Int. J. Electrochem. Sci., 5 **(2010)** 1962 - 1971

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Cyclic Voltammetric Investigations of Dopamine at Alizarin Modified Carbon Paste Electrode

K.R. Mahanthesha, B.E. Kumara Swamy[*]*, K.Vasantakumar Pai, Umesh Chandra, B.S Sherigara*

Department of P.G .Studies and Research in Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta – 577451, Shimoga(D), Karnataka (S), India.
[*]E-mail: kumaraswamy21@yahoo.com

Received: 2 September 2010 / *Accepted:* 1 November 2010 / *Published:* 1 December 2010

Electrochemical response of dopamine at alizarin modified carbon paste electrode has been studied by cyclic voltammetric technique in 0.1M acetate buffer solution at pH 7.0. The modified electrode exhibited strong promoting effect and stability towards the detection of dopamine. From the studies of scan rate effect the overall electrode process was found to be both adsorption and diffusion controlled. The concentration effect reveals that the detection limit of dopamine was 2.37 x 10^{-7} M and pH effect suggested that equal number of protons and electrons were involved in the electrochemical oxidation of dopamine. Alizarin modified carbon paste electrode showed excellent electrocatalytic effect towards the detection of dopamine.

Keywords: Dopamine, alizarin, modified carbon paste electrode and cyclic voltammetry.

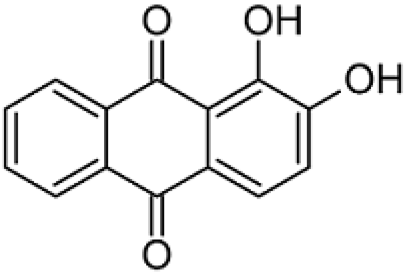
1. INTRODUCTION

Electrochemical sensors for neurotransmitter determination have attracted a great deal of interest due to their analytical performances, such as low detection limits, wide linear response range, good stability and reproducibility. The use of bare electrodes has revealed some drawbacks because of the electrode surface fouling with insulating polymer films or by-products resulting from phenol derivatives oxidation or reduction. Modifying the surface with inorganic or organic coatings has eliminated these drawbacks and allowed the preparation of stable and selective new electrochemical sensors. Inorganic coatings consisting of transition metal hexacyanoferrates, such as Prussian blue [PB, ferric ferrocyanide (Fe4 III[FeII(CN)6]3)], have been used in the reparation of electrochemical sensors, as well as of amperometric biosensors [1–4]. On the other hand, conducting polymers such as polypyrrole, polyaniline, polythiophene, polyazulene, and their derivatives have been also used for the construction of electrochemical sensors based on modified electrodes. Thin polymer films of azulene and its derivatives showed good electrochemical stability, electrocatalytic activity and conductivity [5–10]. The preparation of hybrid inorganic–organic coatings capable of fast bulk and interfacial electron transfer is a method of choice for analytical devices construction. Recently, hybrid inorganic–organic coatings containing transition metal hexacyanoferrates and conducting polymers have been prepared as bilayer structures on electrode surfaces [11,12]. It has been demonstrated that the inorganic compound acts as a redox mediator, while the organic component plays the role of a stable matrix or a permselective membrane. By this approach, most stable, highly conducting, and selective coatings can be easily deposited onto electrode surfaces.

Dopamine (DA), the most significant among the class of catecholamines, plays an important role in the function of the central nervous, cardiovascular, renal and hormonal systems [11-13]. The determination of DA is a subject of great importance for investigating its physiological functions and diagnosing nervous diseases resulting from DA abnormal metabolism, such as epilepsy, senile dementia, Parkinsonism, schizophrenia and HIV infection [14-19]. DA is an important neurotransmitter that plays a well-defined role in the function of central nervous, cardiovascular, renal and hormonal system. Due to the coexistence of many interfering compounds the determination of DA is not so easy. Thus, selectivity and sensitivity are important in the development of new analytical methodologies for DA quantification [20–22].

Because of the simple preparation and easy renewal of the surface, carbon has been used extensively as a working electrode for a variety of electrochemical applications. It has also been shown that carbon tends to be more compatible with biological tissues than other commonly used electrode materials [23,24]. Among the carbon electrodes, the carbon paste electrode (CPE) is of particular importance. The ease and speed of preparation and of obtaining a new reproducible surface, the low residual current, porous surface and low cost are some advantages of CPEs over all other carbon electrodes. Therefore, the CPE can provide a suitable electrode substrate for preparation of modified electrodes.

