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Electropolymerisation of L-arginine at carbon paste electrode and its application to the detection of dopamine, ascorbic and uric acid

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ABSTRACT

L-arginine was electropolymerised on a carbon paste electrode (CPE) to form the biopolymer by free radical formation in the electro oxidation process of the amino and carboxylic group containing compound by cyclic voltammetric technique. The modified electrode shows an excellent electrocatalytic activity towards the oxidation of both dopamine (DA) and ascorbic acid (AA). It was demonstrated that the deposited biopolymer has positive charges over the bare carbon electrode surface, which leads to the formation of electrical double layer made the fast electron transfer process could leads to the diffusion of dopamine, ascorbic acid and uric acid on their charge gradient by cyclic voltammetric technique. The response of the sensor was tested towards the different dopamine concentration. The catalytic peak current obtained was linearly related to DA concentrations in the ranges of 5×10^{-5} to 1×10^{-4} M L^{-1} with correlation co-efficient of 0.9924 which reveals the adsorption controlled process. The detection limit for dopamine was 5×10^{-7} M L^{-1}. The interference studies showed that the modified electrode exhibits excellent selectivity in the presence of large excess of ascorbic acid (AA) and response is fast stable, reliable, resistant to biofouling and can be applied for the real sample analysis in medical, pharmaceutical and biotechnological sectors. The adsorption-controlled process and kinetic parameters of the poly(L-arginine) were determined using electrochemical approaches.

1. Introduction

In recent years, efforts have been exerted in the development of voltammetric methods for the determination of DA and AA in biological samples. Dopamine is one of the excitory neurotransmitters that play an important role in physiological events. It is involved in the functioning of renal, cardiovascular, hormonal and nervous systems. Dopamine is involved in neurological diseases such as parkinson's [1], Alzheimr's disease [2] and schizophrenia [3]. As a result of these discoveries, catecholamines, drugs are now widely used in the treatment of bronchial asthma, hypertension, Parkinson's disease, myocardial infraction and cardiac surgery. Consequently various approaches have been made to develop selective and sensitive methods for the determination of DA concentrations. Dopamine is an electrochemically active compound that can be directly oxidized at an appropriate potential and a suitable electrode material. However the oxidation product of DA can cause electrode surface fouling. Dopamine normally present at low concentrations along with the electro active compounds such as ascorbic acid which is at higher concentrations. However, DA and AA usually have overlapping oxidation potentials on the bare solid electrodes. So it is essential to develop simple and rapid methods for their determination is routine analysis. Several methods have been applied to overcome the above problems [4–6]. Based on the ion-exchange membrane coated electrode, selectivity of DA and AA has been achieved [7]. Ion exchange membrane of both anionic and cationic nature has been developed to electrostatically accumulate oppositely charged analyte molecules. They are Nafion [8], polyester sulphonic acid [9], poly(4-vinylpyridine) [10], stearate [11], w-mercapto carboxylic acid [12], poly(monomericeugenol) [13], overoxidised poly(1-(2-carboxyethyl) pyrrole [14], 4-aminophenylacetic acid [15], ionic liquid [16], overoxidised polypyrrole [17,18].

Among many methods for determination of DA and AA in biological samples, polymer modified electrodes have shown to be powerful tool in electrochemical methods. Because of characteristics like film thickness, permeation and charge transport can be controlled by adjusting the electrochemical parameters. Therefore PME's have many advantageous such as improved electrocatalysis, absence of surface fouling and prevention of undesirable reactions competing kinetically with the desired electrode process [19,20]. In future these modified electrocatalytic electrodes which acts as sensors can be used in the medicine and biotechnology field.

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In this present work a covalently modified carbon paste electrode with L-arginine biopolymer was fabricated via the electrooxidation of L-arginine to its analogous cation radicals to form a chemically stable covalent linkage between the nitrogen atom of the amine group and the carbon electrode surface. This electrode was applied to induce the voltammetric separation between DA and AA which make feasible the simultaneous determination of DA and AA in a mixture based on the different electrocatalytic activities of the modified electrode towards these species. A sensitive and selective method for simultaneous determination of DA, AA and UA have been set up for routine analysis in pharmaceuticals and medicine.

2. Materials and methods

2.1. Apparatus

Cyclic voltammetry was performed with EA-201 Electroanalyser working station. The electrochemical cell contained a working electrode was carbon paste electrode (CPE) or poly(L-arginine)/CPE, platinum counter electrode and saturated calomel electrode as reference. All pH were made with MK VI digital pH meter with a combined glass calomel electrode.

2.2. Reagents and chemicals

L-arginine was purchased from Sigma. Dopamine hydrochloride and AA from Merck. All other chemicals used in this investigation were of analytical grade. The 0.1 M acetate buffer solution was prepared by using acetic acid and sodium acetate. The aqueous solutions were prepared with doubly distilled water.

2.3. Preparation of carbon paste electrode and poly(L-arginine)/CPE

The ratio of 70:30 graphite powder and silicon oil was mixed thoroughly until a homogenous paste was obtained. The paste was packed in a PVC tube, was contacted by copper wire. Thus the carbon paste electrode was obtained.

