Full Paper

Sensitive Electrochemical Analysis of Resorcinol using Polymer Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

Chenthattil Raril and Jamballi G. Manjunatha*

Department of Chemistry, FMKMC College, Madikeri, Mangalore University Constituent College, Karnataka, India

*Corresponding Author, Tel.: +91- 08272228334

E-Mail: manju1853@gmail.com

Abstract- Glycine was electropolymerized on a carbon paste electrode (CPE) to form the polymer film in the electrooxidation process of the amino and carboxylic group containing compound by cyclic voltammetric technique and the electrochemical oxidation of resorcinol (RC) was studied in 0.2 M phosphate buffer solution (PBS) having pH 7.0. Modified carbon paste electrode (MCPE) shows a good electrocatalytic activity towards RC compared to bare carbon paste electrode (BCPE). The oxidation of RC at MCPE showed a linear relation versus concentration of RC in the range of 6×10^{-5} to 1×10^{-3} M with a detection limit 8.6×10^{-6} M.

1. INTRODUCTION

Resorcinol (RC) is a phenolic compound (Benzene-1,3-diol) has wide range of application in both chemical and pharmaceutical industry. It is widely used as a medicine to treat some diseases such as Psoriasis, Seborrheic and other skin illness and also used an antiseptic and disinfectants. It is used in hair coloring agent as well. As, such it is essential to

accurately quantify the amount of RC in such formulations. Many methods are proposed to determine RC such as High-performance liquid chromatography [1], Fluorescence [2], Spectrophotometric [3], Electrochemical [4-5].

Voltammetric techniques are the most useful tools in analytical science especially for studies of electroactive species. Modern research laboratories are usually equipped with electrochemical techniques [6]. These methods can be used to study the kinetics and thermodynamics of electron and ion transfer process [7], to investigate the adsorption phenomena that occur at the electrode surface and to study the reaction mechanism. Among the voltammetric methods, cyclic voltammetry (CV) is most popular method to investigate the electrochemical behavior of new redox systems [8].

Among the variety of electrodes, Polymer modified electrodes (working electrode) [9-10] have shown to be powerful tool in electrochemical methods for the determination of electroactive species, because of film thickness, permeation and charge transfer transport can be controlled by adjusting the electrochemical parameters. In future these modified electrodes which act as sensors can be used in the medicine and biotechnology field [11-31].

In this present work carbon paste electrode was modified via electropolymeization of Glycine. Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) were used to examine the reaction mechanism of RC molecule with varying parameters like scan rate, pH, and concentration in 0.2 M phosphate buffer solution (PBS). There is no voltammetric sensor based on PGMCPE for the determination of RC [32,33].
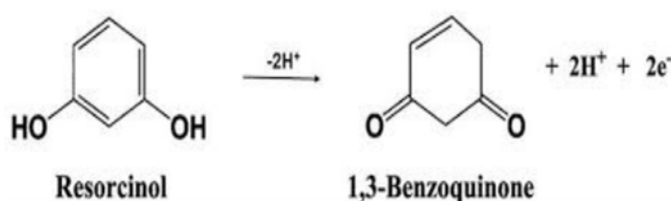

Fig. 1. Structure and the reaction mechanism of resorcinol

2. MATERIALS AND METHODS

2.1. Instrumentation

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on a model 201 (EA-201, Chemilink system, Mumbai, India). Carbon paste electrode (CPE) and polyglycine modified carbon paste electrode (PGMCPE) used as a working electrode. An aqueous saturated calomel electrode (SCE) as the reference electrode and platinum wire employed as the auxiliary electrode.

2.2. Reagents and Chemicals

Graphite, silicone oil, purchased from Nice Chemicals, India. RC obtained from Spectrum Reagents Pvt. Ltd. India. Other chemical were analytical grade and used without further purification. RC stock solution (25×10^{-3} M) was prepared by dissolving in double distilled water and 25×10^{-3} M glycine stock solution was prepared in double distilled water. Phosphate buffer solution (0.2 M) was prepared by mixing the suitable amount of 0.2 M monosodium phosphate and 0.2 M disodium phosphate and having pH 7.0 was used as supporting electrolyte. All the data's were collected at room temperature (25° C).