As a part of our research work on the development of modified electrodes, we extended our work on the detection of dopamine [25-31]. In the present work the modifier chosen for investigation of DA was alizarin. The construction of new electrodes modified with alizarin a commercial dye is reported. The electrochemical properties of these modified electrodes and their responses towards DA have been investigated by using cyclic voltammetry.



Scheme 1. Structure of Alizarin.

Alizarin is an orange-red compound having molecular formula $C_{14}H_8O_4$. The compound is a derivative of anthraquinone, with hydroxyl groups substituted at the 1 and 2 positions (Scheme.1). It is an important dyestuff producing red or violet lakes with metal hydroxide. AZ occurs naturally as the glucoside in madder plant (Rubia tinctorum). It comes under mordant vegetable dye, as the name suggests that these dyes require a mordant [32].

2. EXPERIMENTAL PART

2.1. Reagents and chemicals

Alizarin (AZ) and 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. Graphite powder of 50mm size was purchased from Loba and silicon oil was purchased from Himedia.The acetate buffer (0.1 M pH 7.0) was used as optimum measurments. 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 (3.0mm 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 fallows, 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 amount of AZ in milligrams 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 dopamine

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 amounts of AZ in milligrams. By increasing the amount of AZ from 0.5 mg to 1.5 mg 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.

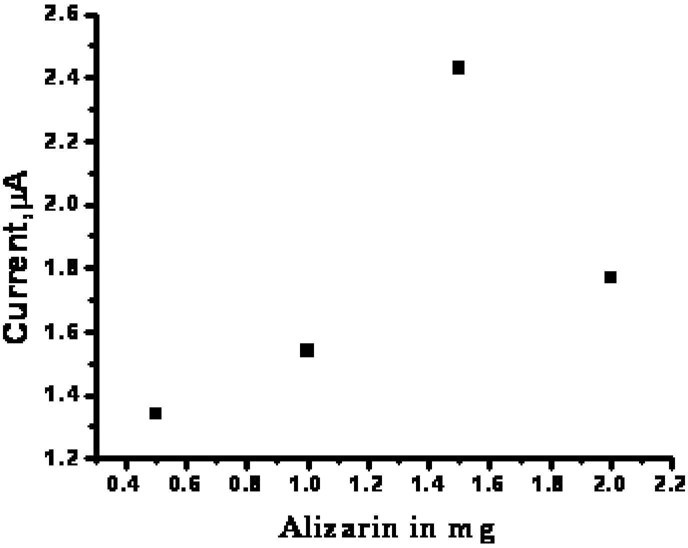


Figure 1. Effect of concentration of AZ on anodic peak current in 50µM DA and 0.2M acetate buffer solution Scan Rate: 100mVs^{-1}

The graph of anodic peak current vs. different amount of AZ in carbon paste electrode was plotted and shown in Fig.1. Maximum current signal was noticed in 1.5 mg AZMCPE, so we have chosen 1.5 mg 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 100mV/s. 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 i_{pa} /i_{pc} 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.

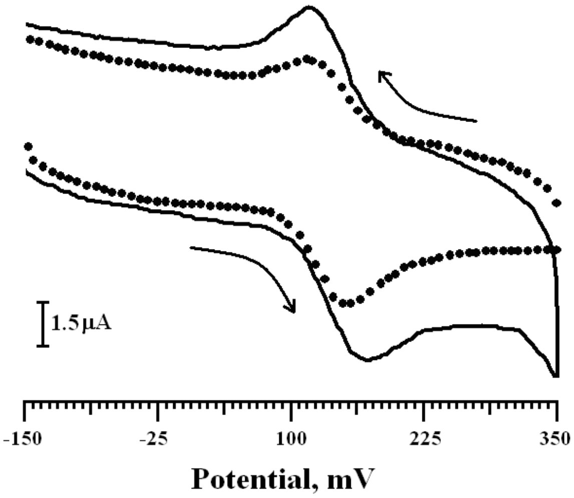


Figure 2. Cyclic voltammogram of BCPE (dotted line) and AZMCPE (Solid line) in the presence of 50μM DA and 0.2M acetate buffer, in pH 7.0 Scan Rate: $100mVs^{-1}$

3.3. Effect of scan rate

According to Randles-sevick's equation the scan rate is directly proportional to peak current. The AZMCPE showed increase in the peak current with increase in scan rate (100mV/s to 400mV/s) for 50 μM DA in 0.2 M acetate buffer solution at pH 7.0.

