Selective determination of dopamine in presence of ascorbic acid and uric acid at hydroxy double salt/surfactant film modified carbon paste electrode

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Abstract
A sensitive and selective electrochemical method using a hydroxy double salt/surfactant film modified carbon paste electrode (HDS/SDS/CPE) was developed for the electrochemical determination of dopamine. The HDS/SDS/CPE shows an excellent electrocatalytic activity towards the oxidation of dopamine in 0.1 M phosphate buffer solution (pH 7.4) and the detection limit of DA was \(1 \times 10^{-10}\) M. The interference studies showed that the modified electrode exhibits an excellent selectivity towards dopamine (DA) in the presence of large excess of ascorbic acid (AA) and uric acid (UA). The separation of the oxidation peak potentials for DA–AA and DA–UA were about 187.8 mV and 110.7 mV respectively. The differences are large enough to determine AA, DA and UA individually and simultaneously. This work provides a simple and easy approach to selectively detect the dopamine in the presence of ascorbic acid and uric acid in physiological samples.

1. Introduction
Dopamine (DA) is one of the most important neurotransmitters which play vital role in the function of the central nervous, renal, hormone and cardiovascular system. Low levels of DA may cause neurological disorders such as schizophrenia and Parkinson’s disease [1], senile dementia [2], HIV infection [3], Huntington’s disease, motivational habit, reward mechanisms and the regulation of extracellular fluid of the central nervous system has received much interest during the past few decades [6].

The successful route to overcome the problems of selectivity is to modify the electrode surface by electropolymerization [8,9], polymer-modified electrode [11,12], carbon ionic liquid electrodes [13,14], nanomaterials modified electrodes [10] and self-assembled monolayers [15], because the modified electrode could decrease the overpotential, improve the mass transfer velocity and effectively enrich the substance. The major consideration is based on the different ion forms of DA and AA at the physiological pH of 7.40. AA exists in the anionic form (pKa = 4.10) while DA is in the cationic form (pKb = 8.87) [16].

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds (HTLCs) or anionic clays are an important class of ionic lamellar solids. Structurally, LDH consists of positively charged brucite-like layers and anion with charge \(\pm x\). Nickel zinc hydroxy nitrate, \(\text{Ni}_3\text{Zn}_2\text{(OH)}_8\text{(NO}_3\text{)}_2\) is an anion-exchangeable hydroxy double salt (HDS), a compound which is structurally similar to layered double hydroxides (LDHs). One of the most important properties of LDHs and HDSs is the anionic exchange capacity. The anions and water...
molecules intercalated into HDS interlayers can be replaced with other organic anions and polar molecules. The positively charged hydrotalcite layers have strong affinity to the negative head of surfactants (such as sodium dodecylbenzenesulfonate, octylphenoxypolyethoxyethanol, sodium octyl sulfate, sodium dodecyl sulfate (SDS)) and the inorganic anions in LDH interlayers can be replaced with long-chain surfactants, yielding modified LDH with hydrophobic surface property, resulting in high adsorptive capacity of modified LDH to nonionic organic compounds [17].

In recent years HDSs and LDHs were reported to be an attractive material for electrochemical biosensor design [20] attributing to its desirable properties, such as good biocompatibility, intense adsorbability, high catalytic activity, low cost, high chemical stability [18], low cytotoxicity, intense adsorbability, and high thermal stability [19]. Clays exhibit a flexible sheet or layered structure with relatively low interlayer bonding which gives rise to swelling properties. So they appear as a good host structure for electroactive guest molecules. Most of the studies on clay-modified electrodes have been done with the swelling cationic clays known as smectite clays. Since 1987, several papers have dealt with the application of synthetic anionic clays to electrode preparation [20]. The LDH has special interest because the hydrotalcite type structure has an anion exchange property and can act as a passive discriminator allowing preconcentration of an analyte or reactant [21]. Generally, most of LDHs have no electroactivity and poor electrical conductivity which also limit their wide applications in electrochemistry. Ni-bearing LDHs are a class of important synthetic materials that display good conductivity in an alkaline medium due to the reversible one-electron redox process of the couple Ni(III)/Ni(II) [18].

Surfactants, a kind of amphiphilic molecules with a hydrophilic head on one side and a long hydrophobic tail on the other, have been widely applied in electrochemistry to improve the property of the electrode/solution interface. Zheng and Zhou [16] reported that SDS formed a mono-layer on CPE surface with high density of negative charged end directed outside the electrode. Wang et al. [24] have investigated the micellar effect on the electrochemistry of dopamine and found that the anodic peak current of dopamine is enhanced in sodium dodecyl sulfate micelle, but the interference coming from AA cannot be eliminated [16]. According to Rusling [25] and Sivagnam and Palaniandavar [26] micellar aggregates (composed by surfactants) may mediate catalytic systems, thus, presenting strong attractive for the development of novel methodologies based on the surfactants at the electrode surface. Among these surfactants attractive for biosensor development, SDS demonstrates unique advantages such as low cytotoxicity, its extremely high adsorbability, high catalytic activity, low cost, high chemical stability, ion exchange property and can act as a passive discriminator for the development of electrochemical sensors [19].

2.2. Apparatus

Electrochemical measurements were carried out with a CHI model 660c. Electrochemical workstation connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three-electrode cell. The bare or HDS/SDS/CPE was used as a working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. All potentials reported were vs the SCE.

Powder X-ray diffraction (PXRD) measurements were performed on a PAN analytical X'pert Pro X-ray diffractometer using Cu Kα radiation (λ = 0.154 nm) at 40 kV, at a scanning rate of 2° min⁻¹. The infrared (IR) spectra of samples were collected using a Nicolet IR200 FT-IR spectrometer using KBr pellets, in the range 4000–400 cm⁻¹ with 4 cm⁻¹ resolution. The interlayer anion (nitrato/acetate) contents were obtained by ion chromatography (IC) using a Metrohm 861 Advanced compact ion chromatograph with Metrosep A Supp5 250 anion column and conductivity detector. The samples were dissolved in 1 N sulfuric acid or hydrochloric acid and diluted suitably for this purpose.

2.3. Preparation of Ni₂Zn₂(µ₃-OH)₄(NO₃)₂·2H₂O

The anionic clay, Nickel–zinc hydroxynitrate, Ni₂Zn₂(µ₃-OH)₄(NO₃)₂·2H₂O was prepared by adding 2.32 g of ZnO (0.028 mol) into a solution containing 12.44 g of nickel nitrate (0.043 mol) in 200 ml of water with continuous stirring. This mixture was aged at 65 °C for 48 h. The solids were washed free of ions with decarbonated water followed by acetone and dried at 65 °C. This sample is hereafter referred as NiZn–NO₃.

2.4. Preparation of Ni₂Zn₂(µ₃-OH)₆(CH₃COO)₄·2H₂O

Ni₂Zn₂(µ₃-OH)₆(CH₃COO)₄·2H₂O was obtained through anion exchange reaction of NiZn–NO₃. About 1 g of NiZn–NO₃ was stirred with an aqueous solution of sodium acetate (2 g in 50 ml) in an air-tight container for 2 days. The resultant solid was filtered, washed with decarbonated water followed by acetone and dried at 65 °C to constant mass. This sample is hereafter referred as NiZn–OAc.

2.5. Preparation of bare carbon paste electrode

The bare carbon electrode was prepared by hand mixing of graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was obtained. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal
diameter) and the electrical contact was provided by a copper wire connected to the paste in the end of the tube.

2.6. Preparation of hydroxy double salt/surfactant film modified carbon paste electrode (HDS/SDS/CPE)

The HDS/SDS/CPE was prepared by hand mixing of 70% graphite powder and 40 mg HDS with 30% silicon oil in an agate mortar to produce a homogenous carbon paste. The paste was packed into the homemade cavity (3 mm in diameter) and then smoothed on a weighing paper and immobilize the 0.1 mm SDS solutions on surface of the HDS/CPE modified carbon paste electrode. The electrical contact was provided by a copper wire connected to the paste in the end of the tube.

3. Results and discussion

3.1. X-ray diffraction study

PXRD patterns of the NiZn–NO₃ and NiZn–OAC are shown in Fig. 1a and b. The pattern is marked by intense and sharp peaks at high 2θ angles and weak and asymmetrical peaks at low 2θ angles. The pattern matches well reported in the literature [30]. The pattern can be indexed based on a hexagonal cell. The basal spacing of the sample is 8.23 Å. The saw tooth peaks at 2θ = 33 and 60° are due to the turbostatic disorder in the sample. The acetate exchanged sample shows a basal spacing of 12.85 Å.

3.2. Infrared spectroscopic study

IR spectra of NiZn–NO₃ and NiZn–OAC are given in Fig. 2a and b. The broad absorption at 3545 cm⁻¹ is due to O–H stretching vibration of the hydroxyl groups of the brucite-like sheets and water in the interlayer space. The O–H bending vibration of the interlayer water is observed at 1630 cm⁻¹. There is a sharp peak at 1384 cm⁻¹ is due to the N–O stretching of nitrate ion in the D₃h symmetry. The acetate exchanged sample shows characteristic peaks at 1571 cm⁻¹ and 1405 cm⁻¹ due to carboxylate stretching vibrations. The broad bands below 900 cm⁻¹ are due to lattice vibrations of the metal cations.

3.3. Electrochemical response of dopamine at HDS/SDS/CPE

Fig. 3a shows the cyclic voltammograms obtained for the electrochemical response of 0.1 mM DA at the bare CPE (dotted line), HDS/CPE (dashed line) and HDS/SDS/CPE (solid line) in 0.1 M phosphate buffer solution at pH 7.4. At bare CPE, the oxidation and reduction peak potentials occur at 162 mV and 115 mV (ΔEₚ = 47 mV) and at HDS/CPE 161 mV and 125 mV (ΔEₚ = 36 mV) respectively. Under identical conditions, the HDS/SDS/CPE produces increased peak current and a more reversible electron process of DA with the oxidation and reduction peak potentials at 174 mV and 142 mV respectively and the peak separation is about (ΔEₚ) 32 mV. It was observed that the peak currents enhanced greatly at the HDS/SDS/CPE surface provides clear evidence to the catalytic electrochemical response of DA.

On the other hand, HDS/SDS/CPE film shows antifouling property. As it is known, dopaminequinone is a product of two-electron oxidation of DA (Eq. (1), Scheme 1). It is undergo ring closure reaction (Eq. (2), Scheme 1) leading to leucodopaminochrome (Eq. (3), Scheme 1). The later can polymerized to form melanin-like product on surface of electrode (Eq. (4), Scheme 1), thus inhibit the electron
transfer reaction. However, the plot of $I_{pa}$ of DA at HDS/SDS/CPE film modified electrode as a function of successive measurements shows that the response stabilizes after two measurements. After equilibration, electrode response is very stable. Relative standard deviation for the successive measurement between the 2nd and 15th was 1.67% which indicated that there was inhibition of the activity of modifier toward DA [29]. Therefore HDS/SDS/CPE film modified electrode has an antifouling property.

3.4. Effect of concentration of SDS and immobilization time

Fig. 3a shows that SDS exhibits a remarkable enhancement effect on the anodic peak current ($I_{pa}$) of DA. However, $I_{pa}$ of DA closely related to concentration of SDS. Fig. 4a depicts the relationship between the $I_{pa}$ of DA and the concentration of SDS. The $I_{pa}$ increases greatly as SDS concentration increases from 0 to 15 µL and then decreases from 15 to 25 µL. Similarly, immobilization time also influences the $I_{pa}$ of DA. The influence of immobilization time on $I_{pa}$ of DA in the presence of 15 µL SDS have been examined by cyclic voltammetry, and results shown in Fig. 4b. The peak current increases with immobilization time over the time of 0–540 s and then decreases. In this work, the concentration of SDS and immobilization time were chosen to be 15 µL and 540 s respectively, for a higher peak current and a low background current.

3.5. Effect of scan rate on the peak current of DA

Fig. 5a shows the cyclic voltammograms of 0.1 mM DA at HDS/SDS/CPE in different scan rates. This was carried out in order to investigate the kinetics of the electrode reactions and verify whether diffusion is the only controlling factor for mass transport.
or not. The observation shows that with the increased scan rate \( (v) \), the redox peak current also increased gradually (Fig. 5a). The graph of anodic peak current \( (I_{p_a}) \) vs square root of scan rate \( (\sqrt{v}) \) was plotted (Fig. 5b). The graph obtained was good linearity between the square root of scan rate \( (\sqrt{v}) \) and \( I_{p_a} \). In the range from 100 to 500 mV s\(^{-1}\) the redox peak currents were proportional to the square root of scan rate \( (\sqrt{v}) \) and the obtained correlation coefficient was 0.9980, which indicates that the electron transfer reaction was diffusion controlled.

3.6. Effect of pH

The electrochemical response of DA at HDS/SDS/CPE was generally dependent on pH. The voltammograms of DA were recorded at 0.1 M phosphate buffer solution of different pH by cyclic voltammetric method. Fig. 6a demonstrates the pH dependence of DA at HDS/SDS/CPE at sweep rate of 100 mV s\(^{-1}\). Both anodic and cathodic peak potentials were shifted to less positive side with increasing in the pH values. The anodic peak potential of DA shifted from 244 to 108 mV with increase in the pH 6–8. The potential diagram was constructed by plotting the graph of \( E_{p_a} \) vs pH of the solution (Fig. 6b). The graph shows good linearity with a slope of 64 mV/pH this behavior is nearly obeyed the Nernst equation for equal number of electron and proton transfer reaction \([31,32]\). From the graph of \( I_{p_a} \) vs pH, maximum current was obtained at pH 7.0 (Fig. 6c). The electrochemical investigation of DA at physiological pH and simultaneous determination in presence of AA and UA was carried out.

3.7. Effect of concentration of dopamine

As the concentration of dopamine was varied from 0.1 to 0.5 mM and cyclic voltammograms were recorded (Fig. 7a)
0.1 M phosphate buffer solution at pH 7.4. The anodic peak current obtained were found to increase linearly with increase in concentration of dopamine (Fig. 7b).

3.8. Electrocatalytic oxidation of AA and UA at HDS/SDS/CPE

Fig. 8a shows the oxidation of AA at HDS/SDS/CPE in 0.1 M phosphate buffer solution of pH 7.4 at sweep rate of 100 mV s\(^{-1}\). It can be noticed that the oxidation peak of AA (1 mM) at bare carbon paste electrode anodic potential was found around at 211 mV. However, at HDS/SDS/CPE, the oxidation peak for AA was shifted towards negative direction; the anodic peak potential was located at −28 mV. This shifting of peak potential confirms the electrocatalytic activity of HDS/SDS/CPE towards AA. Fig. 8b the UA (0.1 mM) shows its anodic peak at 258 mV at bare CPE at 100 mV s\(^{-1}\) sweep rate in 0.1 M phosphate buffer solution of pH 7.4. The obtained voltammogram at bare CPE was less sensible. However, the voltammogram obtained at HDS/SDS/CPE for UA in the same condition leads more current signal comparing to bare CPE. The anodic peak potential was located at 295 mV. This result of enhancement in current signal showed very good sensor activity of HDS/SDS/CPE for UA.

3.9. Simultaneous determination of DA, AA and UA

DA, AA and UA usually coexist in physiological samples, generally the concentrations of AA, UA were much higher than that of DA. Since, the oxidation potential of both AA and UA were nearly same as that of DA result in an overlapped voltammetric response at bare CPE. Fig. 9a showed the cyclic voltammetric response of DA (0.04 mM) in presence of UA (0.1 mM) and AA (2 mM) in 0.1 M phosphate buffer solution of pH 7.4 at bare CPE (a), HDS/CPE (b)
and modified electrode HDS/SDS/CPE(c) at sweep rate of 100 mV s$^{-1}$. The voltammogram obtained for mixture of sample at bare CPE was broad, less sensible and overlapped wave at the potential of 201 mV. However, the modified HDS/SDS/CPE shows separations. The resulted voltammogram had oxidation peak potentials of DA, AA and UA were at 174 mV, 13 mV and 285 mV respectively. The peak to peak separation of DA–AA was 187 mV and that of DA–UA was 111 mV. This results were large sufficient to identify DA in presence of AA and UA at HDS/SDS/CPE.

