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Original scientific paper

Enhanced voltammetric detection of paracetamol by using carbon nanotube modified electrode as an electrochemical sensor

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Abstract

New aspects associated with electro-catalytic activity of poly(methyl orange) modified carbon nanotube paste electrode (PMMCNTPE) towards the detection of paracetamol (PC) which is typically used worldwide as a pain reliever, were explored through implementation of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. Bare carbon nanotube paste electrode (BCNTPE) was modified by methyl orange using the electro-polymerizing method. The effect of pH and influence of potential scan rate were resolved by means of CV technique. It was found that under optimized experimental conditions, PMMCNTPE imparts the analytical curve for PC in the concentration range of 2.0×10^{-6} – 5.0×10^{-5} M with detection limit of 3.8×10^{-8} M and limit of quantification of 1.2×10^{-8} M. The proposed sensor exhibited acceptable reproducibility, admirable stability, and adequate repeatability. The interference study of PC with dopamine (DA) and folic acid (FA) showed good selectivity of the designed sensor. The feasibility of the constructed electrochemical sensor to detect PC was successfully tested in some pharmaceutical formulations.

Keywords

Voltaammetric studies; electropolymerization; methyl orange; paracetamol; detection limit

Introduction

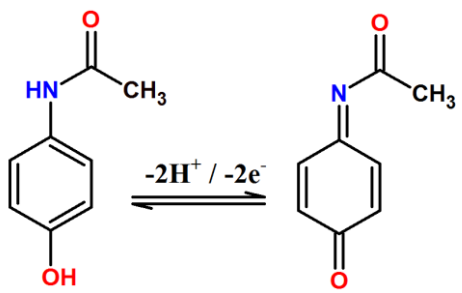
The quality of human health was vastly upgraded in last fifty years, what is predominantly due to well-developed medicines, education, and lifestyle. At the present time, an increase in daily use of pharmaceuticals to prolong life and avoid or cure various diseases, has additionally been recorded [1-2]. One of the most frequently used drugs is painkillers. Among several painkillers, paracetamol (PC) has commonly been used for fever of viral and bacterial sources and pain relief [3]. PC (acetaminophen, N-acetyl-p-aminophenol) diminishes mild-moderate pain related with headache, migraine, toothache, backache, muscular aches, and postoperative pains [4-6]. It is the best

substitute for patients who are sensitive to aspirin, which is also used as an analgesic [7-8]. Normally, PC does not have any harmful side effects, as it is completely metabolized into inactive metabolites that can easily be excreted *via* urine [9], whereas the overdoses of PC can lead to hepatic-toxicity and nephron-toxicity [10-13]. Due to its growing use, defecated PC together with PC disposal in manufacturing industrial effluents raise its presence in water source systems [14]. To control and evade these problems, the monitoring of PC becomes essential.

Drug analysis in biological systems provides valuable information in pharmacokinetic studies, and clinical diagnosis. The literature surveys revealed a number of already developed techniques for determining PC in different samples [15]. These techniques include titrimetric determination [16–18], liquid chromatography-mass spectroscopy [19-20], high performance-liquid chromatography [21-22], liquid chromatography [23], capillary electrophoresis [24], chemiluminescence [25], UV–Vis spectrometry [26-27], infrared spectroscopy [28], and flow [29-30] and batch [31] injection analyses. These methods offer high sensitivity, selectivity and accuracy, but difficulties of their use such as time-consuming measurement process, highly expert technicians required for the operation, and high cost instruments, limit their extensive applications. The electrochemical approach, however, provides simple, quick, and selective analyte detection with inexpensive and durable instruments. Recently, electrochemical methods have attracted great attention because compared to traditional methods, they are simpler and more sensitive. Also, electrochemical methods offer excellent stability and repeatability and require short analytical time. The construction of novel electrochemical sensors based on carbonaceous materials such as carbon nanotubes (CNTs), graphene and graphite, has an outstanding importance in the development of electroanalytical techniques. This is due to their uncomplicated preparation, low cost, high conductivity, and biocompatibility. CNTs are one of the carbonaceous materials that have already been well inspected for the design of electrochemical sensors with fabulous physical and chemical properties, including high conductivity and large surface area [32-33].