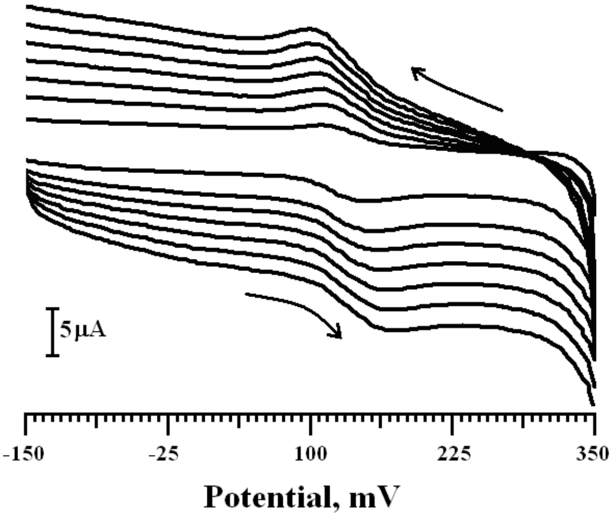


Figure 3(a). Cyclic voltammograms of different scan rate in the presence of 50μM DA and 0.2M acetate buffer, in pH 7.0 Scan Rate: $100mVs^{-1}$-400 mVs^{-1}

Cyclic voltammogram of DA at AZMCPE surface was shown in Fig.3a. The graph of current anodic peak current (i_{pa}) vs. scan rate (υ) and square root of scan rate ($\upsilon^{1/2}$) were plotted. The graph obtained were nearly straight lines shown in Fig.3b.and Fig.3c. In the range from 100 mV/s to 400 mV/s the anodic peak currents were proportional to the scan rate (υ) and also the to the square root of scan rate ($\upsilon^{1/2}$) with correlation coefficient 0.9980 and 0.9979 for i_{pa} vs. υ and i_{pa} vs. $\upsilon^{1/2}$ respectively. This indicates that, the electrode transfer reaction was both adsorption controlled and diffusion controlled.

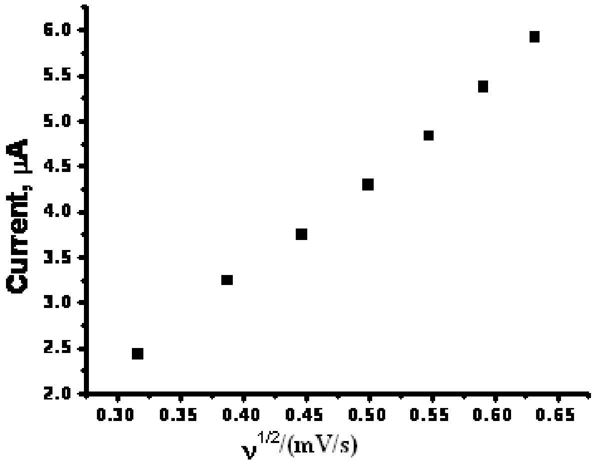


Figure 3(b). Effect of variation of square root of scan rate on the anodic peak current of 50µM DA in 0.2M acetate buffer, at pH 7.0, Scan Rate: 100mVs^{-1}-400 mVs^{-1}

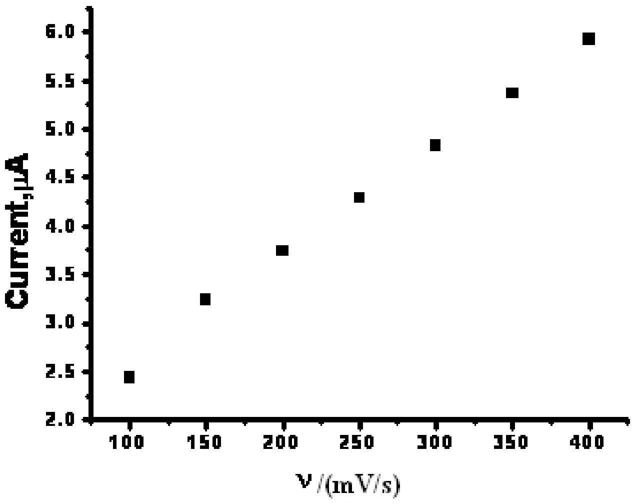


Figure 3(c). Effect of variation of scan rate on the anodic peak current of 50µM DA in 0.2M acetate buffer, at pH 7.0