DPV was used for the determination of DA, AA and UA because it has more sensitivity and selectivity. The simultaneous study was carried out in the potential range from 200 to 500 mV (Fig. 9b) and DPV showed the simultaneous determination of DA, AA and UA with well separated three anodic peaks corresponding to their oxidation at HDS/SDS/CPE. The 0.04 mM DA showed its $E_{pa}$ at 133 mV, 2 mM AA was at –76 mV and 0.1 mM UA was at 245 mV. The peak separation between DA–AA was 209 mV and for DA–UA the peak separation was 112 mV which were greater differences when comparing to peak separation occurred by CV technique.
3.10. Interference study

The simultaneous determination of DA, AA and UA in the mixture was carried out at HDS/SDS/CPE when concentration of one species changed, whereas the others kept constant. From the Fig. 10a it can be seen that the peak current of DA was proportional to its concentration, which was increased from 0.02 to 0.16 mM when keeping the concentration of UA 0.1 mM and AA 1 mM. There were no change in the peak current and peak potential occurred for AA and UA. Similarly in Figs. 10b and 10c self explains the concentration effect of AA from 1.5 to 2.5 M mM and UA from 0.18 to 0.3 mM respectively. These results shows that the DA and UA were exist independently in their mixtures of samples.

To study the effect of concentration of DA, differential pulse voltammetric technique was used [9]. The simultaneous determination of DA, AA and UA in the mixture was carried out at HDS/SDS/CPE when concentration of one species changed, whereas the others kept constant. From the Fig. 10a it can be seen that the peak current of DA was proportional to its concentration, which was increased from 0.02 to 0.16 mM when keeping the concentration of UA 0.1 mM and AA 1 mM. There were no change in the peak current and peak potential occurred for AA and UA. Similarly in Figs. 10b and 10c self explains the concentration effect of AA from 1.5 to 2.5 M mM and UA from 0.18 to 0.3 mM respectively. These results shows that the DA and UA were exist independently in their mixtures of samples.

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4. Conclusions

In this work HDS/SDS/CPE has shown good selectivity towards DA in presence of excess of AA and UA. The scan rate effect was found to be diffusion-controlled electrode process. The concentration effect and pH effect was well investigated by using cyclic voltammetric technique. The NiZn–OAc(HDS) used as biosensor because of good biocompatibility, high catalytic activity, low cost, high chemical stability, low cytotoxicity high thermal stability and having excellent conductivity. The HDS modified electrode acts as a good sensor for DA and it can be further applied for the investigation of other neurotransmitter.

References

Clay modified carbon paste electrode for the voltammetric detection of dopamine in presence of ascorbic acid

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1. Introduction

Among all the chemical sensors reported in the literature, electrochemical sensors are the most attractive because of their remarkable sensitivity, experimental simplicity and low cost [1]. In the recent years, a new approach to electrocatalysis emerged using molecular materials attached to electrode surfaces, since the kinetics of an electrochemical reaction and sometimes even the electrode reaction product may depend on the composition of the electrode. Research arose focusing on the preparation and the characterization of electrodes modified with inorganic structured materials such as zeolites and clays. The key features of inorganic matrixes. Among these methods, entrapment within hydrophilic gels of the formula M (OH)2 and it is an ordered stacking of neutral layers such as zeolites and clays. The key features of inorganic matrixes. Among these methods, entrapment within hydrophilic gels of the formula M (OH)2 and it is an ordered stacking of neutral layers
surfactants i.e.; surfactants might combine with the substrate in certain forms and strengthen their adsorption on the electrode surface, which facilitated the electron or the substance transfer between the electrode and the solution (CPE). Wen et al. [18] have investigated the micellar effect on the electrochemistry of dopamine and found that the anodic peak current of dopamine is enhanced in sodium dodecyl sulfate micelle, but the interference coming from AA cannot be eliminated [17]. Chenghui Hu and Shengshui Hu [16] reported that CTAB formed a compact monolayer on the electrode surface with high density of positive charges and Jianbin Zheng and Xiaoli Zhau [17] reported that SDS formed a monolayer on CPE surface with high density of negative charged end directed outside the electrode.

At the physiological pH, Dopamine (DA) and ascorbic acid (AA) existing in different ion forms, AA is in the anionic form (pKα = 4.10) while DA in the cationic form (pKα = 8.87). Taking advantage of the opposite micelle effect of DA and AA, these two bioactive compounds can be simultaneously determined in the ionic micelles or by using surfactant-modified electrodes [19,20]. On the other hand, surfactants have proven effective in the electroanalysis of biological compounds and drugs. For example, it was recently shown that surfactants are highly effective in stabilizing the voltammetric response of serotonin by protecting the electrode surface from fouling [21,22].

DA and AA are compounds of great biomedical and neurochemical interest playing a potential role in human metabolism. DA is one of the most significant catecholamine, functioning as a neurotransmitter in the central nervous system and a medicament to drug addiction and Parkinson’s disease [23]. These neurotransmitters are an important group of biological compounds and recently there has been considerable effort in the development of voltammetric methods for the determination of these compounds. It is generally believed that direct redox reactions of these species at bare electrode are irreversible and therefore require high over potentials [24]. Moreover, the direct redox reaction of DA and AA (about 10^3 times higher than DA in biological samples) species at the bare electrode take place at very similar potentials and often suffer from a pronounced fouling effect, which results in rather poor selectivity and reproducibility [25].

The design, fabrication and application of sensitive and selective electrochemical sensors have been of considerable interests. In recent years anionic clays (HDS, LDHs etc.) were reported to be an attractive material for electrochemical biosensor design [4,26]. In this work, our aim was to fabricate novel electrode modification material with low cytotoxicity, high stability, good catalytic activity and an excellent conductivity to achieve the challenge of simultaneous determination of DA in presence of excess amount of AA in physiological pH. The modified carbon paste electrode by α-cobalt (II) hydroxide (α-Co-SO4/CPE) electrode was tightly packed into a PVC tube (3 mm internal diameter) and the electrical contact was provided by a copper wire connected to the paste in the end of the tube.

The bare carbon paste was prepared in a standard three-electrode cell. The bare or α-Co-SO4/CPE was used as a working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. All potentials reported were versus the SCE.

Powder X-ray diffraction (pXRD) measurements were performed on a PAN analytical Expert Pro X-ray Diffractometer using Cu Kα radiation (λ = 0.154 nm) at 40 kV, at a scanning rate of 2°·min⁻¹. The infrared (IR) spectra of samples were collected using a Nicolet IR200 FT-IR spectrometer using KBr pellets, in the range 4000 to 400 cm⁻¹ with 4 cm⁻¹ resolution. The interlayer anion (sulfate) contents were obtained by ion chromatography (IC) using a Metrohm 861 Advanced Compact ion chromatograph with Metrosep A Supp5 250 anion column and conductivity detector. The samples were dissolved in 1 N hydrochloric acid and diluted suitably for this purpose.

2.2. Apparatus

Electrochemical measurements were carried out with a CHI model 660c. Electrochemical Workstation connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three-electrode cell. The bare or α-Co-SO4/CPE was used as a working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. All potentials reported were versus the SCE.

2.3. Synthesis of α-cobalt (II) hydroxide

α-Cobalt (II)hydroxides was prepared by the addition of cobalt sulfate and 0.5 mole excess sodium sulfate in 50 ml of 0.5 M NH₃ solution with constant stirring. The solid product formed was immediately centrifuged, washed free of anions with water followed by acetone, and dried in air at room temperature. The obtained product called as α-Co-SO4.α

2.4. Preparation of bare carbon paste electrode

The bare carbon paste was prepared by hand mixing of graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was obtained. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and the electrical contact was provided by a copper wire connected to the paste in the end of the tube.

2.5. Preparation of α-Co-SO4/surfactant film modified carbon paste electrode (α-Co-SO4/CPE)

The α-Co-SO4/CPE was prepared by hand mixing of 70% graphite powder and 30 mg α-Co-SO4 with 30% silicon oil in an agate mortar to produce a homogenous carbon paste. The paste was packed into the homemade cavity (3 mm in diameter) and then smoothed on a weighing paper and immobilized with 0.1 mm SDS solutions on surface of the α-Co-SO4/CPE electrode. The electrical contact was provided by a copper wire connected to the paste in the end of the tube.

3. Results and discussion

3.1. X-ray diffraction study

Fig. 1. shows the pXRD pattern of α-cobalt hydroxy sulfate (α-Co-SO₄). All the reflections are considerably broadened. This pattern displays a low angle reflection at 7.92 A° attributed to 003 and an asymmetric characteristic saw-tooth-shaped broad peaks due to the 2-dimensional (10) and (11) reflections arising out of turbostratic disorder [27,28]. The turbostratic disorder is a direct consequence of the mismatch between the crystallographically defined interlayer sites generated within a crystal with rhombohedral symmetry and the tetragonal symmetry of the SO₄²⁻ ions. Due to the mismatch the SO₄²⁻ ions are unable to anchor the metal hydroxide slabs in an ordered stacking sequence.

3.2. Infrared spectroscopic study

The FT-IR spectra of α-Co-SO₄ shown in Fig. 2 provides the information of the α-Co hydroxide intercalates, an intense broad band centered at 3440 cm⁻¹ represents the stretching vibrations of the
O–H groups of the inorganic layers and the interlayer water. Another common frequency for this type of materials is the presence of the bending vibrations of water molecules at 1625 cm$^{-1}$ and the S–O bonding of the sulfonate groups at 1115 cm$^{-1}$. The broad bands below 900 cm$^{-1}$ are due to lattice vibrations of the metal cations.

3.3. Electrochemical response of dopamine at α-Co-SO$_4$/SDS/CPE

Fig. 3A shows the cyclic voltammograms obtained for the electrochemical responses of 0.1 mM DA at (a) bare, (b) α-Co-SO$_4$/CPE and (c) α-Co-SO$_4$/SDS/CPE in 0.1 M phosphate buffer solution at pH 7.0. At bare CPE, the oxidation and reduction peak potentials occur at 159 mV and 110 mV ($\Delta E_p = 49$ mV) and at α-Co-SO$_4$/CPE 154 mV and 107 mV ($\Delta E_p = 47$ mV) respectively. Under identical conditions, the α-Co-SO$_4$/SDS/CPE produces increased peak current and a more irreversible electron process of DA with the oxidation and reduction peak potentials at 147 mV and 112 mV respectively and the peak separation is about ($\Delta E_p = 35$ mV). It was observed that the peak currents enhanced greatly at the α-Co-SO$_4$/SDS/CPE surface provides clear evidence to the catalytic electrochemical response of DA.

Fig. 3B shows that there is no characteristic peak of the modifier in the blank PBS solution (curve a) and exhibited the redox nature of the DA in the PBS solution (curve b).

3.4. Effect of concentration of SDS

Fig. 4 shows that SDS exhibits a remarkable enhancement effect on the anodic peak current $I_{pa}$ of DA closely related to concentration of SDS. Fig. 4 depicts the relationship between the $I_{pa}$ of DA and the concentration of SDS. The $I_{pa}$ increases greatly as SDS concentration increases from 0 to 9 µL and then decreases from 9 µL to 15 µL. In this work the concentration of SDS was 9 µL chosen for experimental work.

3.5. Effect of scan rate on the peak current of DA

Fig. 5A shows the cyclic voltammograms of 0.1 mM DA at α-Co-SO$_4$/SDS/CPE in different scan rates. This was carried out in order to...
investigate the kinetics of the electrode reactions and verify whether diffusion is the only controlling factor for mass transport or not. The observation shows that with the increased scan rate (v), the redox peak current also increased gradually (Fig. 5A). The graph of anodic peak current (Ipa) Vs scan rate (v) was plotted (Fig. 5B). The graph obtained was good linearity between the scan rate (v) and Ipa. In the range from 100 to 500 mV s\(^{-1}\), the redox peak currents were proportional to the scan rate (v) and the obtained correlation coefficient was \(r^2 = 0.9980\), which indicates that the electron transfer reaction was adsorption-controlled.

### 3.6. Effect of pH on the oxidation of DA

In order to investigate the mechanism of electrochemical reactions of DA on \(\alpha\)-Co-SO\(_4\)/SDS/CPE, the effect of pH on the formal potential and Ipa was investigated in CV in the solution containing 0.1 mM DA and the results are shown in Fig. 6A, B and C. From the Fig. 6B the peak potential shifted negatively with the increase of solution pH indicating that protons were directly involved in the electrochemical reaction of DA. The anodic peak potential (Epa) of DA was proportional with the solution pH in the range of 6–8. The linear regression equation for DA was Epa (V) = 0.594–0.0612 pH, with the correlation coefficient \(r^2 = 0.9980\). A slope of 0.0612 V/pH, revealing that the proportion of the electron and proton involved in the reactions was 1:1. As the DA oxidation is a two-electron process, the number of protons involved is also predicted to be two. This was shown in the mechanism of DA oxidation (in Scheme 1) and the oxidation peak current (Ipa) of DA increases gradually with increasing pH from 6.0 to 7.0 and the maximum current achieved at pH 7.0 (Fig. 6C). With the further increasing pH value a great decrease in the Ipa values.

Considering the sensitivity of the determination of DA, the values of pH 7.0 were chosen for the subsequent experiments.

![Fig. 5. A. Cyclic voltammograms of 0.1 mM DA at different scan rate (a–i; 0.1 V/s to 0.5 V/s) at \(\alpha\)-Co-SO\(_4\)/SDS/CPE. B. Graph of anodic peak current (Ipa) Vs scan rate (v).](image)

![Fig. 6. A. Cyclic voltammograms of 0.1 mM DA for different pH (a–e; from 6 to 8 pH) at \(\alpha\)-Co-SO\(_4\)/SDS/CPE. B. Graph of Epa vs pH. C. Graph of Ipa vs pH.](image)

**Scheme 1.** Mechanism of DA oxidation at \(\alpha\)-Co-SO\(_4\)/SDS/CPE.
3.7. Effect of concentration of dopamine

To study the effect of concentration of DA, differential pulse voltammetric (DPV) technique was used [29–31], because of its more sensitivity than cyclic voltammetric (CV) technique. The electrocatalytic oxidation of dopamine was carried out at α-Co-SO4/SDS/CPE by varying its concentration from $5 \times 10^{-7}$ to $1000 \times 10^{-7}$ M shown in Fig. 7A. Fig. 7B shows that the graph of peak current vs concentration of DA shows two linear relationships ranges $5 \times 10^{-7}$–$50 \times 10^{-7}$ and $50 \times 10^{-7}$–$1000 \times 10^{-7}$ M with the linear regression equations as $I_{pa} (A) = 9.1983 \times 10^{-7} + 0.1858 \, C$ M/L and $I_{pa} (A) = 9.018 \times 10^{-7} + 0.1465 \, C$ M/L, respectively. The correlation coefficient for the first linearity was $r^2 = 0.99755$ and for the second it was found to be $r^2 = 0.9910$. The decrease of sensitivity (slope) in the second linear range is likely to be due to kinetic limitation[32]. The detection limit for DA in the lower range region was found to be $2.5 \times 10^{-7}$ M and quantification limit was $5.3 \times 10^{-7}$ M. The detection limit and quantification limit were calculated by using the formulas (1) and (2) [29,33] where S is the standard deviation and M is the slope obtained from the calibration plots.

\[
\text{LOD} = \frac{3S}{M} \quad (1)
\]

\[
\text{LOQ} = \frac{10S}{M} \quad (2)
\]

3.8. Simultaneous determination of DA and AA

DA and AA usually coexist in physiological samples, generally the concentrations of AA was much higher than that of DA. Since, the oxidation potential of AA was nearly same as that of DA results in an overlapped voltammetric response at bare CPE [34]. Fig. 8A showed the cyclic voltammetric response of DA (0.04 mM) in presence AA (1 mM) in 0.1 M phosphate buffer solution of pH 7.0 at bare CPE (a) and modified α-Co-SO4/SDS/CPE (b) with sweep rate of 100 mV s$^{-1}$. The voltammogram obtained for mixture of sample at bare CPE was broad, less sensible and overlapped wave at the potential of 199 mV. However, the modified α-Co-SO4/SDS/CPE shows the separations. The voltammetric separation resulted voltammogram had oxidation peak potentials of DA, and AA were at 180 mV and $-30$ mV respectively. The peak to peak separation of DA-AA was 210 mV. This results were large sufficient to identify DA in presence of AA at α-Co-SO4/ SDS/CPE.