2.3. Fabrication of the modified electrode

Graphite powder and silicone oil in the ratio of 70:30 was mixed thoroughly until a homogeneous paste was obtained, CPE was obtained by packing the paste on the surface of teflon tube having cavity 3 mm diameter. The bare CPE was placed in 0.2 M PBS at pH 5.7 containing 1×10^{-3} M glycine solution. Poly (glycine) film was prepared by electropolymerization of glycine in the potential window between 500–1800 mV at the scan rate of 100 mV/s for ten cycles (Fig. 2). Poly (glycine) modified electrode was rinsed with water in order to remove the unreacted glycine and used for the RC determination. Oxidation current decreases after 10 cycles because of increase in thickness of polymeric film will hinder the movement of electron transfer on the electrode surface. Therefore, 10 electropolymerization cycles were selected.
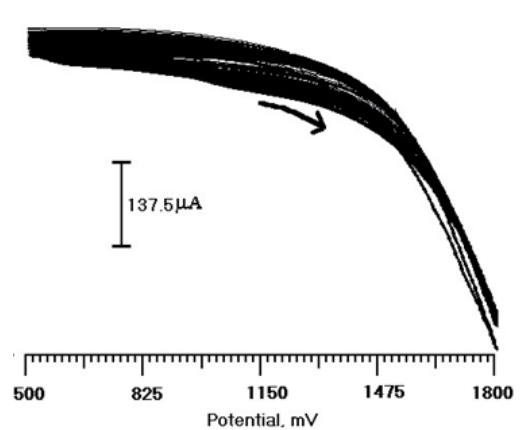

Fig. 2. Cyclic voltammogram for the electrochemical polymerization of 1×10^{-3} M glycine on a carbon paste electrode (CPE) in 0.2 M PBS (5.7 pH) at the scan rate 100 mV/s

3. RESULT AND DISCUSSION

3.1. Surface analysis of BCPE and PGMCPE

Field emission scanning electron microscopy (FESEM) was used to characterize the Surface morphology BCPE and MCPE. Fig. 3 shows the morphological features of BCPE (Fig. 3a) and PGMCPE (Fig. 3b). The FESEM image clearly shows the typical uniform arrangements of poly (glycine) on the surface of carbon paste electrode where BCPE shows irregular shaped with graphite. This confirms that CPE was coated by poly (glycine) film.
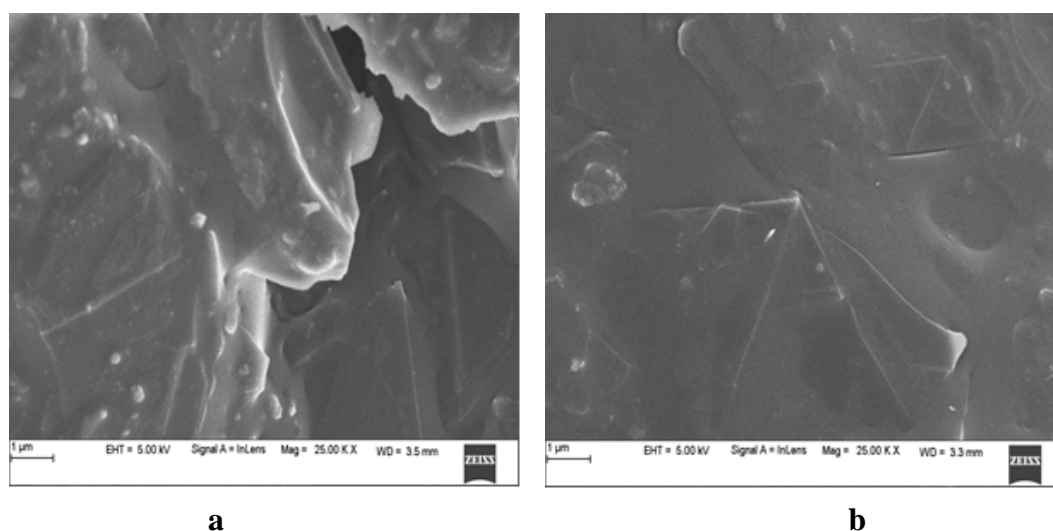

