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# Cyclosporine/SDS Modified Carbon Paste Electrode for Electrochemical Study of Dopamine: A Cyclic Voltammetric Study

Tanuja SB,  
Kumara Swamy BE and  
Vasantakumar Pai K

Department of PG Studies and  
Research in Industrial Chemistry,  
Kuvempu University, Jnana Sahyadri,  
Shankaraghatta, Shimoga, Karnataka,  
India

**Corresponding author:** Kumara Swamy BE

✉ kumaraswamy21@yahoo.com

Department of PG Studies and Research in  
Industrial Chemistry, Kuvempu University,  
Jnana Sahyadri, Shankaraghatta, Shimoga,  
Karnataka-577 451, India.

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## Abstract

A sensitive electrochemical sensor was developed by cyclosporine and sodium dodecyl sulphate for the electrochemical detection of dopamine (DA). The modified Cyclosporine carbon paste electrode was further modified by immobilization of sodium dodecyl sulphate (SDS) as a surfactant. The Modified Cyclosporine/SDS carbon paste electrode showed an excellent electro catalytic activity towards the oxidation of dopamine. Cyclosporine/SDS modified carbon paste electrode enhanced the anodic peak current as compared to bare carbon paste electrode at pH 7.4, the electrochemical parameters like scan rate and concentration of dopamine was investigated. Interference study at Cyclosporine/SDS modified carbon paste electrode reveals the excellent selectivity of electrode towards the dopamine, ascorbic acid and uric acid.

**Keywords:** Dopamine; Cyclosporine; Modified carbon paste electrode; Sodium dodecyl sulphate (SDS); Cyclic voltammetry

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## Introduction

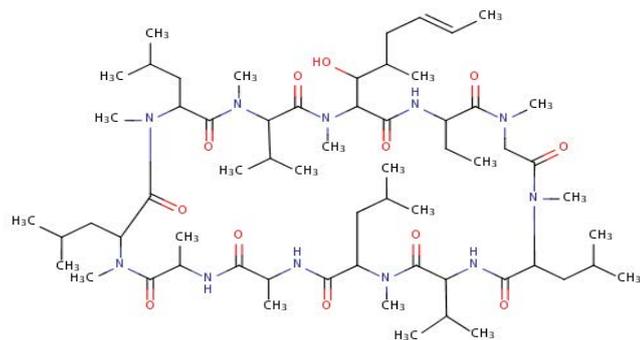
Cyclosporine (CSA) is a neutral compound soluble only in organic solvents or lipids with very low water solubility [1]. It is a powerful immunosuppressant, drug immune system is made of special type of cells like proteins, tissues, and organs defend the body against germs and microorganisms. Cyclosporine is used to prevent the rejection of transplanted organs [2]. Cyclosporine is blocking reversibly, the early events in T cell as well as in B cell and natural killer cell response leads to the alteration of immune response [3,4] and it may also have clinical application in the treatment of autoimmune disorders (**Scheme 1**). Cyclosporine can also used for transdermal applications [5].

Dopamine (DA) is an important monoamine neurotransmitter belongs to catecholamine family. It found in neurons of both the central and peripheral nervous system major dopamine containing area of the brain is the corpus striatum [6]. The DA is also known as 4-(2-Aminoethyl)-1, 2-benzenediol. In 1958 Arvid Carlsson and Nils-Ake Hillarp discovered the function of dopamine as a neurotransmitter in the mammalian central nervous system. It plays an important role in controlling emotions, pleasure, movement and incoming information. It facilitates transmission of signals between brain cells or neurons. And it

plays very important role in the life of the mammalian central nervous system. The Low level of dopamine causes neurological disorders, such as Parkinson's disease [7,8] schizophrenia disease [9,10] and Alzheimer's disease [11]. Dopamine plays a role in drug addiction [12] and some manifestation of HIV [13]. It is an electrochemically active compound hence it can be easily determined by electrochemical methods based on the anodic oxidation [14]. Therefore, it is a challenging task to develop sensitive and simple methods for the determination of dopamine. There are methods were introduced to determine the dopamine such as spectroscopy, chromatography, and electrochemistry [15-18]. The electrochemical method received a lot of interest due to its simplicity, sensitivity and eco-friendly and this method even suitable for coloured samples [19].