DPV technique was used for the determination of DA and AA because of its sensitivity and selectivity. The simultaneous study was carried out in the potential range from $-200$ to $400$ mV (Fig. 8B) and DPV showed the simultaneous determination of DA and AA with well separated two anodic peaks at modified electrode. The 0.04 mM DA showed its $E_{pa}$ at 125 mV and 1 mM AA was at $-91$ mV. The peak separation between DA–AA was 216 mV which was more differences when comparing to peak separation occurred by CV technique.

3.9. Interference study

The simultaneous determination of DA in the presence of AA was carried out at α-Co-SO4/SDS/CPE film modified electrode when concentration of DA changed, whereas the AA remained kept constant.
From Fig. 9 it can be seen that the peak current of DA was proportional to its concentration, which was increased from $50 \times 10^{-7}$ to $1000 \times 10^{-7}$ M at constant concentration of 1 mM AA. There was no change in the peak current and peak potential occurred for AA. These results show that the DA and AA exist independently in their mixtures of samples.

3.10. Reproducibility and stability

To investigate the precision of the determination, the ability to generate a reproducible electrode surface was examined using cyclic voltammetric data’s from eight separately prepared $\alpha$-Co-SO4/SDS/CPE’s, obtained in optimum solution pH. The calculated RSD for 0.1 mM DA at sweep rate of 100 mV s$^{-1}$ was 1.89% indicating that surface reproducibility was satisfactory. In addition, the long-term stability of the eight $\alpha$-Co-SO4/SDS/CPEs was tested over a three-week period. When CVs were recorded after the modified electrode was stored at room temperature, the peak potential for DA oxidation was unchanged and the modified electrode showed negligible decreases in anodic peak current as time lapses for 1 week time intervals. The RSD of the determination of 0.1 mM DA in optimum solution pH at sweep rate 100 mV s$^{-1}$ was 4.13% shows that the electrode is highly stable over a long-period.

4. Conclusion

In the present work, a simple and easy approach to selectively detect the dopamine in the presence of ascorbic acid in physiological samples using $\alpha$-Co-SO4/SDS/CPE was used. The modified electrode showed excellent sensitivity, selectivity, biocompatibility, low cytotoxicity, reproducibility, stability, anti-fouling properties and exhibited strong electrocatalytic activity toward the oxidation of DA and AA. The detection limit of DA was $2.5 \times 10^{-7}$ M and also resolved the overlapping anodic peak of DA and AA. Therefore this approach can readily be applied to the development of electrochemical sensors for dopamine and related neurotransmitters.

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References


Fig. 9. Differential pulse voltammograms of DA for different concentrations (a–m; $50 \times 10^{-7}$–$1000 \times 10^{-7}$) in 0.1 M phosphate buffer solution of pH 7.0 in the presence of 1 mM AA at $\alpha$-Co-SO4/SDS/CPE with scan rate of 50 mV s$^{-1}$.
Electrochemical Investigation of 4-Aminophenol at CTAB Modified Carbon Paste Electrode: A Cyclic Voltammetric Technique

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Abstract- 4-aminophenol is the main impurity present in preparations of paracetamol. Using the cyclic voltammetry, the electrode behaviour of 4-aminophenol has been studied in 0.1 M phosphate buffer solutions at carbon paste electrode and surfactant modified carbon paste electrode. The optimal potential window of wide range from -0.4 V to 0.7 V was selected. The electron transfer kinetics of the CTAB/CPE in the detection of analyte was determined by the scan rate effect and concentration variation studies. The scan rate effect showed the electrode process is adsorption controlled. The oxidation peak currents represented a linear dependence on 4-aminophenol concentration from 1 mM to 4 mM with correlation coefficient $r^2=0.9942$. The effect of cationic surfactant shows good high sensitivity and stability for the redox process of the 4-amino phenol. The detection limit was found to be $1 \times 10^{-7}$ M.

Keywords- 4-aminophenol, CTAB Modified Carbon Paste Electrode, PBS, Cyclic Voltammetry
1. INTRODUCTION

4-aminophenol has highly toxic and mutagenic effects and induces DNA cleavage in mouse and human lymphoma cells [1,2]. Aminophenols are interesting electrochemical materials [3,4-6]. This is because, unlike aniline [7] and other substituted anilines [8], they have two oxidizable groups (NH₂ and OH) providing more reactive sites. Therefore, in principle, they could show electrochemical behavior resembling anilines [9] and phenols [10]. This compound is an intermediate in the degradation of azo dyes [11]. However, little is known about the metabolism of 4-aminophenol by bacteria [12]. 3-Nitrophenol-grown cells of Ralstonia eutropha JMP 134 convert nitrobenzene to hydroxylaminobenzene, 2-aminophenol and 4-aminophenol [13]. Hydroxylamino benzene is transformed by 3-nitrophenol-grown cells of Pseudomonas putida 2NP8 to 1,4-benzenediol via 4-aminophenol [14]. A number of reports indicated that 4-aminophenol might be a key intermediate in the biodegradation of nitrobenzenes and amines [11, 14]. 4-aminophenol is a well-known compound that has been used as a redox agent in photography [6]. In neutral media, it is oxidized to a complex oligomeric dye that can be used in enzymatic assays [15]. Voltammetric studies[16] showed that the first step of the oxidation of 4-aminophenol in organic and aqueous media on gold electrodes probably results in the uptake of one electron, producing an intermediate oxidation product (semiquinoneimine) in agreement with the literature[17,18]. Heras et al. [18] studied the electrochemical oxidation of 4-aminophenol on a mercury electrode in aqueous medium. They indicated that the electrooxidation of 4-aminophenol occurs by the loss of one proton and one electron. The next step is the loss of another electron and of a second proton to yield p-quinoneimine that is hydrolyzed to p-benzoquinone. Investigations of the modification of platinum [19-21], graphite [4] and gold [22] by polymers derived from 4-aminophenol have been carried out. Graphite electrodes coated with poly (4-aminophenol) are efficient for the immobilization of purine bases [4]. In the present work, it describes the electrochemical investigation of 4-aminophenol on CTAB modified carbon paste electrodes. Many of the analytes have been detected by cyclic voltammetric technique by our research group [23,24]. The aim of the work reported here was to investigate the electrochemical properties of 4-aminophenol on carbon paste and CTAB/CPE as well as the electrochemical characterization of electrodes by cyclic voltammetric technique. It can be applied to routine investigations of pharmaceutical preparations in the form of tablets by using the cyclic voltammetric technique.

2. EXPERIMENTAL SECTION

2.1. Reagents

4-aminophenol obtained from Sigma-Aldrich, dissolved in ethanol to prepare 10 mM standard stock solutions and stored at dark place. CTAB was dissolved in double distilled
water to form 5 mM solutions. All solutions were prepared with double distilled water, were of analytical grade and used without further purification. Phosphate buffer solution (PBS) was prepared by standard method. All experiments were performed at room temperature.

2.2 Apparatus and Procedure

The electrochemical experiments were carried out using a Model CHI-660c electrochemical work station. All experiments were carried out in a conventional three-electrode system. The electrode system contained a working carbon paste electrode, homemade cavity of 3 mm diameter, a platinum wire as counter electrode and saturated calomel electrode as reference electrode. Bare carbon paste electrode was prepared by grinding 70% graphite powder and 30% silicon oil in an agate mortar by hand mixing for about 30 min to get homogenous mixture. The paste was packed into the cavity of CPE and smoothened on weighing paper.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Investigation of 4-amino phenol.

4-amino phenol was studied at CTAB/CPE by cyclic voltammetric study. Fig. 1 shows the cyclic voltammograms of 4-amino phenol which exhibited two good anodic peaks and a cathodic peak current at 0.1886 V, 0.3983 V and 0.1217 V respectively. At bare carbon paste electrode the reduction peak is good compared over the oxidation peak current. But at the CTAB/CPE both the oxidation peak current and reduction peak current were increased. At bare carbon paste electrode the anodic peak current could have not been properly observed. CTAB immobilized on the carbon paste electrode has formed a uniform layer which possessed a positive charged group on the electrode; the 4-amino phenol undergoes oxidation and forms a positive charge. Due to the electrostatic interaction between the positive charged 4-amino phenol and the CTAB/CPE increases the peak current which results in the good sensitivity. Scheme.1 shows the 4-aminophenol undergone oxidation with the loss of one electron and hydrogen transfer and it undergoes reduction with addition of one electron to the oxidised product of 4-aminophenol. The current sensitivity may be due to the electrostatic repulsion between the quinone moiety of the 4-aminophenol and the positively charged CTAB modified carbon paste electrode. Electron-withdrawing groups accelerate reduction whereas electron donating groups lowers reduction. Since 4-aminophenol undergoes reversible reaction the hydroxyl group of the phenol was deprotonated which gave well defined oxidation peak and followed by reduction peak.
The probable electrochemical reactions of 4-aminophenol has shown in the Scheme.1

\[
\begin{align*}
\text{PhOH} & \quad \quad \quad -\text{H}^+ -\text{e}^- \\
\text{NH}_2 & \quad \quad \quad +\text{H}^+ +\text{e}^- \\
\text{PhNH}_2 & 
\end{align*}
\]

**Scheme. 1.** Mechanism of electrochemical redox reaction of 4-aminophenol at CTAB/CPE

**Fig. 1.** Cyclic voltammogram of 1 mM \(\text{p-aminophenol}\) at (a) Bare Carbon paste electrode (b) CTAB/CPE in 0.1 M PBS of 7.5 pH; Sweep rate- 100 mVs\(^{-1}\)

**3.2. Effect of scan rate**

The effect of scan rate on the redox of 4-aminophenol was examined in 0.1 M phosphate buffer solution of pH-7.5 as a supporting electrode. Fig. 2(a) shows both the anodic and the cathodic peak currents linearly increase with the scan rate over the range of 50 to 500 mVs\(^{-1}\), suggesting that the electron transfers for 4-aminophenol at the CTAB modified CPE is adsorption controlled reaction. Fig. 2(b) shows the linear relationship between the scan rate vs. anodic peak currents of 4-amino phenol at CTAB/CPE. The cathodic peak shifted towards positive potential with increased in scan rate.

**3.3. Effect of concentration of 4-amino phenol**

Fig.3(a) shows the CV curves of different concentration of 4-aminophenol at CTAB/CPE was increased from 1 mM to 5 mM in 0.1 M phosphate buffer solution at pH-7.5 at a sweep rate of 100 mVs\(^{-1}\). Both the anodic and cathodic peak current increases linearly with the
concentration of 4-aminophenol and the plot of current versus concentration obeys Randles-Sevc equation, which implies that the electrode process is adsorption controlled reaction.

**Fig. 2(a).** Cyclic voltammograms of 1 mM para amino phenol in 0.1 M phosphate buffer solution at pH 7.5 using a CTAB/CPE at scan rates of (curve a) 50 mVs⁻¹, (curve b) 100 mVs⁻¹, (curve c) 150 mVs⁻¹, (curve d) 200 mVs⁻¹, (curve e) 250 mVs⁻¹, (curve f) 300 mVs⁻¹, (curve g) 350 mVs⁻¹, (curve h) 400 mVs⁻¹, (curve i) 450 mVs⁻¹, (curve j) 500 mVs⁻¹, (b). Plot of anodic peak current vs. scan rate.

As the concentration increases the first anodic peak potential is followed by the another anodic peak with the peak potential difference of 230 mV is due to the adsorption of first oxidised product and allowed the following scan at stepwise oxidation process. It was also observed that the cathodic peak potential shift towards negative values and anodic peak potential shift towards positive side. This kind of shift in $E_p$ in the cathodic and anodic direction with increasing concentration of the 4-aminophenol indicates that the product of 4-aminophenol molecules are adsorbed over the electrode surface. The plot of current versus the concentration gives correlation coefficient value of $r^2=0.9942$ (Fig. 3b) which revealed the electrode process is adsorption controlled process. The detection limit of 4-aminophenol at CTAB/CPE was $10^{-7}$ M.

3.4. Effect of pH variation of buffer solution

In most cases, the solution pH is important to the electrochemical reaction. The pH was varied in the range from 5.0 to 9.0 with the 0.5 interval difference using 0.1 M phosphate buffer as the supporting electrolyte. Fig. 4(a) shows the cyclic voltammograms of the 4-aminophenol at different pH. The anodic peak potential shifted towards positive side and
cathodic peak potential $E_{pc}$ shifted towards more negative potential. The anodic and cathodic peak current of 4-aminophenol increased at pH 7.5. Fig. 4(b) shows the graph of different pH versus peak current, it could be confirmed that at pH 7.5 the electrode acts as a good sensor.

Fig. 3(a). Cyclic Voltammograms of different concentration of para amino phenol (a-g: 1 mM to 4 mM) at CTAB/CPE in 0.1 M PBS. Sweep rate – 100 mVs$^{-1}$ (b). Plot of peak current vs. concentration of 4-aminophenol. Scan rate: 100 mV/s

Fig. 4(a). Effect of pH on the oxidation of 4-aminophenol at the CTAB modified CPE (b). Plot of the relationship between solution pH and the oxidation peak current
3.5. Effect of Surfactant

Surfactants even in trace quantities can exert a strong effect on the electrode process. Adsorption of such substances at the electrode may inhibit the electrolytic process, bring about the irregularity in the voltammogram and cause shift in the wave to negative potential [26, 27]. The effect of surfactant concentration on 4-amino phenol oxidation/reduction peak currents are shown in Fig. 5(a) for immobilized form modified carbon paste electrode. The CTAB/CPE could increase the peak current due to the electrostatic interaction between the modifier and 4-aminophenol. 4-aminophenol has slight hydrophillic character which leads to the uniform distribution in the aqueous media. The peak current increases linearly with the increase in concentration of surfactant and optimised at 10 μL above which the voltammogram peak current could not be observed due to their high background current. The oxidation peak potential shift towards positive side and the reduction peak potentials tends to shift towards negative side. Hence the CTAB modified carbon paste electrode acts as good sensor for the determination of dopamine.

![Graph showing effect of CTAB concentration on current](image)

**Fig. 5.** Effect of different concentration of CTAB immobilised on the carbon paste electrode for cyclic voltammogram of 1 mM 4-aminophenol. Sweep rate- 100 mVs⁻¹

3.6. Stability and reproducibility of CTAB/CPE

Modified carbon paste electrode was switched into the sample was kept at room temperature and used the same without made it changes for the determination of 4-amino phenol. The current sensitivity of the modified electrode has been kept for one week is almost same as that of the freshly prepared modified electrode. Hence the relative stability of the CTAB/CPE is good and reproducibility upto 98%.
4. CONCLUSION

The modified electrode increased the amplitude of the current signal of 4-aminophenol when compared to non-coated carbon paste electrode and produced good response. A modified CTAB/CPE study revealed that 10 μL CTAB in carbon paste electrode enhanced the electrocatalytic activity of 4-aminophenol. The effect of the CTAB surfactant showed the formation of monolayer on the bare carbon paste electrode which could have made the better sensor for the detection of 4-aminophenol and also exhibited the good reproducibility.

REFERENCES

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

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A B S T R A C T
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 $5 \times 10^{-5}$ to $1 \times 10^{-4}$ M L$^{-1}$ with correlation co-efficient of 0.9924 which reveals the adsorption controlled process. The detection limit for dopamine was $5 \times 10^{-7}$ 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.