For further enhancing of electrode properties, however, electrode surfaces should be modified. To modify CNT paste electrode (CNTPE), electro-polymerization is one of frequently used modification methods in which a certain thickness of polymer films on the electrode is obtained by regulating the number of cycles or potential values applied to an electrode. The modified CNTPE is worthy for enhancing electrode conductivity and stimulating the transfer of electrons [34-35].

The present work targets the fabrication of the electrochemical sensor based on the bare CNTPE (BCNTPE) modified with methyl orange and the fabricated PMMCNTPE sensor was implemented to the detection of PC by CV technique. The voltammetric response of PC at PMMCNTPE showed a quasi-reversible redox behavior and remarkable improvement in current sensitivity. According to reports available in the literature, BCNTPE modified with methyl orange as an electrochemical sensor was not yet utilized for the determination of PC using CV technique. The constructed sensor was successfully employed to the determination of PC, dopamine (DA) and folic acid (FA) simultaneously. The electro-oxidation mechanism of PC is shown in scheme 1.



***Scheme 1**: Electro-oxidation mechanism of PC*

Experimental

Reagents and solutions

PC was procured from Tokyo Chemical Industry Company Ltd. (Japan). CNTs were purchased from the Sisco Research Laboratories Pvt. Ltd. Mumbai, Maharasthra (OD: 30-50 nm and length: 10-30 μm). Silicone oil and methyl orange were obtained from Nice Chemicals, India. Monosodium hydrogen phosphate (NaH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) were acquired from Molychem, India. All analytical grade chemicals were used without any further treatment. Stock solutions of PC (25×10^{-4} M) and methyl orange (25×10^{-4} M) were prepared in distilled water. PBS (0.2 M) solutions of proper pH for particular experiments were prepared by mixing appropriate amounts of 0.2 M NaH_2PO_4 and 0.2 M Na_2HPO_4 and used as supporting electrolytes. All voltammetric experiments were carried out at the room temperature (25±1 °C).

Instrumentation

The voltammetric measurements were performed by using an electrochemical working station CHI-6038E (CH-Instruments-USA), integrated to the personal computer. The electrochemical analyzer was fitted with an electrochemical cell consisting of three-electrode compartment that comprised BCNTPE or PMMCNTPE as a working electrode, a platinum wire as an auxiliary electrode, and the standard calomel electrode (SCE) as a reference electrode. All the potential values were referred against SCE. The EQ-610 model digital pH meter was used to provide the solution with the relevant pH for the experiment. All peak current measurements were taken with the background current. The DST purse lab, Mangalore University, provided the FESEM characterization of the bare and modified electrodes.

Fabrication of PMMCNTPE

In the first stage of preparation of the modified electrode, BCNTPE was constructed by hand mixing of CNTs and silicone oil in the ratio 60:40 in an agate mortar and grinding with the help of pestle until a homogenous CNT paste was obtained. The resultant homogenous CNT paste was then firmly packed into the cavity of the teflon tube and smoothed on a tissue paper to obtain the uniform surface. A copper wire was introduced into the teflon tube to provide the electrical contact. Afterwards, PMMCNTPE was fabricated by electrodeposition of methyl orange on the surface of the prepared BCNTPE. Electrodeposition was carried out in 0.2 M PBS of pH 7.0 in the presence of 1×10^{-4} M methyl orange, for 15 continuous potential cycles between -0.6 to 1.4 V at a scan rate 0.1 V s^{-1}. After electrochemical polymerization, the surface of the prepared PMMCNTPE was thoroughly washed with the distilled water and used for the further electrochemical analysis.

Results and siscussion

Electrochemical polymerization of methyl orange on BCNTPE

Methyl orange (MO) is a redox indicator undergoing polymerization. Electrochemical polymerization of MO was carried out on the surface of BCNTPE between -0.6 V and 1.4 V for 15 cycles at the scan rate 0.1 V s^{-1}, and an adequate polymer growth was attained. Figure 1 shows cyclic voltammograms (CVs) of the electrochemical polymerization of 1×10^{-4} M MO in 0.2 M PBS of pH 7.0 indicating satisfactory development of the polymer on the surface of BCNTPE. Two anodic peaks and one reduction peak in CVs are related to the redox behavior of MO. The electrochemical polymerization of MO has been already reported [36-38].