Ascorbic acid is a water-soluble vitamin and plays very important role in the metabolic process of living organisms. Due to its powerful antioxidant property, it protects the body against oxidative stress [20]. It defends the body from cold, infertility, and mental illness [21,22] it is used to prevent the scurvy disease.

Uric acid is one of the non-protein nitrogen constituent of the blood produced by purine metabolism and it is filtered in the



**Scheme 1** Structure of Cyclosporine.

kidney and excreted in the urine. The concentration of uric acid plays a very important role. The normal uric acid range for males is between **3.6 mg/dL** and female is **2.3-6.6 mg/dL** [23]. High concentration of uric acid in the body leads to several disorders such as gout, Lesch-Nyhan syndrome, Hyperuricemia, cardiovascular disease and multiple sclerosis [24,25].

Surfactants are surface active agents and they are in amphiphilic nature. Due to their unique molecular structure surfactants have been extensively used in the fields of cleaning uses, preparation of paints, pigments and manufacture of rubber, resins. Due to adsorption at interface and aggregation in to supramolecular structures, they have ability to modify and control the properties of electrode surface and enhance the rate of reaction therefore they are beneficially used in electrochemistry [26-30].

In the present work the modified carbon paste electrode was prepared by using cyclosporine as a modifier, it was further modified by immobilization of SDS surfactant. The modified Cyclosporine/SDS carbon paste electrode showed a good electro-catalytic activity for dopamine and uric acid. The modified new carbon paste electrode has more advantages, including high sensitivity, rapid response and simplicity.

## Experimental Part

### Reagents and chemicals

Cyclosporine was kindly supplied by PerkinElmer (Waltham, MA, USA). Dopamine (DA) was obtained from Himedia chemical company with analytical grade used without further purification. 25 mM DA stock solution was prepared in 0.1 M Perchloric acid, Sodium dodecyl sulphate, potassium ferro cyanide and KCl 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 7.4) was used as supporting electrolyte.

### Instrumentation

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

## Electrode preparation procedure

**Preparation of bare carbon paste electrode:** The carbon paste electrode was prepared by graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar by hand mixing to get homogenous paste. The prepared carbon paste was tightly packed into the cavity of a homemade carbon paste electrode then smoothed the surface of a weighing paper.

**Preparation of modified carbon paste electrode:** The modified carbon paste electrode was prepared by using 4 mg of cyclosporine, graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar by hand mixing to get homogenous paste. The modified carbon paste electrode was tightly packed into the cavity of a homemade carbon paste electrode then smoothed the surface on a weighing paper. The modified Cyclosporine electrode was further modified by immobilization by adding an SDS solution (10  $\mu$ L) on the surface of Cyclosporine MCPE and allowed for 5 min. Later electrode was thoroughly rinsed with distilled water to remove the unabsorbed modifier and dried in air at room temperature.

## Results and Discussion

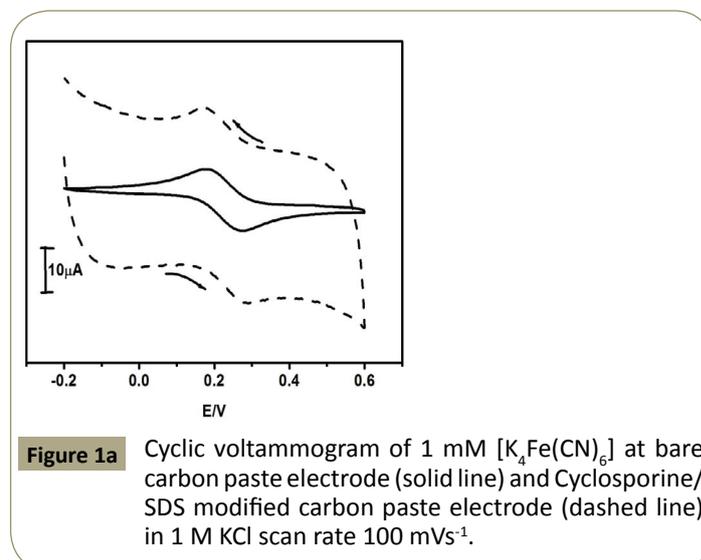
### Cyclic voltammetric studies of $K_4Fe(CN)_6$ at Cyclosporine/SDS MCPE