The bare CPE was placed in 0.1 M acetate buffer solution at pH 5.6 containing 2.5 mM L-arginine solution. The poly(L-arginine) film was prepared by repetitive potential cycling between −200 and 1500 mV s^{-1}. After polymerization, the poly(L-arginine) film was washed thoroughly using ABS of pH 5.6 to remove unreacted L-arginine.

3. Result and discussion

3.1.1. Electrochemical modification of L-arginine at CPE surface

L-arginine provides a single broad and irreversible oxidation peak at −31 mV on CPE in 0.1 M acetate buffer solution. No cathodic peak can be observed on the reverse scan. When the scan rate was increased up to 1500 mV s^{-1} indicating that the species obtained after the first electron transfer undergoes a chemical reaction and forms the second anodic peak at 170 mV. The one electron oxidation of the amino group turns it into its corresponding cation radical [21]. These cation radicals form carbon-nitrogen linkages at the carbon electrode surface [22]. The developments of progressively increasing redox waves and the increase of the current with each potential cycle indicated that the formation of the electroactive biopolymer film on the surface of the carbon paste electrode. As increasing number of deposition cycles were leading to the formation of a thickened polymer [23].

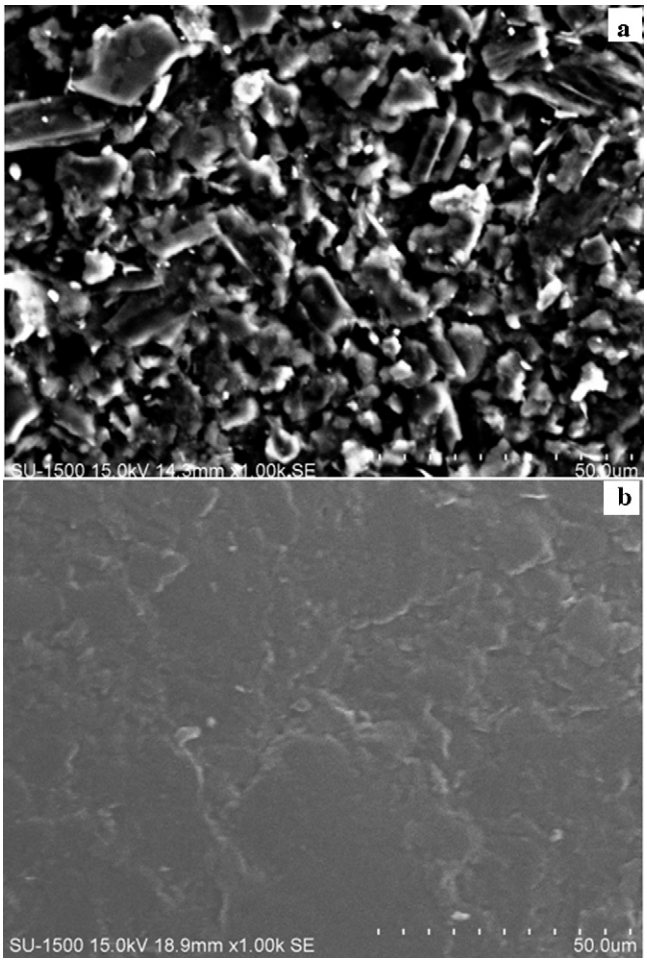

Fig. 1. Scanning electron microscopic image of (a) bare carbon paste electrode and (b) poly(arginine)/CPE.

Fig. 1 reveals the surface morphology of bare carbon paste electrode (a) and poly(arginine) modified carbon paste electrode (b) using scanning electron microscopy. The surface of bare carbon paste electrode was irregularly shaped with the flakes of graphite. However, the poly(arginine) film coated carbon paste electrode has typical uniform arrangement of poly(arginine) molecules on the surface of carbon paste electrode. This confirms that the carbon paste electrode was coated by poly(arginine) film, leads to the change in the surface activity of the poly(arginine)/CPE.

3.2. Electrochemical studies of AA at the poly(L-arginine)/CPE

Detecting dopamine is a complicated task in the presence of other electro active compounds such as ascorbic acid [24]. Ascorbic acid can interfere with the measurement of biochemical parameters leading to inexact results [25] due to the co-oxidation of AA [26]. Fig. 2A demonstrated the cyclic voltammograms of AA at bare CPE (a), poly(L-arginine)/CPE (c). AA has shown a broad and irreversible anodic peak at 180 mV at the bare CPE versus $Hg/Hg_2Cl_2/KCl(sat)$ electrode. The biopolymer poly(L-arginine)/CPE shows an anodic peak at 6 mV with increase in peak current. This poly(L-arginine) modified CPE has positive charged surface showed an improved catalytic activity towards AA which reveals that the faster electron transfer kinetics of the oxidation of AA and the oxidation potential was negatively shifted [27]. The cyclic voltammograms (b) of the blank solution at the modified electrode showed diffused broad peak at the potential 180 mV, the same as that of the peak potential at the bare carbon paste elec-