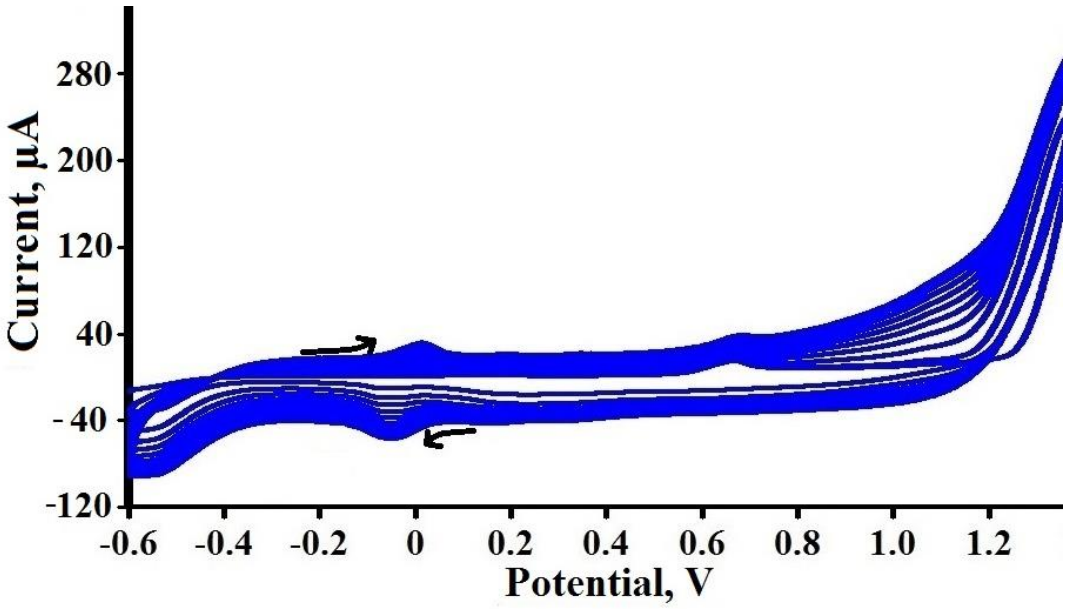


Figure 1. *Electrochemical polymerization of methyl orange at BCNTPE*

Surface morphology characterization of BCNTPE and PMMCNTPE

The surface morphologies of BCNTPE and PMMCNTPE were probed with FESEM. Figures 2(a) and 2(b) present FESEM images of BCNTPE and PMMCNTPE, respectively. The FESEM image of BCNTPE discloses a rough surface morphology with a tube-like CNT structure, while the smooth surface morphology in FESEM image of PMMCNTPE shows formation of uniform polymeric film of MO on the surface of BCNTPE. Therefore, by comparing FESEM images of BCNTPE and PMMCNTPE, it can clearly be seen that electrodeposition of MO on the surface of BCNTE was successfully achieved forming poly-MO film by electrochemical polymerization.