3.4. Effect of Concentration of DA

According to electrochemical response, the redox peak current increased with increasing the concentration of analyte. Concentration of DA was increased from 50 µM to 500 µM as shown in Fig.4a and the plot of anodic peak current against concentration of DA shown a linear relationship between the i_{pa} in the range 50µM to 500µM as shown in Fig.4b[33-38]. The detection limit of DA was calculated by using the formula (1) [39, 40] and it was found to be 2.37×10^{-7} M.

$$\text{LOD} = 3S/M \qquad (1)$$

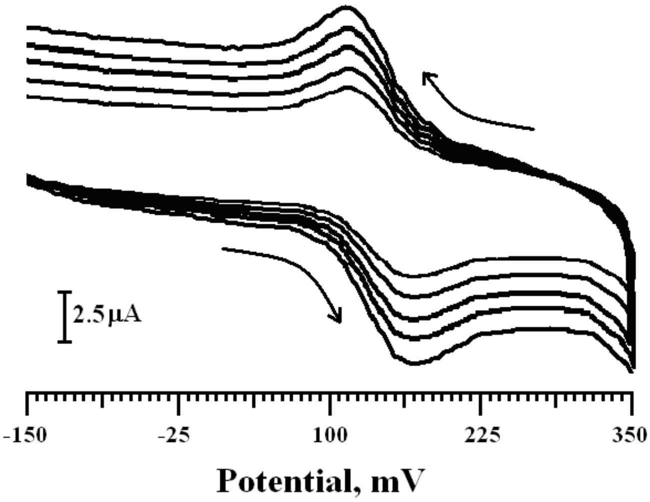


Figure 4(a). Cyclic voltammogram of variation of concentration of DA from 50μM-500μM in presence of acetate buffer solution at pH 7.0

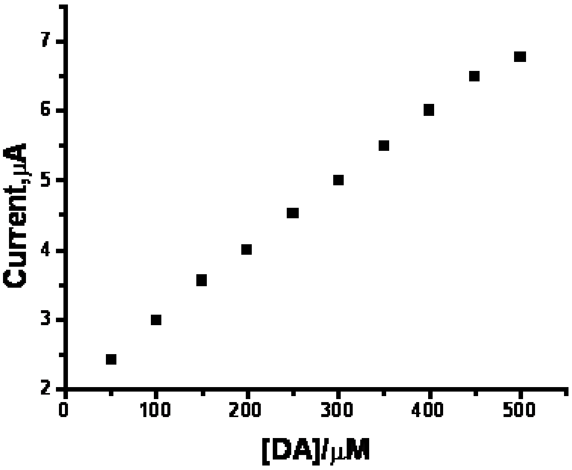


Figure 4(b). Effect of variation of concentration of DA on the anodic peak current of 50μM DA in acetate buffer solution at pH 7.0, Scan rate: 100mVs^{-1}

3.5. Effect of pH

Fig.5a. shows the effect of pH on the electrocatalytic oxidation of DA at AZMCPE. The anodic peak current was increased with increasing pH from 3.0 to 7.0 and then decreased for higher pH values. The better sensitivity and shape of the voltammogram was observed at pH 7.0 suggested it as optimal pH value. The graph of anodic peak potential vs pH was plotted (Fig.5b). The graph shows the linear relationship between the anodic peak potential and pH with the slope value 65 mV suggested that equal number of protons and electrons were involved in the electrochemical oxidation of DA [41, 28].

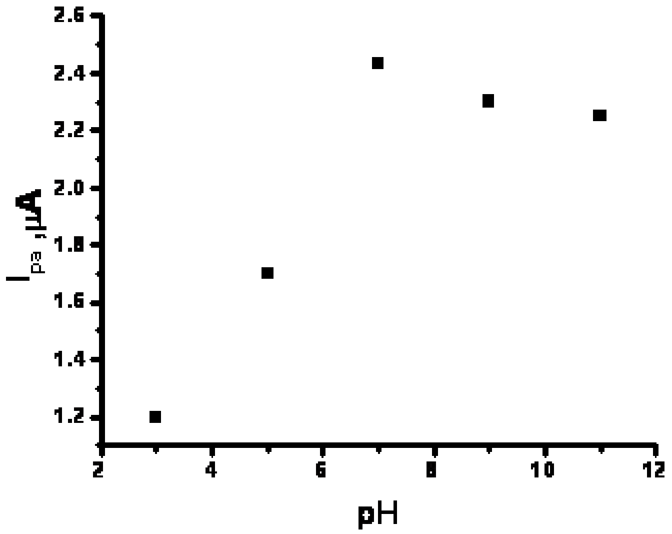


Figure 5(a). Effect of variation of pH on the anodic peak current of 50μM DA in acetate buffer solution at AZMCPE.