The cyclic voltammetric response at Cyclosporine/SDS MCPE was studied using 1mM  $[K_4Fe(CN)_6]$  in 1M KCl as a supporting electrolyte with the scan rate 100  $mVs^{-1}$  was shown in **Figure 1a**.

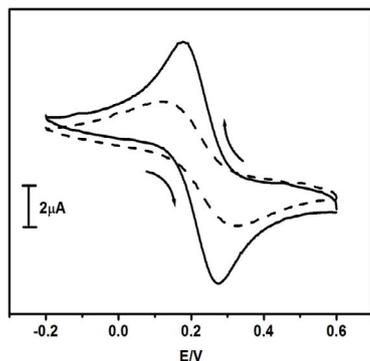
The cyclic voltammogram at modified Cyclosporine/SDS CPE shows excellent enhanced peak current (dotted line) as compared to the bare carbon paste electrode. The trace amount of SDS on the surface of Cyclosporine MCPE alter the electrochemical response of  $[K_4Fe(CN)_6]$  and influence the rate of electron transfer.

### Cyclic voltammetric studies of $K_4Fe(CN)_6$ at Cyclosporine MCPE

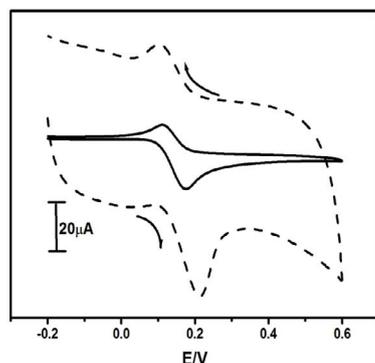
The cyclic voltammetric response at Cyclosporine/MCPE was



**Figure 1a** Cyclic voltammogram of 1 mM  $[K_4Fe(CN)_6]$  at bare carbon paste electrode (solid line) and Cyclosporine/SDS modified carbon paste electrode (dashed line) in 1 M KCl scan rate 100  $mVs^{-1}$ .



**Figure 1b** Cyclic voltammogram of 1 mM  $[K_4Fe(CN)_6]$  at bare carbon paste electrode (solid line) and Cyclosporine modified carbon paste electrode (dashed line) in 1 M KCl scan rate  $100\text{ mVs}^{-1}$ .



**Figure 2a** Cyclic voltammogram in 0.2 M phosphate buffer solution pH 7.4 at bare carbon paste electrode (solid line) and Cyclosporine/SDS modified carbon paste electrode (dashed line) of 1 mM DA with scan rate of  $100\text{ mVs}^{-1}$ .

studied using  $1\text{ mM } [K_4Fe(CN)_6]$  in  $1\text{ M KCl}$  as a supporting electrolyte with scan rate  $100\text{ mVs}^{-1}$  was shown in **Figure 1b**.

The cyclic voltammogram at modifying Cyclosporine/MCPE shows decrease in current signal as compared to BCPE (solid line).

### Cyclic voltammetric studies of DA at Cyclosporine/SDS MCPE

The cyclic voltammetric response of DA at Cyclosporine/SDS MCPE and BCPE was shown in **Figure 2a**. The cyclic voltammograms of dopamine in 0.2 M phosphate buffer at pH 7.4 and scan rate  $100\text{ mVs}^{-1}$  at Cyclosporine/SDS MCPE showed a good enhancement of peak current (dashed line) as compared to BCPE. In the presence of trace amount ( $10\ \mu\text{l}$ ) of SDS surfactant on the surface of Cyclosporine modified carbon paste electrode greatly influence the enhancement of electrochemical reaction and it was confirmed by the enlargement of peak currents [31].