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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 excitatory 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], Alzheimer’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 infarction 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], polyether sulphonic acid [9], poly(4-vinylpyridine) [10], stearate [11], w-mercapto carboxylic acid [12], poly(monomercugenol) [13], overoxidised poly(1-(2-carboxyethyl) pyrrole [14], 4-aminophenylacetic acid [15], ionic liquid [16], overoxidised polyppyrrrole [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 PMEs 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.
In this present work a covalently modified carbon paste electrode with L-arginine biopolymer was fabricated via the electro-oxidation 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 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/Hg₂Cl₂/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-
trode. When the poly(L-arginine)/CPE was immersed in the solution containing 2 mM AA has shown an anodic peak at 6 mV and also diffused peak at the same potential to that of poly(L-arginine) modified CPE in blank solution of 180 mV. The oxidation peak potential was observed that shifted slightly positive with the increase in the scan rate. The experimental error bar graph is shown as per the number of trials of the experiment (scan rate variation) in Fig. 2B. A remarkable correlation co-efficient ($r^2 = 0.9976$) existed between the current and the scan rate which confirmed that the electrode reaction was an adsorption-controlled process.

3.3. Electrocatalytic oxidation of DA at the poly(L-arginine)/CPE

Cyclic voltammograms of DA at bare CPE (a) and poly(L-arginine)/CPE (b) in 0.1 M acetate buffer solution of pH 5.6 is shown in Fig. 3(A). At the bare CPE, DA exhibited a poor electrochemical response. But at the modified electrode the voltammograms showed a redox peaks with the potential value of the anodic and cathodic peaks of 280 mV and 213 mV respectively due to the electrostatic interaction between positively charged modifier and dopamine. Under the identical conditions, the poly(L-arginine)/CPE produced significantly increased peak current and gives a clear evidence of the catalytic effect.

Fig. 3(B) shows the voltammograms of dopamine concentration variation at the poly(L-arginine)/CPE at 0.1 M ABS of pH 5.6 revealed that the increase in both the anodic peak current and cathodic peak current linearly with increasing the concentration of dopamine and negligible shift in peak potential towards positive side. The linearity was found between the anodic peak current and the dopamine concentration variation with the correlation co-efficient value of 0.9924.

3.4. Effect of scan rate and pH on the determination of dopamine at poly(L-arginine)/CPE

The cyclic voltammograms of 0.1 mM DA on the poly(L-arginine) modified CPE at different scan rate is shown in Fig. 4. The observation was made to investigate the kinetics of the electrode reaction. With the increase of the scan rate, the redox peak current also increased gradually, indicating that direct electron transfer between DA and the modified electrode surface. In the range from 50 to 150 mV s$^{-1}$ the redox peak current were proportional to the scan rate ($i_{pa}(10 \mu A) = 16.290 + 1.147v$) and the correlation coefficient was 0.9995 which indicates that the electron transfer reaction was adsorption-controlled process.

The effect of pH on the formal potential was investigated by cyclic voltammetry in the solution containing 1 mM DA. Cyclic voltammograms obtained at poly(L-arginine)/CPE in 0.1 M acetate buffer solutions of different pH values at scan rate of 50 mV s$^{-1}$. The anodic and cathodic peak potentials of DA were shifted to a less positive potential with the increase of pH value because the negative carboxylic acid group on the poly(L-arginine) electrode surface increases with decreasing solution pH. So more DA cations were attracted to the electrode surface [27]. The values of $\Delta E_p$ which were dependent on the pH value of the buffer solution. The experimental error bar graph of peak potential difference versus pH variation is shown in Fig. 4B. The peak potential of DA oxidation shifted negatively at a slope of $-65$ mV/pH unit, indicating equal number of electrons and protons involved in the oxidation process.
0.2 mM uric acid solution and the anodic peak potential makes a negligible shift towards positive side. The voltammogram curve a and c shows the uric acid at bare and PLE/CPE respectively, curve b shows for blank solution voltammogram at poly(β-arginine)/CPE.

3.6. Simultaneous voltammetric studies in mixed solution of AA, DA and UA

Construction of effective methods for resolution of responses and simultaneous determination of AA and DA is very important in analytical and clinical chemistry. Many attempts have been performed for the preparation of modified electrodes that are able to resolve the voltammetric responses and provide the possibility of simultaneous detection of AA and DA [29,30]. Fig. 6 shows that the cyclic voltammograms of 2 mM AA, 0.1 mM DA and 0.2 mM UA of the different concentration in 0.1 M ABS of pH 5.6 at a BCPE (curve a). While three distinct anodic peaks were obtained at the poly(β-arginine)/CPE (curve b). The observation clearly indicates that the BCPE failed to separate each voltammetric signals of AA, DA and UA. The fouling effect of the electrode surface with the oxidized products of AA–DA are the reasons for the single broad peak for AA and DA mixture [5]. Poly(β-arginine)/CPE exhibited three well defined oxidation peaks at 20, 305 and 483 mV corresponding to AA, DA and UA respectively. Since the oxidation peak potential of AA was shifted to negative potential than that of DA. The difference between the oxidation peak potentials of AA–DA was 285 mV and DA–UA was 178 mV. The results showed that the sensitivity of the method for DA was more than AA. A reason for this sensitivity may be the more reversibility, antibiofouling, large surface area and faster kinetics of the electron transfer for the anodic oxidation of AA relative to DA.

Interference studies were also studied by the differential pulse voltammogram that were obtained for the oxidation of dopamine, ascorbic acid and uric acid at the poly(arginine)/CPE in 0.1 M ABS. The peak potential difference between the AA–DA, AA–UA and DA–UA were found to be 264 mV, 436 mV and 172 mV respectively could be observed in Fig. 7(A). Interestingly the peak current for dopamine was increased linearly with the increase in dopamine concentration at 256 mV has shown in Fig. 7(B). The interference of ascorbic acid oxidation peak was much in dopamine at bare carbon paste electrode. Fig. 7(C) shows the DPV that were obtained at the poly(arginine) during the change of concentration of ascorbic acid from $1 \times 10^{-3}$ M to $7 \times 10^{-3}$ M and 0.1 mM DA. This results indicated that the interference of AA with DA was resolved at the poly(arginine)/CPE. The dopamine limit of detection was found to be $1 \times 10^{-7}$ M L$^{-1}$.

3.5. Voltammetric response of UA at PLE/CPE modified electrode

Fig. 5 shows the cyclic voltammogram of UA at poly(β-arginine)/CPE and BCPE in 0.1 M L$^{-1}$ ABS of pH 5.6 illustrated that the oxidation peak current of UA at poly(β-arginine)/CPE was more than three times higher to that of bare carbon paste electrode in

which is close to the theoretical value of 59 mV/pH unit for one electron and one proton [28].

**Fig. 4.** (A) Cyclic voltammograms of $1 \times 10^{-4}$ M DA at different scan rate (a-k; 50, 60, 70, 80, 90, 100, 110, 120, 130, 140 and 150 mV s$^{-1}$) in 0.1 M ABS (pH 5.6). (B) Graph of $E_m$ vs different pH.

**Fig. 5.** Cyclic voltammogram of bare CPE (curve a) and poly(β-arginine)/CPE (curve b and c) in presence of $0.5 \times 10^{-3}$ M UA (curve a and c) and in the absence of UA (curve b) in 0.1 M ABS of pH 5.6 at scan rate 50 mV s$^{-1}$.
3.7. Analysis of dopamine injection sample

The applicability of the modified electrode as an electrochemical sensor was tested for the determination of DA hydrochloride injection. The concentration of DA hydrochloride in the injection was determined by applying a calibration plot using the procedure proposed in the effect of concentration studies in the standard dopamine solution. The results obtained after the standard addition method are presented in Table 1. Recoveries from 97 to 102.5% of dopamine were obtained for dopamine hydrochloride injection samples (n = 5 repetitions). This is an evidence of the accuracy of the proposed procedure. The statistical calculations for the results suggested good precision for the cyclic voltammetric method which indicating that the poly(l-arginine) modified carbon paste electrode can be used for determinations of dopamine hydrochloride injection samples.

4. Conclusion

In the present work, the electropolymerisation of l-arginine on the carbon paste electrode produced a stable polymeric film. This study has shown that the poly(l-arginine)/CPE not only exhibited strong electrocatalytic activity towards the oxidation of DA, AA and UA were also resolved the overlapping anodic peak of DA and AA into two-well resolved peaks. The high sensitivity and selectivity together with the very easy preparation and surface regeneration of the modified electrode and the reproducibility of the voltammetric response made this characteristics modified electrode was very useful in the construction of sample devices for the simultaneous determination of dopamine in the presence of interfering compounds such as ascorbic acid and uric acid in the field of electroanalytical chemistry and also it can be used as sensors in the medicine field for the diagnosis of dopamine deficiency.

Table 1

<table>
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<tr>
<th>No</th>
<th>Spiked DA (mg)</th>
<th>DA found (mg)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
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<td>2.98</td>
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</table>

Fig. 7. (A) Differential pulse voltammogram of 0.1 mM DA, 2 mM AA and 0.5 mM UA at Modified electrode in pH 5.6 ABS. Scan rate: 10 mVs⁻¹. (B) Differential pulse voltammogram of different DA concentration (a–g: 10–70 μM). (C) DPV recordings of DA at poly(l-arginine)/CPE in the presence of different concentrations of AA (mM): (a) 1; (b) 2; (c) 3; (d) 4; (e) 5; (f) 6 and (g) 7.

References


Synthesis of MgFe₂O₄ nanoparticles and MgFe₂O₄ nanoparticles/CPE for electrochemical investigation of dopamine†

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Magnesium ferrite nanoparticles (MgFe₂O₄ NPs) were prepared by a solution based method using magnesium sulphate (MgSO₄), ferrous sulphate (FeSO₄), dl serine and NaOH as a precipitant and the obtained precipitation was calcinated under 500 °C for 4 h. The resulting material was characterized by using X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The MgFe₂O₄ NPs were used for preparation of MgFe₂O₄ NPs/carbon paste electrode (MgFe₂O₄ NPs/CPE) and applied for electrochemical investigation of dopamine (DA) which exhibits good electrocatalytic activity for investigation of DA at physiological pH 7.4. The effect of pH range from 5.5 to 8.0 was studied and the result shows that the redox peak current was maxima at pH 7.5 and the redox peak was pH dependent with a slope of 0.061 V/pH. The scan rate effect was found to be an adsorption-controlling electrode process. The electrocatalytic currents increased linearly with an increase in DA concentration in the range 0.1–1.2 μM and the detection limit was found to be 7.7 × 10⁻⁵ M. The proposed method was successfully applied to the determination of DA in injection samples.

1. Introduction

Magnesium ferrite, MgFe₂O₄, as a soft magnetic n-type semiconductor, is an important member of the spinel family. Apart from the applications of its magnetic properties, it can be used as a heterogeneous catalyst, adsorption and humidity sensor, oxygen sensor, sensor technology and it has been demonstrated that this material can be used for thermal coagulation therapy, in which tumors are locally heated by an application of alternating magnetic fields.

It is well known that properties of ferrite materials strongly depend on the preparation conditions. At present, chemical methods, including coprecipitation method have been reported and recently the synthesis of leaf-like CuO nanoparticles and a Nafion/GOD/CuO modified electrode was used for detection of glucose, the synthesis of CuO nanoparticles and their modified gold electrode was used for investigation of rutin, NiFe₂O₄/MWCNTS/GCE was used for electrochemical investigation of hydrazine, silver pentacyanonitrosylferrate films modified electrode was used for investigation of L-cysteine, gold nanoparticles modified carbon paste electrode was used for determination of acetaminophen and atenolol.

Quantitative determination of dopamine (DA) in human physiological fluids is of considerable significance in both biochemical and clinical diagnosis. Methods for the detection of DA include chemiluminescence, fluorimetry, ultraviolet-visible spectrometry, capillary electrophoresis (CE-luminescence) and electrochemical methods. The electrochemical method detection is a simple, sensitive and environmentally friendly detection method that is even suitable for the analysis of colored or turbid samples. Particularly the development of voltammetric sensors for the determination of secretion neurotransmitters, such as dopamine (DA) and other catecholamine, that exist in the mammalian central nervous system has received a lot of interest. Among the catecholamines, DA has attracted much interest because the change in DA levels has proved to be a very effective route towards understanding brain functions, such as learning and memory formation, and the physiological and pathological process of Parkinson’s disease.

Electrochemical detection of DA and AA by using LaFeO₃ nanoparticles, CdO nanoparticles, chemically modified carbon paste electrode, poly (Naphthol Green B) film graphite pencil electrode and gold nanoparticles modified ITO electrode has been reported. So in this work, a simple solution based method previously reported was used for the preparation of MgFe₂O₄ NPs with average crystalline size 15 nm and SEM morphology shows particle like small nanograins with average size 20–50 nm. The MgFe₂O₄ NPs/CPE exhibits enhancement of current...
response for investigation of dopamine at pH 7.4 in 0.2 M phosphate buffer solution and the electrocatalytic current increases linearly with increase in concentration of DA and the detection limit was found to be \(7.7 \times 10^{-4}\) M. The proposed method was successfully applied to the determination of DA concentration in injection samples.

2. Experimental

2.1. Apparatus

Cyclic voltammetric experiments were performed with a Model 660c (CH Instruments) Potentialstat/Galvanostat. A conventional three electrode cell is employed and the bare or MgFe\(_2\)O\(_4\) NPs/CPE (3.0 mm diameter) as a working electrode, a saturated calomel electrode as a reference electrode and a platinum electrode as a counter electrode. XRD studies using a Phillips (with X’lerator detector) X-ray diffractometer. Structural morphology of the synthesis NPs was studied using a JEOL JSM-848 scanning electron microscope (SEM).

2.2. Chemicals and solutions

Magnesium sulphate (MgSO\(_4\)), ferrous sulphate (FeSO\(_4\)) and perchloric acid (HClO\(_4\)) were purchased from sd. fine chemicals. Dopamine hydrochloride, sodium dihydrogen ortho phosphate (NaH\(_2\)PO\(_4\)), disodium hydrogen phosphate (Na\(_2\)HPO\(_4\)) and silicon oil from Hi Media chemicals. dl-Serine, absolute ethanol (99.9%), sodium hydroxide (NaOH) and graphite powder was from Merck chemicals and all chemicals are of analytical grade quality. DA stock solutions (25 mM) were prepared by adding DA to 0.1 M perchloric acid. Phosphate buffer is prepared by adjusting the pH 7.4 with 0.2 M NaH\(_2\)PO\(_4\) and Na\(_2\)HPO\(_4\) solution. All the aqueous solution was prepared by using double distilled water.

2.3. Preparation of MgFe\(_2\)O\(_4\) NPs

In a typical experiment, the first solution 0.2 M MgSO\(_4\), 0.4 M FeSO\(_4\) and 1.2 M dl serine was dissolved in 250 ml of deionized water and the second solution was prepared by 3 M NaOH pallets in 250 ml of deionized water and the first solution was added to second solution with continuous stirring. The obtained precipitate solution was taken in the condenser and boiled at 100\(^\circ\)C temperature for about 2 h then the hot solution was filtered by using whatmann filter paper (grade-41) and dried at 80\(^\circ\)C in a hot air oven for about 1 h. The dried precipitate was transferred to a silica crucible and ignited at 500\(^\circ\)C for about 4 h. Then the obtained powder was washed with ethanol three to four times to remove impurities present in MgFe\(_2\)O\(_4\) NPs.

2.4. Preparation of bare CPE and modified CPE

The bare CPE (BCPE) was prepared by hand mixing of 70% graphite powder with 30% silicon oil in an agate mortar for about 30 min to produce a homogenous carbon paste. The paste was packed into the homemade cavity and smoothed on weighing paper. The MgFe\(_2\)O\(_4\) NPs/CPE was prepared by adding 10, 20, 30 and 40 mg MgFe\(_2\)O\(_4\) NPs to the above mentioned graphite powder and silicon oil mixture.

3. Results and discussion

3.1. Characterization

X-ray diffraction patterns were recorded using Cu-K\(_{\alpha}\) (\(\lambda = 1.5438\) Å) radiation sources for identification of the crystalline structure and average crystalline size of MgFe\(_2\)O\(_4\) NPs. Fig. 1 shows that the obtained diffraction pattern reflects (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes belonging to a cubic spinel structure which are in good agreement with the standard pattern (JCPDS 17-0465). The average crystallite diameter can be determined from the full-width at half-maximum (FWHM) of the (311) diffraction peak by using the Scherrer formula:

\[
D = \frac{0.89 \lambda}{(\beta \cos \theta)}
\]

where \(\lambda\) is the X-ray wavelength, \(\theta\) is the Bragg diffraction angle, and \(\beta\) is the full-width at half-maximum. The calculated value is 15 nm. SEM observations reveal that all the products consist of a large quantity of small nanograins with average size around 20–50 ± 1 nm, as shown in Fig. 2.