a　　　　　　　　　　　　　　　　　　　**b**

Fig. 3. FESEM image of BCPE (a) PGMCPE (b)

3.2. Determination of electrochemical surface area

The surface area available for the electron transfer in the solution can be calculates by Randles – Sevcik equation. This equation is related to the peak current with square root of scan rate.
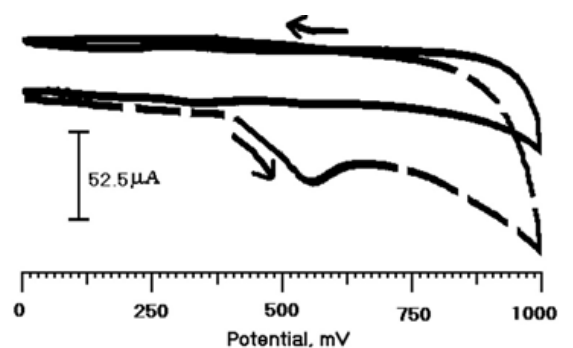

Fig. 4. Cyclic voltammogram of PGMCPE with RC (1×10^{-3} M) (dashed line) and without RC (solid line) in 0.2 M PBS, pH 7.0 without 1×10^{-3} M RC (dashed line)

For the irreversible reaction, $I_p = 2.69 \times 10^5 n(\alpha n)^{1/2} A D^{1/2} C v^{1/2}$, Where I_p is the peak current (A), n is the number of electrons, A is the electroactive area (cm^2), D is the diffusion co-efficient (cm^2/s), C is the concentration of the electroactive species (mol/cm^3) and $v^{1/2}$ is the square root of scan rate (V/s). The diffusion coefficient value obtained from the slope of I_{pa} Vs $v^{1/2}$ plot (data not shown). The surface area of the polymer modified electrode is calculated using the randles equation and obtained as 0.033 cm^2.

3.3. Electrochemical investigation of RC at PGMCPE

As shown in Fig. 4 in the absence (solid line) of RC which is characterized by CV within the potential 0–1000 mV at a scan rate of 100 mV/s (0.2 M PBS, pH 7.0) no redox peak appears for PGMCPE. But under identical condition and in presence of 1×10^{-3} M RC (dashed line) broader oxidation peak was observed at 560 mV with an oxidation peak current of 66.8 µA. It means the electrochemical behavior of RC can be improved by this modified electrode.

3.4. Voltammetric behavior of RC at PGMCPE

Cyclic voltammetric behavior of RC (1×10^{-3} M) in 0.2 M PBS of pH 7.0 at the scan rate of 100 mV/s at BCPE (solid line) and PGMCPE (dotted line) has studied and shown in Fig. 5. BCPE showed the poor electrochemical response compared to the MCPE, and the oxidation of RC occurs irreversibly at PGMCPE with an increased peak current (I_{pa}=66.8 µA) with anodic peak potential of 560 mV, clearly indicates that the good catalytic activity of RC at PGMCPE compare to BCPE.
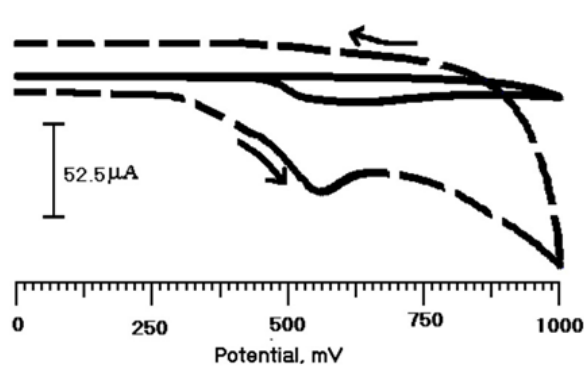