### Cyclic voltammetric studies of DA at Cyclosporine MCPE

The cyclic voltammetric response of DA at Cyclosporine MCPE

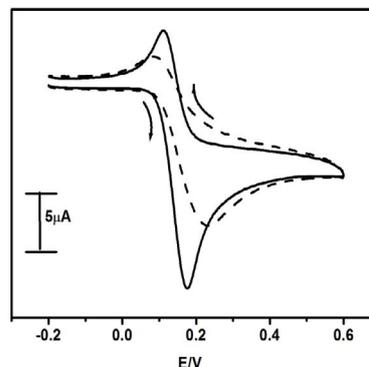
and BCPE was shown in **Figure 2b**. The cyclic voltammogram of dopamine in the absence of SDS at modifying Cyclosporine carbon paste electrode shows low signal as compared to BCPE (solid line).

### Effect of scan rate on Cyclosporine/SDS MCPE

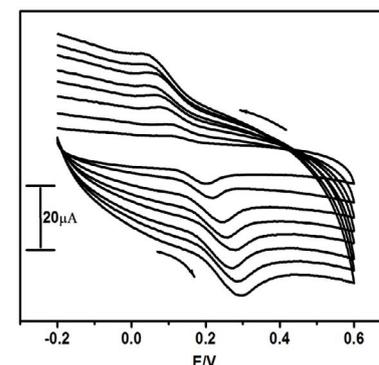
**Figure 3a** shows the cyclic voltammograms of dopamine recorded for different scan rates in 0.2 M phosphate buffer of pH 7.4 as a supporting electrolyte at Cyclosporine/SDS MCPE. This observation was carried out to investigate the kinetics of the electrode reaction and to verify the mass transport process involved in electrochemical processes, whether diffusion or adsorption-controlled. The scan rate varying study showed that current improved linearly with the square root of scan rate range of  $50$  to  $400\text{ mVs}^{-1}$ . The graph of anodic peak current ( $I_{pa}$ ) versus the square root of scan rate showed a linear relationship of  $I_{pa}$  and scan rate. The correlation coefficient was found to be 0.9950. **Figure 3b** it indicates that the electrode process was diffusion controlled [32-35]. The difference between the anodic and cathodic peak potential ( $\Delta E_p$ ) increasing with increasing the scan rate [36-38].

### Concentration effects of DA on Cyclosporine/SDS MCPE

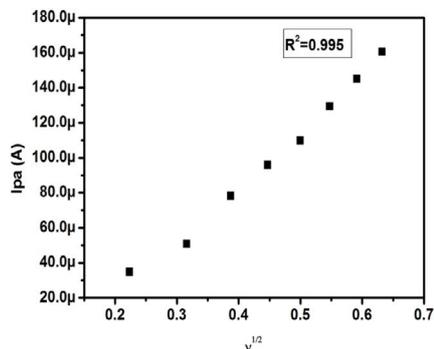
The cyclic voltammograms of different concentration of dopamine



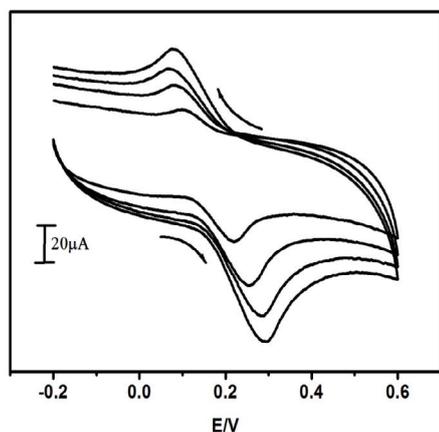
**Figure 2b** Cyclic voltammogram in 0.2 M phosphate buffer solution pH 7.4 at bare carbon paste electrode (solid line) and Cyclosporine modified carbon paste electrode (dashed line) of 1 mM DA with scan rate of  $100\text{ mVs}^{-1}$ .