3.2. Effect of MgFe\(_2\)O\(_4\) NPs in CPE for investigation of DA

The effect of MgFe\(_2\)O\(_4\) NPs in the CPE on the peak current for the investigation of 1\(\times\)10\(^{-4}\) M DA in 0.2 M phosphate buffer solution for investigation of dopamine at pH 7.4 in 0.2 M phosphate buffer solution and the electrocatalytic current increases linearly with increase in concentration of DA and the detection limit was found to be \(7.7 \times 10^{-4}\) M. The proposed method was successfully applied to the determination of DA concentration in injection samples.

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solution at pH 7.4 was studied by cyclic voltammetry technique. The modified CPE with 20 mg of MgFe₂O₄ NPs enhanced high anodic peak current as compared with the BCPE, 10, 30 and 40 mg of MgFe₂O₄ NPs as shown in Fig. 3.

3.3. The response of DA at the bare CPE, and MgFe₂O₄ NPs/CPE

Fig. 4 shows the electrochemical responses of 1×10⁻⁵ M DA in 0.2 M phosphate buffer solution of pH 7.4 at the BCPE and the MgFe₂O₄ NPs/CPE with scan rate 0.1 V s⁻¹. At the BCPE, the difference between the anodic peak potential ($E_{pa}$) 0.136 V and the cathodic peak potential ($E_{pc}$) 0.085 V is reversible wave with $\Delta E_{p}$ 0.051 V. However, DA peak currents significantly increased at the MgFe₂O₄ NPs/CPE, with the anodic peak 0.124 V and the corresponding cathodic peak potential is 0.087 V and corresponding $\Delta E_{p}$ 0.037 V.

Compared with BCPE the remarkable enhancement in the peak currents with reduction of over potential showed catalytic effects of the MgFe₂O₄ NPs. The mechanism may be MgFe₂O₄ NPs combined with the hydrogen bond of the hydroxyl of DA, which activated hydroxyl, weakened the bond energy of O–H and improved the electron transfer rate. At the same time, high surface area of the MgFe₂O₄ NPs improved the electrode contact area of DA.

3.4. Effect of pH value on the determination of DA at the MgFe₂O₄ NPs modified CPE

The pH of the supporting electrolyte has a significant influence on the DA electrocatalysis at the MgFe₂O₄ NPs/CPE by affecting both peak current and peak potential. The effect of pH value on the determination of DA in PBS solution at MgFe₂O₄ NPs/CPE was carefully investigated in a wider pH range of 5.3–7.7 of 1×10⁻⁵ M DA in the different pH solutions. The cyclic voltammograms in Fig. 5 and Fig. 6, illustrate the dependency of the DA anodic peak current and formal potential ($E^0$ (V)) on the buffer solution pH. It can be seen that the peak current of DA increases with increasing pH value until it reaches 7.5 (shown with closed circles (●)). The formal potential of DA shifts negatively with the increase of the pH value of solution and depends linearly on the pH value in the range of 5.3–7.7 with a slope of 0.061 V/pH ($R^2 = 0.991$) (shown with line (○)). It demonstrates that the redox of DA undergoes a two-electron and two-proton process, which is consistent with that reported in literature.[34–37]

3.5. Effect of scan rate on the peak currents

The effect of scan rate for 1×10⁻⁵ M DA in 0.2 M PBS at pH 7.4 was studied by cyclic voltammetry at MgFe₂O₄ NPs/CPE as shown in Fig. 7. MgFe₂O₄ NPs/CPE showed an increase in the redox peak current with increasing scan rate (0.05 to 0.45 V s⁻¹). The graph of redox peak current ($I_{pa}$) vs. scan rate ($ν$) was plotted. The graph obtained has good linearity between the scan rate and redox peak current (Fig. 8). In the range from 0.05–0.45 V s⁻¹ the redox peak currents were proportional to $ν$. The correlation coefficient ($R^2$) was 0.9993, which indicates the
3.6. Concentration effect of DA

The differential pulse voltammetric technique was used for analysis of DA concentration which was varied from 0.1 to 12 μM as shown in Fig. 9. For the MgFe₂O₄ NPs/CPE, the corresponding graphs of anodic peak current versus concentration of DA shows two linear relationship ranges 0.1 to 0.6 μM and 0.8 to 12 μM with the linear regression equations as

\[ I_{pa} (A) = \frac{15.28 C_m}{C_0^{1.00}} + \frac{4.628}{C_0^{0.10}} \]

and

\[ I_{pa} (A) = \frac{4.776 C_m}{C_0^{1.00}} + \frac{5.696}{C_0^{0.10}} \]

respectively. The correlation coefficient for the first linearity was 0.987, the detection limit for DA in the linear range region was found to be 7.7 μM for MgFe₂O₄ NPs/CPE which was calculated according to the equation of

\[ LOD = \frac{KS}{0.1} \]

where \( K \) is a constant related to the confidence level.

According to the}

![Fig. 6](image1.png)  
**Fig. 6** Shows the dependence of the DA oxidation peak current in closed circles (●) and with line (○-○) for formal redox potential versus pH with the scan rate of 0.1 V s⁻¹.

![Fig. 7](image2.png)  
**Fig. 7** Cyclic voltammograms of MgFe₂O₄ NPs/CPE in 0.2 M PBS solutions containing 1 × 10⁻⁵ M DA at different scan rates (0.05–0.45 V s⁻¹).

![Fig. 8](image3.png)  
**Fig. 8** Graph shows the linear relationship between the peak current and the scan rate.

![Fig. 9](image4.png)  
**Fig. 9** Differential pulse voltammogram of (a) 1.0 × 10⁻⁷ M, (b) 2 × 10⁻⁷ M, (c) 3 × 10⁻⁷ M, (d) 4 × 10⁻⁷ M, (e) 6 × 10⁻⁷ M, (f) 8 × 10⁻⁷ M, (g) 1 × 10⁻⁶ M, (h) 2 × 10⁻⁶ M, (i) 3 × 10⁻⁶ M, (j) 4 × 10⁻⁶ M, (k) 5 × 10⁻⁶, (l) 6 × 10⁻⁷, (m) 8 × 10⁻⁷, (n) 1.0 × 10⁻⁵ and (o) 1.2 × 10⁻⁵ M DA in 0.2 M phosphate buffer solution of pH 7.4 at MgFe₂O₄ NPs/CPE.

electrode reaction was adsorption controlled which was supported by previously reported literatures.³⁸–⁴⁰

3.6. Concentration effect of DA

The differential pulse voltammetric technique was used for analysis of DA concentration which was varied from 0.1 to 12 μM as shown in Fig. 9. For the MgFe₂O₄ NPs/CPE, the corresponding graphs of anodic peak current versus concentration of DA shows two linear relationship ranges 0.1 to 0.6 μM and 0.8 to 12 μM with the linear regression equations as

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and

\[ I_{pa} (A) = \frac{4.776 C_m}{C_0^{1.00}} + \frac{5.696}{C_0^{0.10}} \]

respectively. The correlation coefficient for the first linearity was 0.987, the detection limit for DA in the linear range region was found to be 7.7 μM for MgFe₂O₄ NPs/CPE which was calculated according to the equation of \( LOD = \frac{KS}{0.1} \), where \( K \) is a constant related to the confidence level.
Table 1 Detection of DA in injection samples (n = 5)

<table>
<thead>
<tr>
<th>Tested Sample</th>
<th>Added (µg mL⁻¹)</th>
<th>Found (µg mL⁻¹)</th>
<th>RSD (%)</th>
<th>Recovery (%)</th>
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suggestion of IUPAC, the value of K is 3 at the 99% confidence level, S⁰ is the standard deviation of ten blank-solution measurements (no added DA) and S is the slope of the calibration graph, the proposed electrode showed relatively lower detection limits than recently reported and calculated by using the same formula.

3.7. Analytical application

The modified electrode was applied to the determination of dopamine hydrochloride injection. The DA injection sample purchased from Sterile Specialities India Pvt Ltd had a specified content of DA 40.0 mg mL⁻¹ and the sample was used after suitable dilution. The results are shown in Table 1 and the sample was used for application of determination of biological active compounds, injection sample and other neurotransmitters.

Conclusions

MgFe₂O₄ NPs with average crystalline size 15 nm have been synthesized by solution based method and MgFe₂O₄ NPs/CPE shows good sensor application for electrochemical investigation of DA with detection limit 7.7 × 10⁻⁸ M. The proposed methods can be applied to the detection of DA in injections. Hence this current synthetic method extended too many metal oxides, ferrites for synthesis and their modified electrode used as sensor for application of determination of biological active compounds, injection sample and other neurotransmitters.

Acknowledgements

The authors are very thankful to the University Grant Commission, Government of India, New Delhi for the fellowship and funding given throughout project F.No 35-156 \ 2008 (SR).

Notes and references

Synthesis of ZnO and its surfactant based electrode for the simultaneous detection of dopamine and ascorbic acid

Mohan Kumar, a B. E. Kumara Swamy, b Sathish Reddy, b T. V. Sathisha b and J. Manjanna a

ZnO was synthesized by a mechanochemical method and characterized by powder X-ray diffraction, UV-visible absorption, scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). ZnO/CTAB and ZnO/TX-100 modified carbon paste electrodes were used as electrochemical sensors for dopamine. The Triton-X 100 (TX-100) modified carbon paste electrode shows electrocatalytic properties and an enhancement in the peak currents for dopamine. CTAB modified carbon paste electrodes are less sensitive for the determination of dopamine. The effect of ZnO concentration, scan rate and concentration of dopamine (DA) and ascorbic acid (AA) was varied and a simultaneous determination of DA and AA at the ZnO/TX-100 CPE was carried out.

1 Introduction

Semiconductor particles are currently receiving a lot of attention for a wide range of new applications in various fields. Zinc oxide (ZnO) is a versatile material that has achieved application in chemical sensors, piezoelectric transducers, transparent electrodes, photo catalysts and solar cells. 1-3 Zinc oxide, a representative II–VI compound semiconductor, has attracted considerable attention due to its many striking properties, such as a wide and direct band gap of 3.37 eV and a large exciton binding energy of 60 MeV at room temperature. 4-5 There are many methods to synthesise rod shaped ZnO, such as the sonochemical method, 6 low temperature, 7 solvothermal-assisted heat treatment method 8 and electrochemical. 9 The ZnO was prepared using a solution free mechanochemical method based on a modified version of the method reported in the literature 10 and the obtained rod shaped ZnO was further conjugated with surfactant and used as an electrochemical sensor for the detection of dopamine.

DA and AA are compounds of great biomedical and neurochemical interest, playing a potential role in human metabolism. DA is one of the most significant catecholamines, functioning as a neurotransmitter in the central nervous system and a medicament to drug addiction and Parkinson’s disease. 10-12 AA is an essential vitamin for humans, and has been used in preventing and treating colds, mental illness, infertility, cancer and other diseases. 13 There are many methods for the detection of DA, including UV-visible spectroscopy, 14 fluorimetry, 15 chemiluminescence, 16 capillary electrophoresis 17 and electrochemical methods. 18 Among these methods, electrochemical detection is an important technique because of its low cost, fast speed, low detection limits and high accuracy. 19 The fabricated ZnO electrode was used for the electrochemical detection of DA.

For selective and sensitive determination of the DA concentration, the electrochemical technique has been proved as an advantageous one. The major problem is the interference of AA, which is also present in biological fluids at a very high concentration compared to the DA level. 20-21 The irreversibility and requirement of a high potential of bare electrode for the direct oxidation of DA and AA moreover oxidized at almost similar potential and often suffers from a pronounced fouling effect, which results in poor selectivity and reproducibility. 22-24 Various modified oxide particle electrodes such as CuO, MnO2, CdO, MoO3 and Mg2Fe2O4 have been studied in order to increase their sensitivity and selectivity. 25-29 Among different oxide particle modified electrodes, ZnO modified carbon paste based electrodes have been extensively studied. 30-37 Among the many modified carbon paste electrodes (MCPE) which determine DA in presence of AA, electro-active-polymer coated electrodes displayed excellent selectivity and sensitivity. 30

The present work describes the mechanochemical synthesis of rod shaped ZnO. The ZnO/CTAB modified electrode shows a decrease in sensitivity towards DA, and the ZnO/TX-100 electrode shows an increase in sensitivity towards DA. The prepared ZnO is characterized by powder XRD, UV-visible spectroscopy, SEM and EDS. The modified ZnO/TX-100 CPE was studied for an electrochemical investigation of the low concentration of DA in...
the presence of a high concentration of AA, in a phosphate buffer at pH 7.4. Thus the present study also presents an excellent method for the selective and sensitive detection of DA in the presence of AA and vice versa.

2 Experimental

2.1 Reagents and stock solution

The reactant, zinc acetate, Zn(CH$_3$COO)$_2$, was purchased from Nice Chemicals, and the oxalic acid, H$_2$C$_2$O$_4$·2H$_2$O, from SD Fine Chemicals. Dopamine hydrochloride (DA), ascorbic acid (AA), disodium hydrogen phosphate (Na$_2$HPO$_4$), sodium dihydrogen orthophosphate (NaH$_2$PO$_4$), CTAB, TX-100 and the silicone oil were procured from Himedia chemicals. The graphite powder (µm particle size) was supplied by Merck chemicals. All chemicals are of analytical grade quality and were used as supplied without further purification.

The stock solution of dopamine (25 mM) was prepared in 0.1 M perchloric acid, phosphate buffer of pH 7.4 (0.2 M) and ascorbic acid, prepared in double distilled water.

2.2 Preparation of ZnO particles

The rod shaped ZnO were synthesized according to the solution free mechanochemical method described elsewhere, with a slight modification. In a typical experiment, a mixture of 0.1 M of Zn(CH$_3$COO)$_2$ and 0.12 M of H$_2$C$_2$O$_4$·2H$_2$O was ground for about 30 min at room temperature in an agate mortar. The mixture was then taken for thermal decomposition at 450 °C for 30 min, finally producing the rod shaped ZnO.

2.3 Apparatus

The prepared ZnO was characterized by powder X-ray diffraction (PXRD) using CuK$_\alpha$ radiation (λ = 0.1543 nm) at 40 kV, at a scanning rate of 2° min$^{-1}$, in a PAN analytical ‘X’ PERT PRO X-ray diffractometer. UV-visible spectra were recorded on a UV-visible Spectro Photometer–Shimadzo (1650) using sonicated ZnO in double distilled water. Samples were loaded in a quartz cell and the measurement was taken in the wavelength range 200–800 nm. The structural analysis and composition of the ZnO sample was studied using a JEOL JSM-848 scanning electron microscope (SEM), equipped with energy-dispersive spectroscopy (EDS).

The cyclic voltammetric (CV) measurements and differential pulse voltammetric (DPV) measurements were performed on a Model 660c (CH Instruments). Electrochemical experiments were carried out in a three electrode cell system, which contained a bare carbon paste electrode (CPE), CPE/ZnO/CTAB, CPE/TX-100 or CPE/ZnO/TX-100 as the working electrode, an aqueous saturated calomel electrode (SCE) as the reference electrode and a Pt wire as the auxiliary electrode.

2.3.3 Carbon paste electrode. The carbon paste electrode was prepared by mixing 70% graphite powder and 30% silicone oil in an agate mortar for 30 min. The mixture was then packed into a homemade Teflon cavity and polished using smooth paper.

2.3.4 Modified carbon paste electrode. ZnO/CTAB MCPE was prepared by immobilizing ZnO/CTAB (Scheme 1) on the bare CPE. A 10 µL solution (2, 4, 6 and 8 mg) ZnO and 25 mM CTAB) was spread onto the bare CPE, and was incubated for 5 min. In preparing the ZnO/TX-100 MCPE, the same procedure was followed, but instead of CTAB, TX-100 was used.

