Study on fluorescence property of dopamine and determination of dopamine by fluorimetry. Talanta 2002;57(5):899–907.

[33] Vuorensola K, Sirén H, Karjalainen U. Determination of dopamine and methoxycatecholamines in patient urine by liquid chromatography with electrochemical detection and by capillary electrophoresis coupled with spectrophotometry and mass spectrometry. J Chromatogr B 2003;788(2):277–89.

[34] Seçkin ZE, Volkan M. Flow injection fluorescence determination of dopamine using a photo induced electron transfer (PET) boronic acid derivative. Anal Chim Acta 2005;547(1):104–8.

[35] Mamiński M, Olejniczak M, Chudy M, Dybko A, Brzózka Z. Spectrophotometric determination of dopamine in microliter scale using microfluidic system based on polymeric technology. Anal Chim Acta 2005;540(1):153–7.