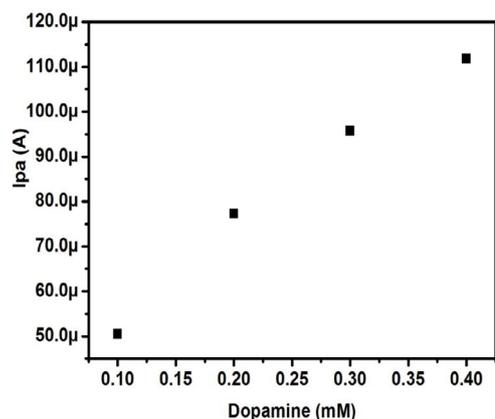
**Figure 3a** Cyclic voltammogram of dopamine at different scan rate.



**Figure 3b** Graph of current V/S square root of scan rate.



**Figure 4a** Cyclic voltammogram of different concentration of DA at Cyclosporine/SDS modified carbon paste electrode in 0.2 M PBS of pH 7.4.



**Figure 4b** Graph of current V/S concentration of DA at scan rate  $100 \text{ mVs}^{-1}$  of pH 7.4.

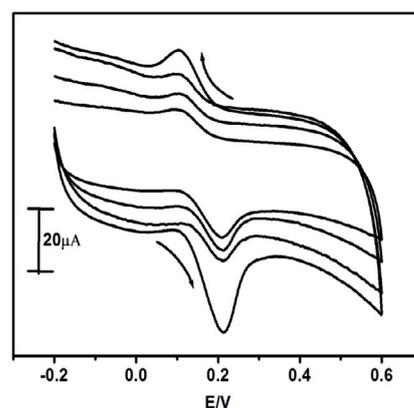
in the 2M phosphate buffer, pH 7.4 and scan rate  $100 \text{ mVs}^{-1}$  at Cyclosporine/SDS MCPE have shown in **Figure 4a**.

The electro catalytic oxidation of dopamine was carried out by varying the concentrations and it shows anodic current increases with increase of dopamine concentration from  $0.1 \times 10^{-3} \text{ M}$  to  $0.4$

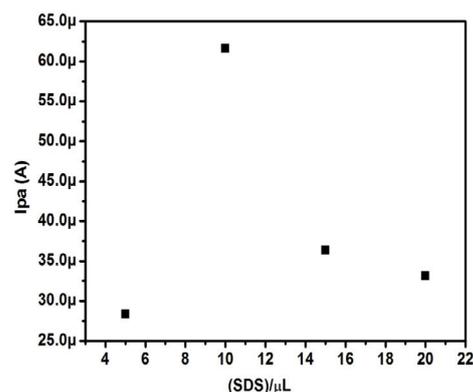
$\times 10^{-3} \text{ M}$ . The electrochemical anodic and cathodic peak currents go on increasing with anodic peak potential shifting towards positive and cathodic peak potential shifting towards negative direction slightly. The **Figure 4b** shows the  $I_{pa}$  versus dopamine concentration and the figure indicates that the concentration of dopamine is directly proportional to the electrochemical anodic peak current.

### Concentration effect of SDS and immobilization time at cyclosporine MCPE

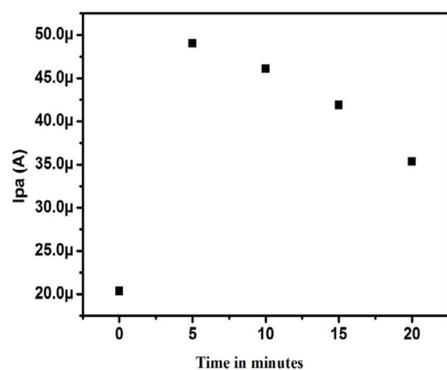
The cyclic voltammograms of dopamine at different concentration of SDS on Cyclosporine MCPE was shown in **Figure 5a**. The **Figure 5b** shows that enhancement of anodic peak current of dopamine was closely related to the concentration of SDS on the surface of Cyclosporine modified carbon paste electrode. Anodic peak current of dopamine goes on increases with increasing the concentration of SDS up to  $10 \mu\text{L}$ , after that it shows the decreases in current signal with increasing the concentration of SDS. Similarly immobilization time also influences the anodic peak current of dopamine. The influence of immobilization time was examined and results shown in **Figure 5c**. The peak current is more with immobilization time 5 min and then decreases.