3 Results and discussions

3.1 Characterization of prepared ZnO

The PXRD pattern of the obtained ZnO particles is shown in Fig. 1. It is indexed to the hexagonal wurtzite structure and matched with JCPDS 36-1451. All peak positions and relative peak intensities show no characteristic peaks of impurities, and the sample is highly crystalline. The UV-visible absorption spectra of the ZnO dispersed in double distilled water, with double distilled water as a reference is shown in Fig. 2. It shows a sharp absorption peak at the wavelength 376 nm and the sample has a bandgap of 3.26 eV that is slightly lower than that of bulk ZnO (3.37 eV). The micro structural analysis of ZnO was carried out using SEM with an EDS attachment. Fig. 3 shows the grown rod shaped ZnO, with a diameter of ~500 nm and a length of about µm, and some irregular shaped particles smaller than 500 nm. The EDS of ZnO shows the presence of zinc and oxygen without containing any impurities as shown in Fig. 4.

3.2 Electrochemical response of dopamine at the ZnO/CTAB modified carbon paste electrode (MCPE)

Fig. 5(a) shows the cyclic voltammograms for the different concentrations of ZnO with the CTAB (cationic surfactant) modified electrode at a scan rate of 100 mV s$^{-1}$, with a dopamine concentration of 2 × 10$^{-4}$ M in 0.2 M phosphate buffer solution (pH 7.4). A decrement in peak current was observed. Fig. 5(b) indicates that increasing the concentration of ZnO with CTAB decreases the anodic peak current. Therefore, the ZnO/CTAB modified electrode shows no electrocatalytic property.

Scheme 1 Modifying the CPE by the immobilization method.
3.3 Electrochemical response of dopamine at the ZnO/TX-100 modified carbon paste electrode

In order to optimize the amount of ZnO/TX-100/CPE, different concentrations of the ZnO conjugate with TX-100 and a nonionic surfactant (Scheme 2) in a CPE were used to determine the amount of $2 \times 10^{-4}$ M dopamine in a 0.2 M phosphate buffer (pH 7.4), at a scan rate of 100 mV s$^{-1}$, as shown in Fig. 6(a). The plot of the maximum peak current versus the different concentrations of ZnO in TX-100, presented in Fig. 6(b), shows the 6 mg ZnO/TX-100 solution response to the maximum current, and this optimized concentration is maintained during further
investigation. Fig. 7 shows the cyclic voltammograms obtained for (a) bare CPE, (b) TX-100 MCPE and (c) ZnO/TX-100 MCPE. The corresponding redox peak-potential difference $\Delta E_p$ was found to be 93 mV, 57 mV and 49 mV respectively, the result indicates that both TX-100 and ZnO/TX-100 MCPE exhibit better electrocatalytic activity than bare CPE. Among them, ZnO/TX-100 MCPE exhibits an enhanced current response, with a slight reduction of over potential than the TX-100 MCPE. This shows that the ZnO/TX-100 MCPE exhibits good electrocatalytic activity.

The schematic illustration of the electrocatalytic activity of DA on the ZnO/TX-100 MCPE is shown in Scheme 3. The cyclic
voltammograms of \( 2 \times 10^{-4} \) M DA at ZnO/TX-100 CPE in Fig. 8(a) show an increase in the anodic and cathodic peak current by increasing the scan rate from 0.05 to 0.5 V s\(^{-1}\). The graph of the anodic peak current \( (I_{pa}) \) vs. the scan rate \( (\nu) \) shows a linear relationship (Fig. 8(b)) and a good correlation coefficient \( (R = 0.99847) \). This linearity indicates an adsorption controlled reaction.

3.4 Electrochemical response of ascorbic acid and dopamine at the ZnO/TX-100 modified carbon paste electrode

Fig. 9 shows the cyclic voltammograms of \( 2.5 \times 10^{-3} \) M AA in a 0.2 M phosphate buffer solution (pH 7.4) at a bare CPE (dashed line) and a ZnO/TX-100 MCPE (solid line). A broad oxidation peak potential occurs at 0.307 V for the bare CPE and at 0.0714 V for the ZnO/TX-100 MCPE, showing a significant shift in oxidation peak potential.

The main aim is the simultaneous detection of AA and DA in a 0.2 M phosphate buffer solution of pH 7.4. Fig. 10 shows the cyclic voltammograms obtained for the electrochemical response of a solution containing \( 2 \times 10^{-4} \) M DA and \( 2.5 \times 10^{-3} \) M AA in a 0.2 M phosphate buffer solution (pH 7.4) at the bare CPE (dashed line) and the ZnO/TX-100 MCPE (solid line). The dashed line shows one broad peak for both analytes, indicating that the oxidation potentials of AA and DA are amalgamated and indistinguishable. The broad peak for the AA and DA mixture is because of the fouling effect of the electrode surface by the adsorption of the oxidation product AA and DA.

Similarly, the solid line shows that AA exhibits well-defined cyclic voltammetry waves, with a good separation from DA, because of the two well-defined oxidation peaks for AA and DA at 0.08 V and 0.19 V respectively, with a potential difference of 0.11 V.

Fig. 11(a) shows that the DPV analysis of AA in the presence of DA in a 0.2 M phosphate buffer solution (pH 7.4) exhibits a linear increase in the anodic peak current with an increase in the concentration of AA. The graph of the peak current versus the concentration of AA also exhibits good linearity as shown in Fig. 11(b). Fig. 12(a) shows that the DPV analysis of DA in the presence of AA in a 0.2 M phosphate buffer solution at pH 7.4 exhibits a linear increase in the anodic peak current with an increase in the concentration of DA. The graph of the peak current versus the concentration of DA also exhibits good linearity as shown in Fig. 12(b).

4 Conclusions

In the present study, rod shaped ZnO was mechanochemically synthesized by the chemical reaction between Zn(CH\(_3\)COO)\(_2\).
and H$_2$C$_2$O$_4$·2H$_2$O, via a bottom-up process, and also demonstrated that immobilizing the ZnO/CTAB and ZnO/TX-100 on to the CPE shows a decrement and an increment in the oxidation peak of DA in a 0.2 M phosphate buffer solution (pH 7.4). The ZnO/TX-100 MCPE exhibits good electrocatalytic activity towards AA in the presence of DA and vice versa, which allows the simultaneous investigation of bioactive molecules or neurotransmitters (AA and DA). It is expected that the high electrocatalytic behavior of the ZnO/TX-100 MCPE could hold great applications in the fields of electroanalytical chemistry and biosensors.

Acknowledgements

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Notes and references

Electrocatalysis of Dopamine by Alizarin and Triton-X 100 Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

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Abstract - The electrocatalytic oxidation of dopamine at alizarin and Triton X-100 modified carbon paste electrode has been studied by means of cyclic voltammetric technique in 0.2 M acetate buffer solution at pH 7.0. This suggests the effectively of surface modification of carbon paste electrode by Triton X-100 a non–ionic surfactant. Cyclic voltammetric investigations demonstrated the improved responses of dopamine. The modified electrode exhibited strong promoting effect and stability towards the detection of dopamine in mobilization and immobilization methods of surfactant. The presence of Triton-X 100 on the alizarin modified carbon paste electrode showed excellent electrocatalytic effect towards the detection of dopamine.

Key words- Dopamine, Alizarin, Modified Carbon Paste Electrode, Electrocatalytic Oxidation, Triton X-100, Cyclic Voltammetry

1. INTRODUCTION

Dopamine (DA) is one of the most significant catecholamines and belongs to the family of inhibitory neurotransmitters that exists in the mammalian central nervous system [1]. Since
its discovery in 1950s, DA has been of interest of neuroscientists and chemists. The loss of DA in the human body may result in some serious diseases such as Parkinsonism [2,3]. Therefore DA is currently the subject of intense research focus to neuroscientists and chemists and it is essential to develop rapid and simple methods for the determination of the concentration of DA. DA can be determined by electrochemical methods because it is an electrochemically active compound. So it is important to establish a fast, sensitive and selective method for the detection of DA [4]. DA is generated in various parts of central and peripheral nervous system and has an agonist action on $\beta$ adrenoceptors. DA has positive chronotropic and ionotropic effects on myocardium which stimulates cardiac contractility and enhances heart beat rate [5].

It is associated with proper functioning of several organs such as the heart, brain, and suprarenal glands. The determination of DA is a subject of great clinical significance for investigating its physiological functions and diagnosing nervous diseases resulting from DA abnormal metabolism, such as epilepsy and senile dementia [6]. There were many methods for the detection of DA, such as titrimetry [7], spectrophotometry [8], chemiluminescence[9], potentiometry [10] and voltammetric methods have been developed for this purpose. Electrochemical techniques have proved to be significantly advantageous to the biosciences. The DA is electroactive and can be detected electrochemically. However, the direct electroanalysis of DA at a bare electrode often suffers from the interferences of other commonly coexisting electroactive substances. The oxidation peak potential of AA is close to that of DA and the working electrode is often fouled owing to the accumulation of oxidized product [11,12]. In order to overcome these problems, different kinds of modifications were done to carbon paste electrode for the determination of DA.

Alizarin is an interesting compound for investigation in electroanalytical chemistry due to formation of conductive, electro-active films which make it as a key constituent, used for modification of electrodes [13]. Alizarin is an anthraquinone derivative, mordant vegetable dye (Scheme 1) and the detailed electrochemical investigation of alizarin by cyclic voltammetric method was reported [27,28].

Surfactant belongs to a class of molecules with surface active properties. This behaviour is due to their amphiphilic structure, which contains both a polar or hydrophilic head and non-polar or hydrophobic tail [14,15]. Surfactants are normally classified according to the head group type [16]. Micellar effects in electrochemistry are a subject of substantial current interest. Adsorption of surfactants on the electrode surface and solubilization of electrochemically active compounds in micellar aggregates might significantly change the redox potential, charge transfer coefficients and diffusion coefficients of electrode processes [17-19]. The addition of trace surfactants to the working solutions could effectively improve the signals of these substances. The applications of surfactants in electrochemistry and electroanalytical chemistry have been widely reported [20-29]. The cetyl trimethyl
ammonium bromide, a cationic surfactant was immobilized on carbon paste electrode and induced iron phthalocyanin modified carbon paste electrode for simultaneous determination of dopamine with ascorbic acid and uric acid by our group [30,31].

In this work, the adsorption of Triton X-100 (TX-100) at chemically modified alizarin carbon paste electrode (TX-100/AZMCPE) was explored by cyclic voltammetric technique which might be able to explain the enhancement effects of surfactants in electroanalytical chemistry. The results revealed not only the adsorptive behavior of TX-100 but also the influences of TX-100 adsorption on the surface of the electrode interface and the redox reactions in solution.

Scheme 1. Structure of Alizarin

2. EXPERIMENTAL PART

2.1. Reagents and chemicals

Alizarin (AZ), Dopamine (DA) and Triton-X 100 (TX-100) were obtained from Himedia chemical company and of analytical grade used without further purification. 25 mM DA stock solution was prepared in 0.1 M perchloric acid. Graphite powder of 50mm size was purchased from Loba and silicon oil was purchased from Himedia. TX-100 surfactant was dissolved in double distilled water to get $1 \times 10^{-5}$ M. The acetate buffer (0.1 M pH 7.0) was used as optimum measurements. Sodium hydroxide and acetic acid were used for increasing and decreasing the pH of the buffer. The water used in all the measurements was double distilled.

2.2. Apparatus

Cyclic Voltammetry (CV) was performed in a model EA-201 Electroanalyser (EA-201 Chemilink system). All experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire as counter electrode and saturated calomel as reference electrode.
2.3. Preparation of bare carbon paste electrode (BCPE) and alizarin modified carbon paste electrode (AZMCPE)

The carbon paste electrode was prepared as follows, 70% graphite powder and 30% silicone oil were mixed by hand about 45 minutes to produce a homogeneous bare carbon paste electrode (BCPE). The paste was then packed into the cavity of a homemade carbon paste electrode and smoothed on a weighing paper. The alizarin modified carbon paste electrode (AZMCPE) was prepared by grinding different percentage of AZ (0.21, 0.41, 0.62 and 0.83%) along with 70% graphite powder and 30% silicone oil.

3. RESULTS AND DISCUSSION

3.1. Effect of AZ as a modifier towards the detection of DA

AZ is a derivative of anthraquinone mordant vegetable dye used as a modifier in the preparation of AZMCPE. The characterization of AZMCPE was investigated by using cyclic voltammetric technique. AZMCPE was prepared of different ratio by adding different percentage of AZ. By increasing the percentage of AZ from 0.21% to 0.62% in the carbon paste electrode, the electrochemical redox peak current of 50 µM DA goes on increasing in 0.2M acetate buffer as supporting electrolyte. Further increase of AZ the current signal of DA decreases. The graph of anodic peak current vs. different percentage of AZ in carbon paste electrode was plotted and shown in Fig. 1. Maximum current signal was noticed in 0.62% AZMCPE, so we have chosen 0.62% AZMCPE as optimum for the study of all other parameters.

3.2. Electrochemical response of DA at AZMCPE

Fig. 2 shows the cyclic voltamogramms of 50 µM DA at BCPE and AZMCPE in 0.2 M acetate buffer solution at pH 7 and scan rate 100 mV s⁻¹. At the BCPE the cyclic voltammogram of DA (dotted line) shows an oxidation peak potential at 155 mV and reduction peak potential at 100 mV with low current signals. The electrochemical response of DA at AZMCPE showed a well defined redox wave of DA with strong increase of the redox peak current (solid line). The oxidation peak potential occurs at 162 mV and reduction peak potential at 104 mV respectively, with the peak potential separation (ΔEₚ) 58 mV. The value of iₚa/iₚc was about 1.15, and negligible shift in the redox peak potentials, shows the characteristics of the reversible natured voltammogram. The modified electrode exhibited strong promoting effect and high stability towards the electrochemical oxidation of DA. It was observed that the peak currents enhanced at the AZMCPE, which provides more evidence for asserting that the AZ in the CPE possessed high electrocatalytic activity towards the DA detection.
Fig. 1. Effect of percentage of AZ on anodic peak current in 50 µM DA and 0.2 M acetate buffer solution scan rate: 100 mV s\(^{-1}\)

![Graph showing the effect of percentage of AZ on anodic peak current](image1)

Fig. 2. Cyclic voltammograms of BCPE (dotted line) and AZMCPE (Solid line) in the presence of 50 µM DA and 0.2 M acetate buffer, in pH 7.0 scan rate: 100 mV s\(^{-1}\)

![Cyclic voltammograms of BCPE (dotted line) and AZMCPE (Solid line)](image2)

3.3. Effect of TX-100 Surfactant

Initially, cyclic voltammograms were recorded for TX-100/AZMCPE in a solution containing DA (50 µM) in 0.2 M acetate buffer solution at pH 7.0. The TX-100/AZMCPE was calibrated by varying the immobilization time interval from 5 min to 25 min. The graph
of $i_{pa}$ vs. different time in minutes was plotted (Fig. 3). The higher current signal was obtained at 10min time intervals. Hence, the 10min time gap was fixed for further investigation. The effect of immobilization study was done by varying the concentration of TX-100 in µL (5 µL to 25 µL) on to the surface of AZMCPE with the immobilization time interval 10 min.

Fig. 3. Graph of $i_{pa}$ vs. time in min at 10 µL of $1 \times 10^{-5}$ M TX-100 on to the surface of AZMCPE in presence of 50 µM DA and 0.2 M acetate buffer at scan rate: 100 mV s$^{-1}$

Fig. 4. Graph of $i_{pa}$ vs. different concentration of $1 \times 10^{-5}$ M TX-100 in µL on to the surface of AZMCPE in presence of 50 µM DA and 0.2 M acetate buffer at pH-7.0 scan rate: 100 mV s$^{-1}$
The graph of $i_{pa}$ vs. different concentration of TX-100 was plotted (Fig. 4). The experimental results revealed that the $1 \times 10^{-5}$ M TX-100 with 10 µL concentration with 10 min time gap showed good electrocatalytic activity towards the detection of DA.