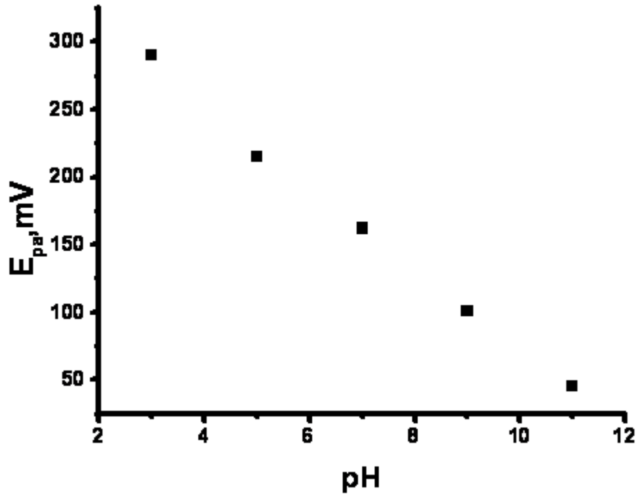


Figure 5(b) Effect of variation of pH on the anodic peak potential of 50μM DA acetate buffer solution at AZMCPE

4. CONCLUSION

In the present work, the AZMCPE was acting as a good sensor for the detection of DA. The modified electrode has been able to show high sensitivity for voltammetric detection of DA. The detection limit of DA was found to be 2.37 x 10^{-7} M. With its low cost, high sensitivity and very easy preparation of the modified electrode and the reproducibility of the voltammetric response make the prepared modified system very useful in the construction of simple devices for the determination of DA in clinical and pharmaceutical preparations.

References

1. R.W. Murray (Ed.), Molecular Design of Electrode Surfaces, Wiley, New York, 1992, p.22.
2. J. Roncali, J. Mater. *Chem.* 9 (1999) 1875.
3. A. Boyer, K. Kalcher, R. Pietsch, *Electroanalysis* 2 (1990) 155.
4. I.L. de Mattos, L. Gorton, T. Laurell, A. Malinauskas, A.A. Karyakin, *Talanta* 52 (2000) 791.
5. S. Lupu, C. Mihailciuc, L. Pigani, R. Seeber, N. Totir, C. Zanardi, *Electrochem. Commun.* 4 (10) (2002) 753.
6. F.Wang, Y.H. Lai, M.Y. Han, *Macromolecules* 37 (2004) 3222.
7. R.J.Waltman, A.F. Diaz, J. Bargon, *J. Electrochem. Soc.* 131 (1984) 1452.
8. G. Tourillon, F. Garnier, *J. Electroanal. Chem.* 135 (1982) 173.
9. J. Bargon, S. Mohmand, R.J.Waltman, *Mol. Cryst. Liq. Cryst.* 93 (1983) 279.
10. P.J. Kulesza, K. Miecznikowski, M.A. Malik, M. Galkowski, M. Chojak, K. Caban, A. Wieckowski, *Electrochim. Acta* 46 (2001) 4065.
11. P. Somani, S. Radhakrishnan, *Mater. Chem. Phys.* 76 (2002) 15.
12. V.S. Vasantha, S.-M. Chen, *Electrochim. Acta.* 51 (2005) 347.
13. M.T. Shreenivas, B.E.Kumara Swamy, Umesh Chandra, S.Sharath Shankar, J.G.Manjunatha, B.S.Sherigara, *Int. J. Electrochem. Sci.*, 5 (2010) 774.
14. J.Oni, T.Nyokong, *Anal.Chim.Acta* 9 (2001) 434.
15. J.E.F.Reynold (Ed) Martindle, *The Extra Pharmacopeia, The Pharmaceutical Press, London*, 1993.
16. H.Yaghoubian, H. Karimi-Maleh, M. AliKhalilzadeh, F.Karimi, *Int. J. Electrochem. Sci.*, 4 (2009) 993.
17. A. M.Othman, N.M.H. Rizka, M.S.E.L.Shahawi .*Anal. Sci*. 20 (2004) 651.
18. Umesh Chandra, B.E. Kumara Swamy, O. Gilbert, M.Pandurangachar, B.S. Sherigara, *Int. J. Electrochem. Sci.*, 4 (2009) 1479.
19. R. Raghavendra Naik, E. Niranjana, B. E. Kumara Swamy, B. S. Sherigara, H. Jayadevappa, *Int. J. Electrochem. Sci.*, 3 (2008) 1574.
20. F. Xu, M. Gao, L.Wang, G. Shi,W. Zhang, L. Jin, J. Jin, *Talanta* 55 (2001) 329.
21. A. Domenech, H. Garcia, M.T. Domenech-Carbo, M.S. Galletero, *Anal. Chem.* 74 (2002) 562.
22. S.-M. Chen,W.-Y. Chzo, *J. Electroanal. Chem.* 587 (2006) 226.
23. R.M. Wightman, L.J. May, A.C. Michael, *Anal. Chem*. 60 (1988) 769A.
24. S. Sharath Shankar, B.E. Kumara Swamy, M.Pandurangachar, Umesh Chandra, B.N. Chandrashekar, J.G.Manjunatha, B.S. Sherigara, *Int. J. Electrochem. Sci.*, 5 (2010) 944 .
25. R. Raghavendra Naik, B.E. Kumara Swamy, Umesh Chandra, E. Niranjana, B.S. Sherigara, H.Jayadevappa, *Int. J. Electrochem. Sci.*, 4 (2009) 855.
26. O.Gilbert, B.E.Kumara Swamy, Umesh Chandra, B.S.Sherigara, *Int. J. Electrochem. Sci.*, 4 (2009) 582.
27. S. Sharath shankar, B.E. Kumara Swamy, Umesh Chandra, J.G.Manjunatha,B.S. Sherigara, *Int. J. Electrochem. Sci.*, 4 (2009) 592.
28. Umesh Chandra, B.E. Kumara Swamy, O.Gilbert, M.Pandurangachar, B.S. Sherigara, *Int. J. Electrochem. Sci.*, 4 (2009) 1479.