Fig. 5. Cyclic voltammogram of RC (1×10^{-3} M) in 0.2 M PBS buffer solution of pH 7.0 at BCPE (solid line) and PGMCPE (dashed line)
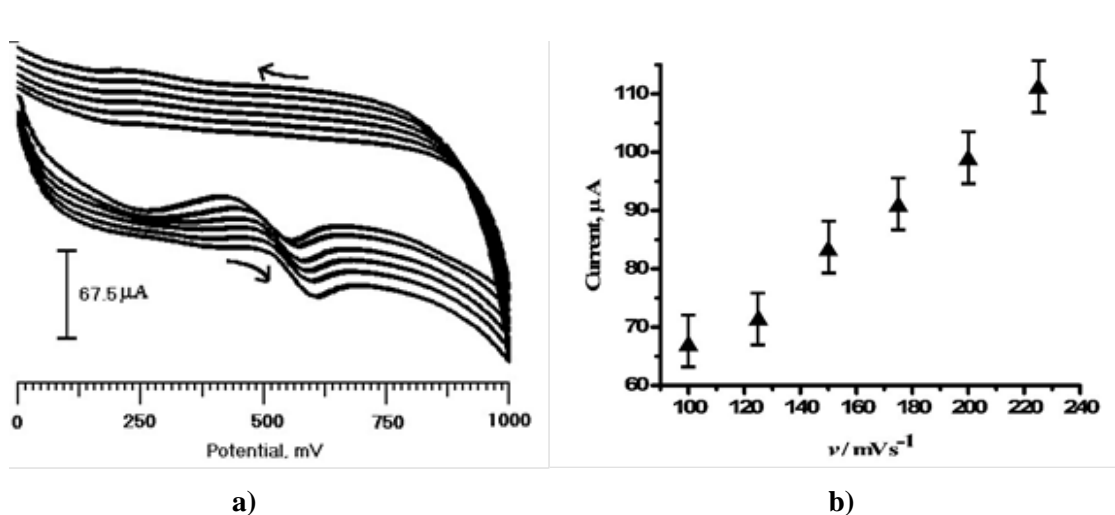
Fig. 6. (a) Cyclic voltammogram of RC (1×10^{-3} M) at PGMCPE in pH 7.0 at various scan rates. From 100, 125, 150, 175, 200, 225 mV/s; (b) Plot of peak current of RC as a function of scan rate
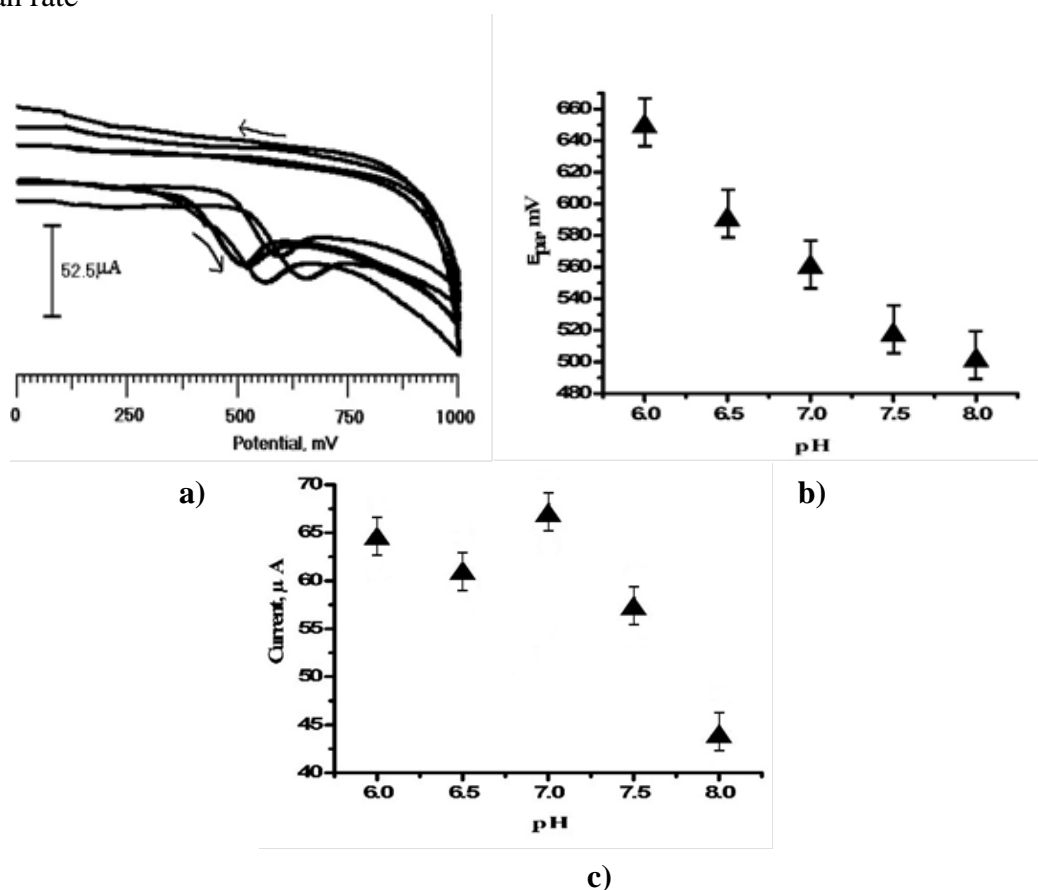