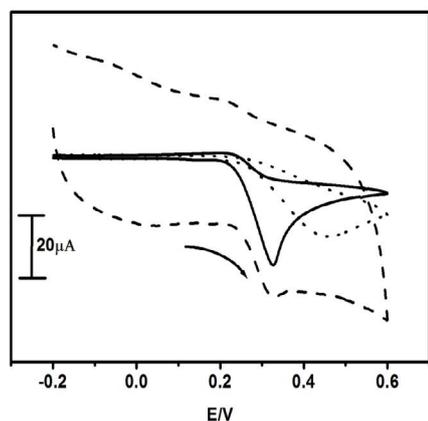
**Figure 5a** Cyclic voltammogram of dopamine at different concentration of SDS at Cyclosporine modified carbon paste electrode in 0.2 M PBS of pH 7.4.



**Figure 5b** Graph of current V/S concentration of SDS at scan rate  $100 \text{ mVs}^{-1}$  of pH 7.4.



**Figure 5c** Graph of current V/S immobilization time of SDS at scan rate  $100 \text{ mVs}^{-1}$  of pH 7.4.



**Figure 6** Cyclic voltammogram of uric acid at bare carbon paste electrode (solid line) and Cyclosporine modified carbon paste electrode (dotted line) and cyclosporine/SDS modified carbon paste electrode (dashed line) in 1 mM UA with scan rate of  $100 \text{ mVs}^{-1}$ .

Therefore 10  $\mu\text{l}$  of SDS and immobilization time 5 min was chosen for further electrochemical studies.

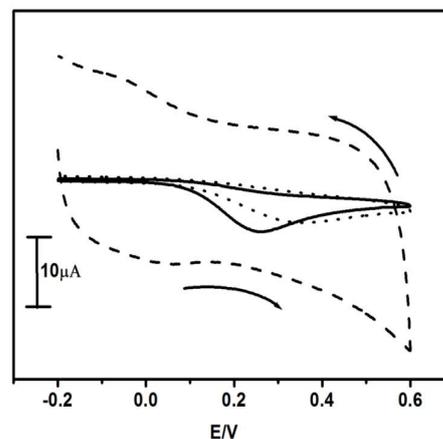
### Cyclic voltammetric response of UA at Cyclosporine/SDS MCPE

The **Figure 6** shows cyclic voltammograms of uric acid in 0.2 M phosphate buffer at pH 7.4 with a scan rate of  $100 \text{ mVs}^{-1}$  at Cyclosporine/SDS MCPE. The cyclic voltammogram of uric acid in the absence of SDS at cyclosporine modified carbon paste electrode shows low signal. However, in the presence of SDS at cyclosporine modified carbon paste electrode showed a good increment in the peak current. The cyclic voltammograms at modifying Cyclosporine/MCPE shows decrease in current signal (dotted line) as compared to bare carbon paste electrode (solid line) the modified Cyclosporine/SDS carbon paste electrode showed a good enhancement of peak current (dashed line) as compare to bare carbon paste electrode.

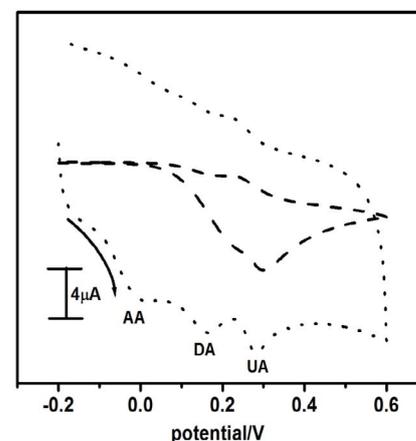
### Cyclic voltammetric response of AA at Cyclosporine/SDS MCPE