The Fig. 5 shows the comparison of bare CPE (dotted line), AZMCPE (dashed line) and TX-100/AZMCPE(solid line) towards the detection of DA. Among all the TX-100/AZMCPE showed the excellent electrocatalytic activity for detection of DA. The mobilization effect of TX-100 towards the electrcrocatalytic oxidation of DA was studied by addition of different concentration of TX-100 in µL (5 µL–25 µL) directly into the solution containing the DA (50 µM) in 0.2 M acetate buffer solution as supporting electrolyte. However, the better redox current signal was obtained at 10 µL addition of TX-100 which could be seen in Fig. 6. The results show the effect of surfactant concentration into the solution that is mobilization method also catalyzes the oxidation of DA. When the surfactant concentration is below 10 µL, the CMC of surfactant at room temperature, both $i_{pa}$ and $i_{pc}$ increases rapidly with the increase of surfactant concentration. The concentration of the surfactant was increased from 5 µL to 25 µL into the solution and onto the surface that is both mobilization and immobilization method as shown in Fig. 6 and Fig. 4 respectively. The redox current signal for DA was superior in immobilization when compared to mobilization method. From this overall we can say that immobilization is more favorable than mobilization method [32].

![Cyclic voltammogram of 50 µM DA at a) BCPE (dotted line) b) AZMCPE (dashed line) c) 10 µL TX-100 (solid line) immobilized AZMCPE in 0.2 M acetate buffer solution (pH 7.0) at scan rate:100 mV s$^{-1}$](image)
4. CONCLUSION

The incorporation of TX-100 as a non-ionic surfactant on the AZMCPE is introduced as a new and very efficient method for enhancement in electrocatalytic effect. From the results of comparative study of BCPE, AZMCPE, TX-100/AZMCPE suggests that TX-100/AZMCPE showed the excellent electrocatalytic activity for detection of DA. The comparative results from the mobilization and immobilization methods, immobilization is more favorable than mobilization method for the detection of dopamine at carbon paste electrode. The experimental results revealed that the $1 \times 10^{-5}$ M TX-100 with $10 \mu$L concentration with 10min time gap showed significant electrocatalytic activity towards the detection of DA. Hence this modified electrode can be applied for the detection of other neurotransmitters.

REFERENCES

Acetanilide Modified Carbon Paste Electrode for the Electrochemical Detection of Dopamine: A Cyclic Voltammetric Study

Abstract - The acetanilide modified carbon paste electrode (ANMCPE) was used for the voltammetric response of dopamine (DA) in an aqueous phosphate buffer solution (PBS). Modified carbon paste electrode was prepared by grinding the 5 mg of acetanilide (AN) with the mixture of graphite powder and silicon oil. Cyclic Voltammetric study improved the reversibility of the DA on the modified electrode. The effect of various experimental parameters such as acetanilide concentration, scan rate, and pH on the voltammetric response of DA was investigated. Under the chosen conditions, the differential pulse voltammetry peak current was found to be linear with DA concentration. The detection limit for modified electrode was found to be $6 \times 10^{-7}$ M for DA determination.

Key Words - Electrocatalytic Oxidation, Acetanilide, Dopamine, Cyclic Voltammetry, Carbon Paste Electrode

1. INTRODUCTION

Carbon paste electrodes have been extensively employed in various electrochemical detection schemes due to their simple and fast preparation, facile surface renewing,
biocompatibility, non-toxic character, and relatively low-background characteristics [1-3]. Furthermore, carbon paste-based electrode material is extremely attractive for its subsequent bulk modification with different modifiers, e.g. electrocatalysts and/or enzymes by simply mixing them into the carbon paste matrix [4–9]. In addition to surface modification of carbon paste electrodes with thin metal films [10-11], (bio)recognition elements [12-14] and or protective membranes [15-16] is/are also widely applicable, although their bulk modification is more convenient and common. Mostly, carbon paste electrodes are used as conventional size electrodes in combination with different holders which facilitate their manipulation and renewing of the electrode surface.

Dopamine (DA) is a neurotransmitter occurring in wide variety of animals; including both vertebrates and invertebrates [17] is produced in several areas of the brain, including the substantia nigra and the ventral segmental area. DA is also a neurochrome released by the hypothalamus. Its main function as a hormone is to inhibit the release of prolactin from the anterior lobe of the pituitary. Dysfunction of the dopaminergic system in the central nervous system is related to neurological disorders such as schizophrenia and Parkinson’s disease [18]. Therefore, real time monitoring of the DA level in real system shows an important issue in diagnosis of diseases. The fact that DA and other catecholamines are easily oxidizable compounds makes their detection possible by electrochemical methods based on anodic oxidation [19-23] Determination of DA has been studied by different modified electrodes [24-33]. Venton et al. reported on the psychoanalytical electrochemistry of dopamine and behavior [34]. The modified electrodes were prepared by using different type of materials [35-39].

Acetanilide is an odorless, white flake solid or crystalline powder and it is used as an inhibitor of peroxides and stabilizer for cellulose ester varnishes. It is also used as a precursor in penicillin synthesis and other pharmaceuticals including painkillers and intermediates. It acts as an intermediate for the synthesis of rubber accelerators, dyes and dye intermediate and camphor (Scheme 1).

In continuation of our studies concerning the preparation of modified electrodes for the detection of DA [40-44], in the present work, we found that acetanilide modified carbon paste electrode (ANMCPE) possessing high stability and good electrocatalytic activity toward the electrocatalytic oxidation of DA. Cyclic voltammetry was used to characterize the electrochemical properties of the ANMCPE and to investigate its electrocatalytic effect on DA oxidation. Differential pulse voltammetry (DPV) was also used to evaluate the analytical performance of the modified electrode.
2. EXPERIMENTAL PART

2.1. Reagents and Chemicals

Acetanilide, Dopamine hydrochloride, Potassium ferrocyanide, was obtained from Himedia chemical company. All chemicals were of analytical grade quality and were used without further purification. The water used was a double distilled. Dopamine stock solutions was prepared by adding dopamine to 0.1M perchloric acid and kept in darkness. In all the measurements, the supporting electrolyte used was 2 M phosphate buffer (pH 7).

2.2. Apparatus and Procedure

Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) were performed on Model EA-201 Electroanalyser (EA-201, Chemilink System). All the experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire counter electrode and a potassium chloride (KCl) saturated calomel reference electrode (SCE).

2.3. Preparation of ANMCPE

ANMCPE was prepared by thoroughly hand-mixing AN (5.0 mg), graphite powder (70%) and silicon oil (30%) in an agate mortar with a pestle for about 30 min to get homogenous ANMCPE. The modified carbon paste was packed into the hole of the electrode body and leveled off with a spatula and smoothed on a weighing paper. The BCPE was prepared without adding acetanilide. The pH was measured with a Digital pH meter MK IV model.

3. RESULTS AND DISCUSSION

3.1. Electrochemical response of K₄Fe(CN)₆ at ANMCPE

The electrochemical response of K₄Fe(CN)₆ at ANMCPE was shown in Fig. 1 at a scan rate of 50 mV s⁻¹. At bare carbon paste electrode (BCPE) the voltammogram of K₄Fe(CN)₆ showed electrochemical response (dashed line) with reversible behavior in 1 M KCl as supporting electrolyte. However, the voltammetric response was apparently improved at
ANMCPE (solid line) with well-defined oxidation and reduction peaks due to the Fe$^{3+}$/Fe$^{2+}$ redox couple were observed. At BCPE the anodic peak potential ($E_{pa}$) was found to be 258 mV and cathodic peak potential ($E_{pc}$) 176 mV (vs. SCE). The separation of redox potential peaks ($\Delta E_p$) 82 mV. At ANMCPE, a pair of redox peak obtained with increase in both anodic and cathodic peak current. The $E_{pa}$ was found at 250 mV and $E_{pc}$ at 181 mV. The separation of redox potential peaks $\Delta E_p$ was found to be 69 mV.

Fig. 1. Cyclic Voltammograms of BCPE (dotted line) and ANMCPE (Solid line) in the presence of 1×10^{-3} M potassium ferrocyanide and 2 M potassium chloride solution, Scan rate 50 mV s^{-1}

3.2. Effect of Acetanilide concentration

By increasing the quantity of acetanilide in the modification, the electrochemical cathodic ($I_{pc}$) and anodic peak current ($I_{pa}$) goes on increasing at certain ratio. The effect of concentration of acetanilide ranging from 1 mg to 11 mg on the CVs of 0.5×10^{-4} M DA in 0.2 M phosphate buffer solution pH 7 was studied. The Fig. 2A shows the plot of anodic peak current verses acetanilide (mg). As the figure illustrates DA oxidation peak is enhanced up-to 5 mg of the modifier and then decreases when the amount of modifier is increased further. Therefore 5 mg is used for the preparation of MCPE.

3.3. Material characterization

To characterize the surface morphology of the electrode scanning electron microscopic images were taken. The SEM image for BCPE and MCPE has shown in Fig. 2B and Fig. 2C and the surface morphology of BCPE and MCPE were entirely different form each other. The SEM image for BCPE shows only the mixture of graphite powder and silicon oil. But for the
acetanilide MCPE the microscopic image has shown the uniform distribution of acetanilide crystal with the mixture of graphite powder and silicon oil. From this observation it is clear that acetanilide crystals were distributed in the carbon paste electrode homogeneously.

3.4. Electro catalytic behaviour of dopamine on ANMCPE

The electrochemical response of $0.5 \times 10^{-4}$ M DA at the BCPE and ANMCPE were shown in Fig. 3 with 50 mV s$^{-1}$ scan rate owing to the complex properties and roughness of the electrode surface. The cyclic voltammogram of DA in the absence of acetanilide was low signal (dashed line), however the voltammetric response was improved in the presence of acetanilide, reflected by the enlargement of both anodic and cathodic peak currents (solid line).

The probable mechanism for this enhancement current was given in scheme 2. During the scanning towards the positive direction the highly electronegative oxygen atom of keto group present in the acetanilide molecule could take the electron towards itself and become more electron rich. This highly electronegative oxygen atom could exert strong electrostatic attraction with the cation present in the dopamine molecule and enhance the rate of electron transfer by converting dopamine to dopa ortho quinone, hence the acetanilide modified carbon paste electrode shows more current enhancement when compared to the bare carbon paste electrode. While in reverse scan both dopa ortho quinone, and anionic acetanilide get back their original position.

**Scheme 2.** Oxidation mechanism of dopamine at the surface of acetanilide modified carbon paste electrode
Fig. 2. A) Plot of current vs. concentration of acetanilide (from 1-11 mg) in $0.5 \times 10^{-4}$ M DA and 2 M PBS 7, Scan rate 50 mV s$^{-1}$, B) Scanning electron microscopic image of bare carbon paste electrode, C) Scanning electron microscopic image of acetanilide modified carbon paste electrode

Fig. 3. Cyclic Voltammograms of $0.5 \times 10^{-4}$ M DA at BCPE (dotted lines) and ANMCPE (solid line) at scan rate 50 mV s$^{-1}$ in 0.2 M PBS (pH 7)
3.5. Scan rate effect

The effect of scan rate on the anodic peak current of DA was investigated experimentally. Fig. 4A shows the CVs obtained from 0.5×10^{-4} M DA in 0.2 M PBS pH 7 at ANMCPE. While increasing the scan rate from 50 to 350 mV s^{-1} both the anodic and cathodic peaks are increasing. The anodic peak current was proportional to the scan rate in the range from 50 to 350 mV s^{-1} as shown in Fig. 4B. The linearity of the plot was good and the correlation coefficient was 0.99771. It was therefore assumed that the electrode reaction of DA at the ANMCPE was typical of an adsorption controlled process. Further the study shows that a good linear relationship was obtained between the anodic peak current and square root of scan rate (Fig. 4C) in the same range with correlation coefficient 0.99759 which indicates a diffusion controlled process occurring at the ANMCPE. The plot of \(i_p/\sqrt{\nu}\) vs. log\(\nu\) (Fig. 4D) indicated an increase in the peak current with an increase in sweep rate and also the slope of log \(i_{pa}\) vs. log\(\nu\) (Fig. 4E) was 0.8608 which is larger than theoretical expected value 0.53 for purely diffusion controlled process [45] from all these results the anodic process is dominated by both adsorption and diffusion controlled for DA simultaneously.

3.6. Effect of concentration of dopamine at ANMCPE

Response of various concentrations of DA at ANMCPE in the range of 0.5×10^{-4}-3×10^{-4} M was studied. From the Fig. 5A. Increasing the concentration of DA both the anodic and cathodic peak increases. The Fig. 5B shows graphical interdependence between concentration and the anodic oxidation current of DA at the ANMCPE. From the plot it is clear that there is a linear enhancement in anodic peak current with the DA concentration.

Table 1. Determination results of DA in injection (n=10)

<table>
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<tr>
<th>Sample</th>
<th>Content (mg mL^{-1})</th>
<th>Found (mg mL^{-1})</th>
<th>Recovery (%)</th>
<th>RSD(%) (n=10)</th>
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</thead>
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<td>10.0</td>
<td>9.9</td>
<td>99</td>
<td>2.3</td>
</tr>
<tr>
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<td>10.0</td>
<td>10.2</td>
<td>102</td>
<td>1.8</td>
</tr>
<tr>
<td>3</td>
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Fig. 4. A) Cyclic Voltammograms for the effect of variation of scan rate of dopamine from 50–350 mV s$^{-1}$ in 0.2 M PBS (pH 7), B) Plot of current vs. scan rate, C) Plot of current vs. square root of scan rate, D) Plot of $i_p/v^{1/2}$ vs. log $v$, E) Variation of the logarithm of peak current with the logarithm of the
Fig. 5. A) Cyclic Voltammograms obtained for different concentration of DA (0.5×10^{-4} to 4×10^{-4} M.) in 0.2 M phosphate buffer solution at pH 7 scan rate 50 mV s^{-1}, B) The plots of the anodic peak as a function of DA concentration, C) Differential pulse voltammograms of ANMCPE in 0.2 M PBS (pH 7) containing different concentrations of DA (a-g): 0.5×10^{-4}, 1×10^{-4}, 1.5×10^{-4}, 2×10^{-4}, 2.5×10^{-4}, 3×10^{-4}, 3.5×10^{-4} M

Fig. 5C shows the differential pulse voltammograms (DPVs) obtained for the oxidation of different concentrations of DA at the ANMCPE. Since DPV has a much higher current sensitivity and better resolution than cyclic voltammetry, it was used to estimate the lower limit of detection of DA. In addition, the charging current contribution to the background current, which is a limiting factor in the analytical determination, is negligible in DPV mode. The DA concentration was varied from 0.5×10^{-4} to 4×10^{-4} M. The anodic peak current of DA
was increased with respect to the concentration of DA without shifting the peak potential and the detection limit was found to be 6×10⁻⁷ M. From the analysis the ANMCPE is stable and does not undergo surface fouling during the voltammetric measurements. This result also demonstrates the fact that the results obtained at the ANMCPE are reproducible.

3.7. Effect of pH

To optimize the electrochemical response of modified carbon paste electrode for the oxidation and reduction of DA, the effect of pH on the electrode response was studied. The effect of solution pH over the range 5 to 9 was investigated. Fig. 6A shows the cyclic voltammogram of 0.5×10⁻⁴ M DA at different pH. As shown in the figure a well distinguishable voltammogram was obtained at pH 7 PBS. The results indicate that at pH 7 the oxidation and reduction of DA was better as compared to other pH. Therefore physiological pH was chosen as the experimental pH value in the electrochemical detection of DA. The influence of pH on the anodic peak potential of DA was also investigated (Fig. 6B) in the pH range from 5 to 9, the anodic peak potential decreases with increase of pH which indicates that uptake of electrons is accompanied by equal number of protons. Since DA involves a two electrons change process the number of electrons and protons will be equal to two.

![Fig. 6. A) Cyclic Voltammograms for the effect of variation of pH of PBS in 0.5×10⁻⁴ DA at scan rate 50 mV s⁻¹ (a-e):5, 6, 7, 8 and 9, B) lot of anodic peak potential vs. pH](image)

3.8. Sample analysis

The modified electrode was also used to analyze the DA in injection samples. The injection samples were used after suitable dilution. The results are shown in Table 1. The
results were satisfactory and the ANMCPE could be efficiently used for the determination of DA in injection.