Fig. 7. (a) Cyclic voltammogram at PGMCPE in 0.2 M PBS in different pH values (a) 6.0 (b) 6.5 (b) 7.0 (d) 7.5 (e) 8.0 containing RC (1×10^{-3} M); (b) Plot of anodic peak potential (E_{pa}) Vs pH at PGMCPE; (c) anodic peak current (I_{pa}) Vs pH for RC

3.5. Effect of scan rate on the determination of RC at PGMCPE

The oxidation peak current of 1×10^{-3} M was measured at PGMCPE by CV at different scan rates from 100 to 225 mV/s (Fig. 6a). It is observed that with the increased scan rate (v), the peak current also increased gradually (shifted towards more negative). The graph of peak current (I_{pa}) Vs scan rate (v) was plotted. The graph obtained was having good linearity between scan rate (v) and peak current (I_{pa}) in the range of 100 to 225 mV/s (Fig. 6b). With a linear regression equation as $I_{pa}(\mu A)=29.21+0.35\ v$ (mVs^{-1}) (Fig. 6b) with a correlation coefficient R=0.99409 [34,35] which indicates that the electron transfer reaction was adsorption controlled.

3.6. Effect of pH on the determination of RC at PGMCPE

The effect of pH was studied by using CV technique over the pH range from 6.0 to 8.0 in 0.2 M PBS. Fig. 7 shows the cyclic voltammogram of 1×10^{-3} M RC. The peak potential was shifted towards positive side by increasing the pH and observed that anodic peak potential (E_{pa}) of RC was proportional with the solution pH in the range of 6.0-8.0. The linear regression equation for RC was $E_{pa}=1080–73.8$ pH (R=0.98293) (Fig. 7a)

A slope of 73.8 close t to the theoretical value 58.5 mV/ pH indicates that, the proportion of electron and proton involved in the reaction was 1:1. As the oxidation of RC is two –electron process [36] (Fig. 1) and oxidation peak current (I_{pa}) of RC maximum achieved at pH 7.0. Considering the sensitivity of the determination of RC, the pH 7.0 was chosen for the experiment.