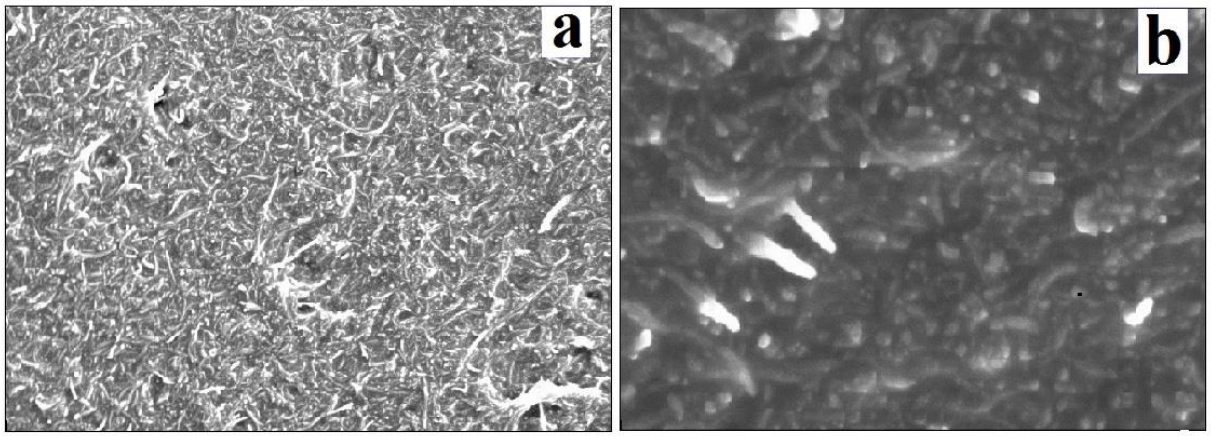


Figure 2. *FESEM magnified image of (a) BCNTPE and (b) PMMCNTPE*

Electrochemical behavior of PC at BCNTPE and PMMCNTPE characterized by CV technique

The electroactivity of PC compound on PMMCNTPE has been analyzed by means of CV method. Figure 3 presents cyclic voltammetric responses of 1×10^{-4} M PC at PMMCNTPE (dashed line) and BCNTPE (solid line) in 0.2 M PBS of pH 7.5, recorded at the scan rate 0.1 V s^{-1} in the potential window 0 V to 0.8 V. BCNTPE offers less significant oxidation peak with a current of 24.2 µA without a reduction peak. PMMCNTPE, however, shows boosted electrocatalytic behavior towards the electro-oxidation of PC with an oxidation peak at 0.357 V having current value of 72.9 µA and a well-defined reduction peak at 0.217 V with current of 41.2 µA, respectively. The redox peak currents of

PC at PMMCNTPE are higher than the redox peak currents of PC at BCNTPE. Also, ΔE_p is 0.14 V, what suggests a quasi-reversible redox performance of the PC on the surface of PMMCNTPE [39]. Hence, PMMCNTPE shows a good electrochemical sensing performance towards the redox behavior of PC.

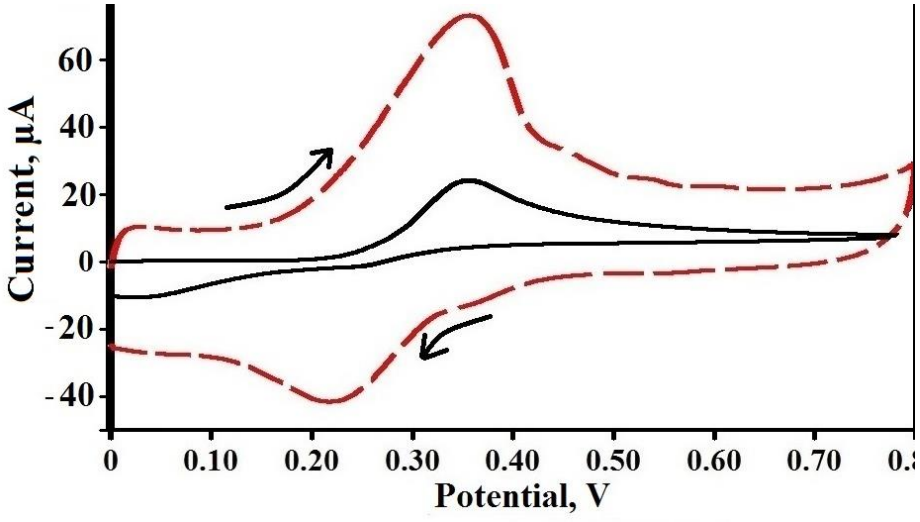


Figure 3. *CVs of PC (1×10^{-4}M) at BCNTPE (solid line), and PMMCNTPE (dashed line) in 0.2 M PBS of pH 7.5, at the scan rate 0.1 V s^{-1}*

Electrochemical response of PC on PMMCNTPE

The electrochemical response of PC at PMMCNTPE was inspected with CV technique. Figure 4 presents CVs at PMMCNTPE without (curve a) and with (curve b) PC in 0.2 M PBS of pH 7.5. CVs were recorded at the scan rate 0.1 V s^{-1} and potential scanned between 0 V to 0.8 V. In the presence of PC, oxidation peak appeared at 0.357 V with a current of 72.9 µA while without PC in the solution, redox peaks were not observed. Therefore, the above result suggests that the analyte PC could be detected by PMMCNTPE by utilizing CV method.