29. O.Gilbert B.E. Kumara Swamy, Umesh Chandra, B.S. Sherigara, *Journal of Electroanal Chem,* 636 (2009) 80.
30. Rekha, B.E. Kumara Swamy, R.Deepa, V.Krishna, O.Gilbert, Umesh Chandra, B.S.Sherigara, *Int. J.Electrochem. Sci.,* 4 (2009) 832.
31. J.G.Manjunatha, B.E. Kumara Swamy, G.P.Mamatha, S.Sharath Shankar, Ongera Gilbert, B.N. Chandrashekar, B.S.Sherigara, *Int. J. Electrochem. Sci.,* 4 (2009) 1469
32. K.R. Mahanthesha, B.E. Kumara Swamy, U. Chandra, Y. D. Bodke, K. V.Pai, B.S. Sherigara, *Int.J.Electrochem.Sci.*4 (2009) 1237.
33. B.E. Kumara Swamy and B.Jill venton, *Anal.chem*. 79 (2007)744.
34. E.Niranjana, R.Raghavendra Naik, B.E. Kumara Swamy, Y. D.Bodke, B.S.Sherigara, H.Jayadevappa , B.V. Badami, *Int.J.Electrochem.Sci.* 3(2008) 980.
35. E.Ramanathan, P.S.M. Kannan, S.Thangavelu, K.S. Udupa,*Bull.Electrochem*. 4 (1988)365.
36. B.Eswarappa, B.S. Sherigara, B.E. Kumara Swamy, *Bull.Electrochem*.20 (2004)1.
37. C.Sliptien, M.Ariel, *J.Electroanal.chem.*75 (1977)551.
38. C.Amatore, J.M. Saveant, D.Tessier, *J.Electroanal.chem.* 146(1988)37.
39. R. N. Hegde, B. E. Kumara Swamy, N. P. Shetty, S. T. Nandibewoor, *J. Electroanal. Chem.*, 635 (2009) 51.
40. Umesh Chandra, B.E. Kumara Swamy, O. Gilbert, B.S. Sherigara, *Electrochim. Acta*, xxx (2010) xxx.
41. Yuzhong Zhang, Guiying Jin, Yanling Wang and Zhousheng Yang, *Sensors*, 3 (2003) 443.