3.7. Repeatability, Reproducibility and stability studies

Repeatability and reproducibility were studied using CV and recorded in 0.2 M PBS (pH 7.0) at the scan rate of 100 mV/s. PGMCPE shows good repeatability for 10 successive measurements with a standard deviation (RSD) of 2.8%. Moreover it exhibits a good reproducibility for 5 individual measurements with an RSD of 2.65%. The stability of fabricated sensor was studied by 50 consecutive cycles and has observed that 98% of the initial current signal was retained even after 50 cycles, shows that fabricated electrode having good stability.

3.8. Response of RC at PGMCPE by DPV

DPV will give higher current density and better resolution than CV. DPV response of 1 mM RC in 0.2 M PBS (pH 7.0) at BCPE and PGMCPE in the potential window 0 to 1000 mV and are shown in Fig. 8.
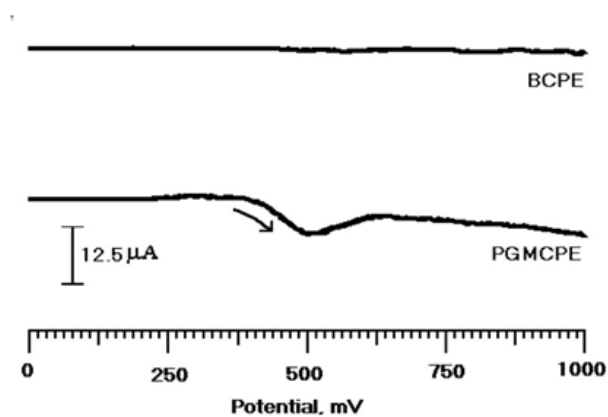
Fig. 8. DPV of a solution containing RC (1×10^{-3} M) in 0.2 M PBS at the BCPE and PGMCPE

The peak potential for PGMCPE is observed at 543 mV with a peak current of 42.4 µA and there was no peak was observed for BCPE, which indicates that, the best electrocatalytic oxidation of RC at PGMCPE.

3.9. Real sample analysis

In order to make sure the application of the fabricated sensor in real sample analysis hair dye powder purchased from local supermarket and measured by using standard addition method. Satisfactory results were obtained for the three measurements.
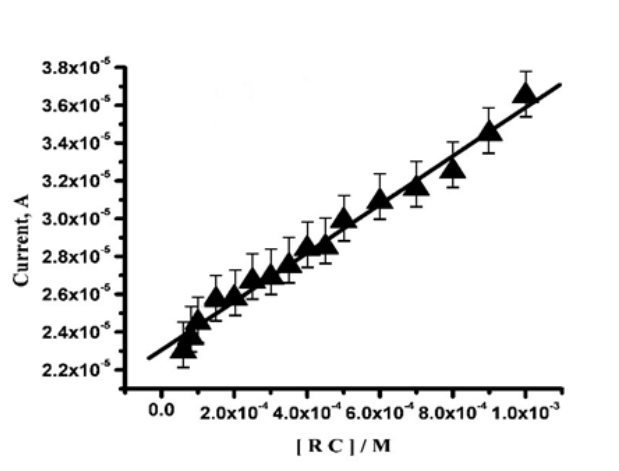

Fig. 9. Calibration plot for the determination of RC at the PGMCPE in pH 7.0 PBS with the scan rate 100 mV/s

Recoveries were obtained from 97.6% to 103.6%, indicates that the modified electrode can be used for the determination of RC in hair dye powder.