**Figure 7** shows cyclic voltammograms of ascorbic acid in 0.2 M phosphate buffer solution of pH 7.4 and scan rate 100

$\text{mVs}^{-1}$  at Cyclosporine/SDS modified carbon paste electrode. The electrochemical response of ascorbic acid at modifying Cyclosporine carbon paste electrode showed decrease in the current signal in the absence of SDS and showed an increase in the current signal in the presence of SDS as compared to the bare carbon paste electrode. The presence of trace amount (10  $\mu\text{l}$  of SDS) surfactant on the surface of cyclosporine modified carbon paste electrode has deeply influenced the enhancement of electrochemical responses. The cyclic voltammograms at modifying Cyclosporine carbon paste electrode shows decrease in current signal (dotted line) as compared to bare carbon paste electrode (solid line). The modified Cyclosporine/SDS carbon paste electrode showed a very good enhancement of peak current (dashed line) as compared to bare carbon paste electrode.



**Figure 7** Cyclic voltammogram of Ascorbic acid at bare carbon paste electrode (solid line) and Cyclosporine modified carbon paste electrode (dotted line) and Cyclosporine/SDS modified carbon paste electrode (dashed line) in 1 mM AA with scan rate of  $100 \text{ mVs}^{-1}$ .



**Figure 8** Cyclic voltammograms of 1 mM dopamine, 2 mM uric acid and 1 mM ascorbic acid in 0.2 M phosphate buffer solution of pH 7.4 at bare carbon paste electrode (dashed line) and Cyclosporine /SDS modified carbon paste electrode (dotted line) with scan rate of  $100 \text{ mVs}^{-1}$ .

### Simultaneous detection of dopamine, uric acid and ascorbic acid

The main objective of the proposed fabricated electrode was detection of dopamine, uric acid and ascorbic acid simultaneously, because they co-exist in physiological samples. The **Figure 8** shows the cyclic voltammograms of a mixture sample having 1 mM dopamine, 2 mM uric acid and 1 mM ascorbic acid in 0.2 M phosphate buffer solution of pH 7.4 at a bare carbon paste electrode (dashed line) and a Cyclosporine/SDS modified carbon paste electrode (dotted line). The bare carbon paste electrode results in an overlapped peak and it fails to locate individual anodic peak potentials for dopamine, uric acid and ascorbic acid, but the Cyclosporine/SDS modified carbon paste electrode clearly shows three well distinct peaks for dopamine, uric acid and ascorbic acid with great enhancement of anodic peak current. The observed result reveals the selectivity of the Cyclosporine/SDS modified carbon paste electrode towards dopamine, uric acid and ascorbic acid.

### Analysis of real sample

In order to estimate the analytical efficacy of the fabricated Cyclosporine/SDS carbon paste electrode, it was used for quantitative determination of dopamine in a pharmaceutical sample. The dopamine injection was purchased from Sterile Specialities India Pvt. Ltd with a specified content of dopamine of

**Table 1** Detection of DA in injection samples (n=3).

Sample	DA added (M)	Found (M)	Recovery (%)
1	$1 \times 10^{-4}$	$0.98 \times 10^{-4}$	98.0
2	$2 \times 10^{-4}$	$1.99 \times 10^{-4}$	99.5
3	$3 \times 10^{-4}$	$2.98 \times 10^{-4}$	99.3

40 mg/mL, the dopamine injection sample was diluted with 0.2 M phosphate buffer solution for suitable concentration. The results were shown in **Table 1** it demonstrates a good performance of the fabricated Cyclosporine/SDS carbon paste electrode with acceptable recovery. The proposed drug based modified carbon paste electrode could be efficiently used for the determination of dopamine in injections with recovery in the range from 98-99.5%.

### Conclusion

In the present work Cyclosporine/SDS modified carbon paste electrode was prepared by immobilization of SDS on the surface of Cyclosporine carbon paste electrode. The modified Cyclosporine/SDS carbon paste electrode shows increasing electrochemical sensitivity towards dopamine, ascorbic acid, uric acid as compared to the bare carbon paste electrode, it resolved the overlapping anodic peaks of dopamine, ascorbic acid and uric acid. The fabricated electrode can successfully be used for the detection of dopamine in real samples. The developed method can also be used as other bioactive molecules in developing the modified sensor.

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