4. CONCLUSIONS

Acetanilide modified carbon paste electrode has been fabricated. SEM has been used to characterize the surface morphology of the working electrode. This study has indicated that the chemically modified acetanilide carbon paste electrode acts as a good sensor, exhibited strong promoting effect and stability towards the electrochemical oxidation of dopamine at pH 7 in phosphate buffer solution. The electrochemical behavior of the modified electrode is strongly dependent on solution pH. Electrochemical process was found to be both adsorption and diffusion controlled. The low cost and easy of preparation; the acetanilide modified carbon paste electrode seems to be great utility for further sensor development. The proposed method has been applied for detecting DA in real sample with satisfactory results.

REFERENCES


Electrochemical Studies of Dopamine at Lithium Zirconate/SDS Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

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Abstract- Li$_2$ZrO$_3$ nanoparticles were synthesized by the Gel Combustion Process. The synthesized nanoparticles were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The synthesized Li$_2$ZrO$_3$ nanoparticles were used for the modification of carbon paste electrode and sodium docylsulphate (SDS) anionic surfactant was further modified by the immobilization technique for the electrochemical determination for dopamine at pH 7.2 phosphate buffer solution. The modified carbon paste electrode SDS/Li$_2$ZrO$_3$ shows excellent electrochemical sensor for dopamine and also in the simultaneous determination dopamine, ascorbic acid and uric acid. The modified electrode showed high sensitivity, high reproducibility, easy preparation and regeneration of the electrode surface.

Keywords- Dopamine, Lithium Zirconate, Modified Carbon Paste Electrode, Electrocatalytic Oxidation, Sodium Docylsulphate (SDS), Cyclic Voltammetry
1. INTRODUCTION

In 1998, lithium zirconate (Li$_2$ZrO$_3$) was proposed by Nkagawa et al. [1,2] In recent years, Li$_2$ZrO$_3$ ceramics have been extensively studied for their applications as electronic devices in batteries and breeder materials for nuclear fusion reactors. [3,4] Li$_2$ZrO$_3$, is a well-known material in the nuclear industry because of its properties, including high-tritium release rate, thermal stability, low thermal expansion, and properties, such as good compatibility with structural materials [5,6]. Generally Li-containing materials, such as lithium zirconate (Li$_2$ZrO$_3$), have been reported to be promising candidates for CO$_2$ capture at high temperatures due to their merits such as high CO$_2$ capture capacity and stability, especially in the presence of steam, and easy regeneration [7].

Dopamine (DA) occurs in the central nervous system naturally in the basal ganglia where its function as a neurotransmitter as well as in the adrenal medulla. DA also known as 4-(2-aminoethyle) bengene -1,2–diol belongs to a member of the catecholamine family. Dopamine (DA) was discovered to be an important neurotransmitter in the mammalian central nervous system in the late 1950 and it is found in high amount (50 nmol/g) in a region of the brain known as “caudate nucleus” [8,9]. It is one of the excitatory neurotransmitters that play an important role in several physiological events. It is involved in the functioning of renal, cardiovascular, hormonal and nervous systems. DA is also involved in neurological diseases such as Parkinson’s disease [10,11], Alzheimer’s disease [12] and Schizophrenia disease [13]. It has been also suggested that DA plays a role in drug addiction [14] and some manifestation of HIV [15]. The fact that DA and other catecholamines are easily oxidizable compounds makes their detect ion possible by electrochemical methods based on anodic oxidation. Dopamine has been determined using various electrochemical methods [16].

Ascorbic acid (AA) is essential in human body due to its importance as an antioxidant. It is widely known as vitamin C, a water-soluble vitamin that is commonly required for metabolism and consumed on a large scale. Studies on the catalytic oxidation of ascorbic acid have been extensively conducted [17,18] Similarly, (AA) has been used for the prevention and treatment of the common cold, mental illness, infertility, and even cancer and AIDS [19,20]. Uric acid (UA) is the primary end product of purine metabolism in the human body [21]. In a healthy human being, the typical concentration of UA in urine is around 2 mM and in the blood is in between 120 μM to 450 μM ranges [22]. Extreme abnormalities of UA levels are symptonic of several diseases, such as, cardiovascular disease [23], hyperuricaemia, uric acid stones, gout and Leseh-Nyhan syndrome [24]. Recently, electrochemical sensors have attracted much attention due to their advantages of simplicity, cheapness, fast analysis along with high sensitivity and selectivity [25].

Surfactants, due to their favorable physicochemical properties are extensively used in many fields of technology and research, i.e. in pharmacy, in cosmetics, textile industry, agriculture, biotechnology [26]. Normally surfactant is a linear molecule with a hydrophilic
(attracted to water) head and a hydrophobic (repelled by water) end. Surfactants, a kind of amphiphilic molecules with a hydrophilic head on one side and a long hydrophobic tail on the other, have been widely applied in electrochemistry to improve the property of the electrode solution interface [27] and also improve the detection limits of some biomolecules. The results showed that the electrochemical responses of these compounds were greatly enhanced in the presence of trace surfactants [28].

As part of our research work on the development of new electrochemical sensors for the determination of DA [29,30]. This work reports for the voltammetric behavior of DA at bare and Li2ZrO3/SDS nanoparticle modified electrode showed an electrocatalytic activity for the oxidation of DA, AA and UA. The results indicate that the modified electrode could be used to detect DA in the presence of AA and UA effectively.

2. EXPERIMENTAL PART

2.1. Reagents and chemicals

Lithium nitrate (98%, sd fine chemicals) and zirconyl nitrate was purchased from Lobo chemicals were used as lithium and zirconia precursor respectively. Glycine was used as fuel. Lithium nitrate, zirconyl nitrate and glycogen were dissolved in double distilled water. Dopamine (DA) were obtained from Himedia chemical company and of analytical grade used without further purification. 25 mM DA stock solution was prepared in 0.1 M perchloric acid, AA and UA was prepared in double-distilled water. Graphite powder of 50 mm size was purchased from Loba and silicon oil was purchased from Himedia. The chemicals for preparation of buffer solution were purchased from Merck. Phosphate buffer (0.2 M pH 7.2) was used as supporting electrolyte.

2.2. Apparatus

Cyclic voltammetry (CV) was performed in a model CHI-660c (CH Instrument-660 electrochemical workstation). All experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire as counter electrode and saturated calomel as reference electrode.

2.3. Preparation of bare carbon paste electrode

The bare carbon paste electrode was prepared by hand mixing of graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was obtained. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and the electrical contact was provided by a copper wire connected to the paste in the end of the tube.
2.4. Preparation of SDS/Li$_2$ZrO$_3$ nanoparticle modified carbon paste electrode

SDS solution (10 µL) was added to the surface of the MCPE prepared from Li$_2$ZrO$_3$ nanoparticles for 5 min. The electrode was later thoroughly rinsed with water to removed unabsorbed modifier and dried in air at room temperature. The same procedure was followed for the preparation of the BCPE.

2.5. Synthesis of Li$_2$ZrO$_3$

Synthesis of Li$_2$ZrO$_3$ was carried out by the gel combustion process. Lithium nitrate (98%, sd fine chemicals) and zirconyl nitrate (Lobo chemicals) were used as lithium and zirconia precursor respectively. Glycine was used as fuel and carefully weighed lithium nitrate, zirconyl nitrate and glycine were dissolved in 125 ml distilled water. Fuel to nitrate ratio (molar ratio) was maintained as 0.35 in the reaction mixture. The beaker containing reaction mixture was placed on a hot plate, and then heat was supplied to the beaker. Nitrates were released during the heating, resulted in gel formation. The reaction was completed by self-ignition combustion leaving behind fine white powder. The formed metal oxide was then calcinated at 500 °C and characterized by SEM and XRD. [31,32]

3. RESULTS AND DISCUSSION

3.1. Electrochemical response of K$_4$Fe(CN)$_6$ at Li$_2$ZrO$_3$/SDS nanoparticle MCPE

Fig. 1A shows the electrochemical response of Li$_2$ZrO$_3$/SDS nanoparticle MCPE was studied by standard 1mM [K$_4$Fe(CN)$_6$] in 1 M KCl as a supporting electrolyte with scan rate 50 mV s$^{-1}$ by CV technique.

At bare carbon paste electrode the voltammetric response of [K$_4$Fe(CN)$_6$] shows low current single owing to the complex properties and the roughness of the electrode surface (solid line). However in Li$_2$ZrO$_3$/SDS nanoparticle MCPE shows excellent enhancement peak current both in cathodic and anodic peak currents with SDS on the surface of electrode (dotted line). SDS is the anionic surfactant, on the surface of electrode which may alter the overvoltage of electrode and influence the rate of electron transfer.

3.2. Electrochemical response of K$_4$Fe(CN)$_6$ at Li$_2$ZrO$_3$ nanoparticle MCPE

At bare carbon paste electrode, the cyclic voltammogram of K$_4$Fe(CN)$_6$ shows the less sensitive current signals (solid line) and in presence of 4 mg of lithium zirconate decreases the current signals (dotted line). This shows as such lithium zirconate is responsible for the decreases the current signals as shown in Fig. 1B. From the fig it is clear that lithium zirconate with SDS is good for the increase in current signals but only in presence of lithium zirconate doesn’t show significant currents as compared to Li$_2$ZrO$_3$/SDS modified electrode.
Fig. 1. A) Cyclic voltammogram of 1 mM [K₄Fe(CN)₆] at BCPE (solid line) and SDS/Li₂ZrO nanoparticle MCPE (dotted line) in 1 M KCl scan rate 50 mV s⁻¹. B) Cyclic voltammogram of 1 mM [K₄Fe(CN)₆] at BCPE (solid line) and Li₂ZrO₃ nanoparticle MCPE (dotted line) in 1 M KCl scan rate 50 mV s⁻¹.

Fig. 2. Cyclic voltammogram in 0.2 M phosphate buffer solution pH 7.2 at BCPE (dotted line) and SDS/Li₂ZrO₃ nanoparticle MCPE (dashed line) of 0.1×10⁻⁴ DA with scan rate of 50 mV s⁻¹.
3.3. Electrochemical response of DA at Li$_2$ZrO$_3$/SDS nanoparticle MCPE

Dopamine is being an easily oxidisable catecholamine its voltammogramm was recorded in the potential range of -0.2 to 0.6 V vs. SCE in the 0.2 M phosphate buffer at pH 7.2 at 50 mV s$^{-1}$.

In Fig. 2 cyclic voltammograms for BCPE (dotted line) shows low redox peak currents with high peak potential difference [$\Delta E_p$=0.067 V] is compared to Li$_2$ZrO$_3$/SDS nanoparticle MCPE shows high redox peak currents with minimization of over peak potential difference [$\Delta E_p$=0.059 V] shows that the modified electrode acts as the electrocatalytic property in Li$_2$ZrO$_3$/SDS MCPE is good for the detection of DA.

![Cyclic voltammogram of DA at different concentration at SDS/ Li$_2$ZrO$_3$ nanoparticle MCPE in 0.2 M PBS of pH 7.2](image)

**Fig. 3.** A) Cyclic voltammogram of DA at different concentration at SDS/ Li$_2$ZrO$_3$ nanoparticle MCPE in 0.2 M PBS of pH 7.2 B) Graph of current Vs concentration of DA at scan rate 50 mV s$^{-1}$ of pH 7.2

3.4. Effect of concentration of DA

Electrocatalytic oxidation of DA was carried out by varying concentration at Li$_2$ZrO$_3$ /SDS nanoparticle MCPE from 0.5 mM to 1 mM shows in the Fig. 3A. By increasing the concentration of DA, both I$_{pa}$ and I$_{pc}$ goes on increasing with negligible shifting E$_{pa}$ and E$_{pc}$. Fig. 3B shows I$_{pa}$ vs. DA concentration that anodic peak current goes on increasing with increasing the DA concentration resulting the electrode processes is diffusion controlled [33-37].
3.5. Effect of concentration of SDS at Li₂ZrO₃ nanoparticle MCPE

Li₂ZrO₃ nanoparticle MCPE was further modified by SDS surfactant from the range 5 µl to 25 µl. The Fig. 4A shows the voltammetric response of SDS concentration at Li₂ZrO₃ nanoparticle MCPE with 0.1 mM DA at pH 7.2. By increasing the concentration of SDS (Eₚₒ) oxidation peak potential shifts positive side and (Eₚᵦ) reduction peak potential shifts negative side. The Fig. 4B shows Iₚₐ V s⁻¹ SDS concentration the anodic peak current goes on increasing with increasing the concentration of SDS. In 20 µl shows high sensitivity in the presence of 0.1 mM DA after there is decrease in the current this is due to SDS surfactant molecule diffuses in the Li₂ZrO₃ nanoparticle MCPE and from a monolayer on the surface of the electrode and subsequently electrostatic interaction between adsorbed substrate and shows hydrophobic character in Li₂ZrO₃/SDS nanoparticle MCPE. This result shows that the method of modification shows maximum increases in the current signals.

![Fig. 4. A) Cyclic voltammogram of SDS at different concentration at SDS/ Li₂ZrO₃ nanoparticle MCPE in 0.2 M PBS of pH 7.2 B) Graph of current V s⁻¹ concentration of SDS at scan rate 50 mV s⁻¹ of pH 7.2](image)

3.6. Electrocatalytic response of DA and AA at Li₂ZrO₃/SDS nanoparticle MCPE

It is well known that ascorbic acid (AA) widely coexists with DA in real biological matrices. Therefore avoiding AA interference is an important target for any DA analytical methods. In Fig. 5, the voltammetric response of DA and AA at Li₂ZrO₃/SDS nanoparticle MCPE at pH 7.2 with scan rate 50 mV s⁻¹. Li₂ZrO₃/SDS nanoparticle MCPE DA exhibited enhanced peak currents in the presence of AA. The two well oxidation peaks and one reduction peak (solid line) separated between DA and AA. The electrocatalytic anodic peak
of DA was obtained at 197 mV and AA was found to be at 50 mV. This result shows that Li$_2$ZrO$_3$/SDS nanoparticle MCPE acts as good sensor for the detection of DA in the presence of AA.

**Fig. 5.** Cyclic voltammogram obtained for oxidation of AA and DA at SDS/Li$_2$ZrO$_3$ nanoparticle MCPE (solid line) at scan rate of 50 mV s$^{-1}$, 0.2 M PBS (pH 7.2)

**Fig. 6.** Cyclic voltammogram obtained for the oxidation of AA, UA and DA at SDS/Li$_2$ZrO$_3$ nanoparticle MCPE (solid line) at bare (dotted line) at scan rate of 50 mV s$^{-1}$, 0.2 M PBS (pH 7.2)
3.7. Voltammetric simultaneous study of DA, AA and UA at Li₂ZrO₃/SDS nanoparticle MCPE

In Fig. 6 shows the voltamograms for solution contains mixture of 1 mM AA, 0.1 mM DA and 0.5 mM UA in phosphate buffer at pH 7.2 in 50 mV s⁻¹. In bare (solid line) showed two oxidation peak and one reduction peak with low current signal currents. However in Li₂ZrO₃/SDS nanoparticle MCPE was able to separate the oxidation peaks of AA, DA and DA by showing three well oxidation peak and one reduction with high enhancement (solid line). The separation peak of DA-UA was 0.190 V and DA-AA was 0.140 V obtained. The AA, DA and UA shows well oxidation peak individually. Hence Li₂ZrO₃/SDS nanoparticle MCPE acts as a good sensor in the simultaneous study of neurotransmitter.

4. CONCLUSION

The bare carbon paste electrode was modified with Li₂ZrO₃ nanoparticle shows small decrease in current but in presence of SDS modified with Li₂ZrO₃ shows very good electrocatalytic property for the determination of dopamine. The modified electrode shows simultaneous determination of DA, AA and UA and the proposed method can be applied for the determination of bioactive molecule and this modified electrode acts as sensor for some neurotransmitters.

REFERENCES