3.10. Effect of concentration of RC

To study the effect of concentration of RC, CV technique was used. Electrocatalytic oxidation of RC was carried out at PGMCPE by varying concentration and is shown in Fig. 9. RC shows a linear relationship in the range of 6×10^{-5} to 1×10^{-3} M with a linear regression equation as $I_{pa}=2.3\times10^{-5}+0.012$ C with a correlation coefficient 0.99284. The limit of detection (LOD) and limit of quantification (LOQ) of RC were calculated by using following formulas, LOD=3 S/M and LOQ=10 S/M [37]. Where S is the standard deviation and M is the slopes obtained from the calibration plot and were obtained as 8.5×10^{-6} and 28.7×10^{-6}. The comparison of detection limit with different related work were reported [4,28,38,39] and shows that the developed sensor exhibit higher sensitivity and having low detection limit (Table. 1).

Table. 1. Detection limit comparison of PGMCPE with some other modified electrode for the determination of RC

Electrodes	Detection limit (µM)	Linear range(µmol L^{-1})	Ref.
SDSMCNTGMPE	5.8	20-1000	[4]
MWNTs/GCE	0.49	1.2-190	[37]
Graphene - chitosan/GCE	0.75	1-550	[38]
MWNTs/multielectrode array	0.6	6-100	[28]
PGMCPE	8.6	60-1000	This work

4. CONCLUSION

A stable polymer film of glycine was produced on CPE by electropolymerization and showed a good sensitivity, selectivity, with good stability. The prepared PGMCPE exhibit highly electrocatalytic activity towards the oxidation of RC. Oxidation peak potential was observed at 560 mV with an oxidation peak current of 66.8 µA. The oxidation process of RC has found to be irreversible, adsorption controlled, two electron–two proton process and the modified electrode shows good electrocatalytic activity, reproducibility, repeatability and good stability. RC shows a linear relationship in the range of 6×10^{-5} to 1×10^{-3} M with a good detection limit of 8.6×10^{-6} M. The practically of the proposed sensor was evaluated by sensing RC in real sample and satisfactory result has obtained.

Acknowledgement

18/126/333, 21/11/2017 and Mangalore University under Research Project order No. MU/DEV/2014-15/D3 D.t:30.04.2016.

REFERENCES

[1] L. Yang, Z. Wang, and L. Xu, J. Chromatogr. A 1104 (2006) 230.

[2] M. F. Pistonesi, M. S. Di Nezio, M. E. Centurion, M. E. Palomeque, A. G. Lista, and B. S. Fernandez Ban, Talanta 69 (2006) 1265.

[3] K. D. Khalaf., B. A. Hasan, A. Morales-Rubio, and M. de la Guardia, Talanta 41 (1994) 547.

[4] J. G. Manjunatha, Asian J. Pharm. Clin. Res. 10 (2017)295.

[5] M. U. Hossain., M. T. Rahman, and M. Q. Ehsan. Int. J. Anal. Chem. (2015) 862.

[6] J. Bard, Electrochemical methods fundamentals and application, second edition, United States of America (2008).

[7] Bagotsky, Fundamentals of electrochemistry, second edition, United States of America (2005).

[8] R. Gulaboski and C. M. Pereira, Electroanalytical Techniques and Instrumentation in Food Analysis, Handbook of Food Analysis Instrument, (2008) 379.

[9] A. Volkov, G. Tourilon, P. C. Lacaze, and J. E. Dubios, J. Electroanal. Chem. 115 (1980) 279.

[10] Y. Ohnuki, T. Ohsaka, M. Matsuda, and N. Oyam, J. Electroanal. Chem. 158 (1983) 158.

[11] H. Wang, X. Qiao, J. Chen, and S. Ding, Colloids Surf A 256 (2005)111.

[12] S. Corona-Avendano, G. Alarcon-Angeles, M. Romero-Romo, A. Cuan, M. T. Ramirez-Silva, and L. Hernandez-Martinez, J. Appl. Electrochem. 40 (2010) 463.

[13] V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, and K. C. Kemp, Chem. Rev. 112 (2012) 156.

[14] J. Du, Y. Li, and J. Lu, Talanta 55 (2001) 1055.

[15] J. Q. Huang, C. C. Hu, and T. C. Chiu, Int. J. Cosmetic Sci. 35 (2013) 346.

[16] F. Welsch, Int. J. Toxicol. 27 (2008) 59.

[17] J.G. Manjunatha, Deraman. M, Basri. N. H and Talib. I. A, Arab. J. Chem. 11 (2018) 149.

[18] J. G. Manjunatha, B. E. Kumara Swamy, M. Deraman, and G. P. Mamatha, Der Pharm. Chem. 4 (2012) 2489.

[19] J. G. Manjunatha, B. E. Kumara Swamy, G. P. Mamatha, O. Gilbert, M. T. Shreenivas, and B. S. Sherigara, Der Pharm. Chem. 3 (2011) 236.

[20] J. G. Manjunatha, B. E. Kumara Swamy, G. P. Mamatha, C. Umesh, E. Niranjana, and B. S. Sherigara, Int. J. Electrochem. Sci. 4 (2009) 187.

[21] J. G. Manjunatha, B. E. Kumara Swamy, M. Deraman, and G. P. Mamatha, Int. J. Pharm. Sci. 5 (2013) 355.

[22] J. G. Manjunatha, B. E. Kumara Swamy, G. P. Mamatha, S. Sharath Shankar, O. Gilbert, and B. N. Chandrashekar Int. J. Electrochem. Sci. 4 (2009) 1469.

[23] J. G. Manjunatha, B. E. Kumara Swamy, G. P. Mamatha, O. Gilbert, and B. S. Sherigara, Anal. Bioanal. Electrochem. 3 (2011) 146.

[24] J. G. Manjunatha, B. E. Kumara Swamy, and M. Deraman, Anal. Bioanal. Electrochem. 5 (2013) 426.

[25] X. Zhu, and X. Lin, Chinese J. Chem. 27 (2009) 1103.

[26] M. Pistonesi, M. E. Centurion, M. Pereyra, A. G. Lista, and B. S. F. Band, Anal. Bioanal. Chem. 378 (2004) 1648.

[27] M. Narita, K. Murakami, and J. Kauffmann, Anal. Chim. Acta. 588 (2007) 316.

[28] D. Zhang, Y. Peng, H. Qi., Q. Gao, and C. Zhang, Sens. Actuators B 136 (2009) 113.

[29] K. Mikame, and M. Funaoka, Polym. J. 38 (2006) 592.

[30] P. Livant, T. R. Webb, and W. Xu, J. Org. Chem. 62 (1997) 737.

[31] Y. Aoyama, Y. Tanaka, H. Toi, and H. Ogoshi, J. Am. Chem. Soc. 110 (1998) 634.

[32] K. Verschueren, Handbook of Environmental Data on Organic Chemicals, 3rd Ed., New York, Van Nostrand Reinhold (1996) 1611.

[33] C. Goebel, T. L. Diepgen, and M. Krasteva. Regulatory Toxicol. Pharmacol. 64 (2012) 459.

[34] T. Alizadeh, M. R. Ganjali, M. Zare, and P. Norouzi., Electrochim. Acta 55 (2010) 1568.

[35] M. Javanbakht, M. R. Ganjali, P. Norouzi, A. Badiei, A. Hasheminasab, and M. Abdouss, Electroanalysis 19 (2007) 1307.

[36] D. Vega, L. Agui, A. Gonzalez-Cortes, P. Yanez–Sedeno, and J. M. Pingarron, Talanta 71 (2007) 1031.

[37] H. Beitollahi, H. Karimi-Maleh, and H. Khabazzadeh, Anal. Chem. 80 (2008) 9848.

[38] S. M. Ghoreishi, M. Behpour, E. Hajisadeghian, and M. Golestaneh, Arab. J. Chem. 9 (2016) 1563.

[39] H. Yin, Q. Zhang, Y. Zhou, Q. Ma, T. Liu, and L. Zhu, Electrochim. Acta 56 (2011) 2748.