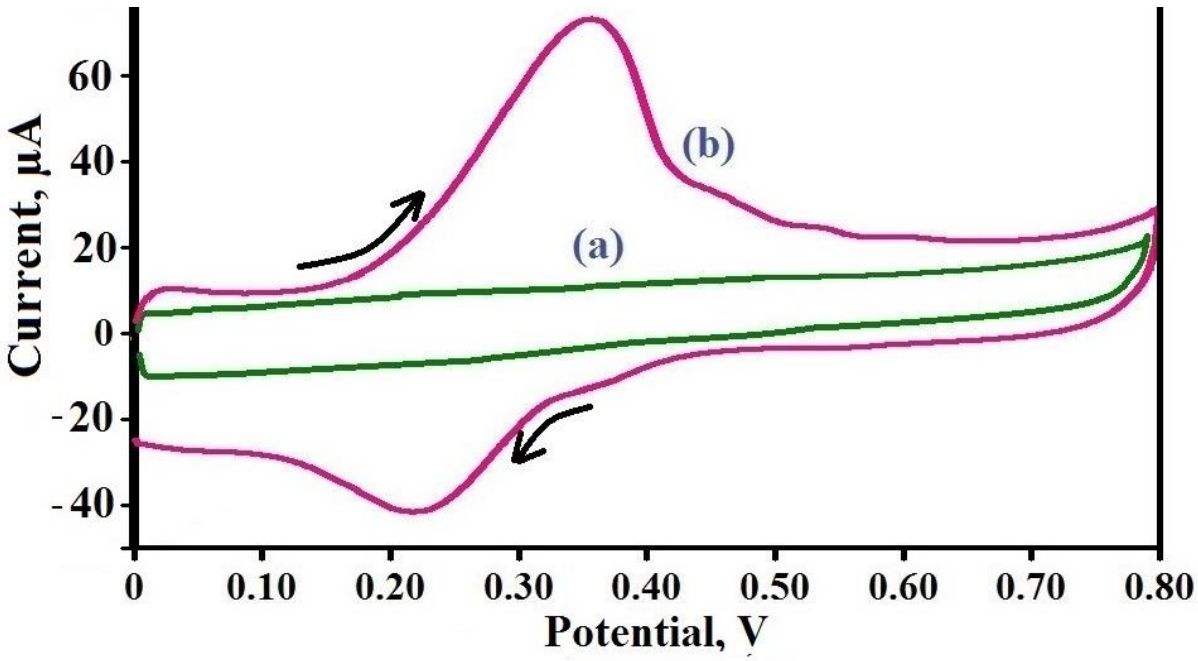


Figure 4. *CVs of PMMCNTPE without PC (curve a) and with 1×10^{-4} M PC (curve b) in 0.2 M PBS of pH 7.5, at the scan rate 0.1 V s^{-1}.*

Effect of pH variation

The pH of the supporting electrolyte is one of the main experimental parameters affecting the voltammetric response of PC at PMMCNTPE. Therefore, an optimum pH is required to maximize the intensity of redox peak currents. Figure 5(a) illustrates voltammetric responses of PC in 0.2 M PBS of pH varying from 6.5 to 8.0, at the scan rate 0.1 V s^{-1}. As can be deduced from CVs in Figure 5(a), the current signal of PC at PMMCNTPE increases with elevating pH value from 6.5-7.5, and after that, the current signal decreases with further increase of pH value. This is clearly shown in Figure 5(b) from the graphical plot of $I_{pa.}$ *vs*. pH. Thus, pH 7.5 was selected as the optimum pH value for further experiments. In Figure 5(c), the graph of E_{pa} *vs.* pH is plotted, showing a linear relationship between the oxidation peak potential and pH value in the range 6.5 to 8.0. The displayed linear regression equation is:

E_{pa} / V = 0.0705 - 0.0453 pH (R^2 = 0.9968)

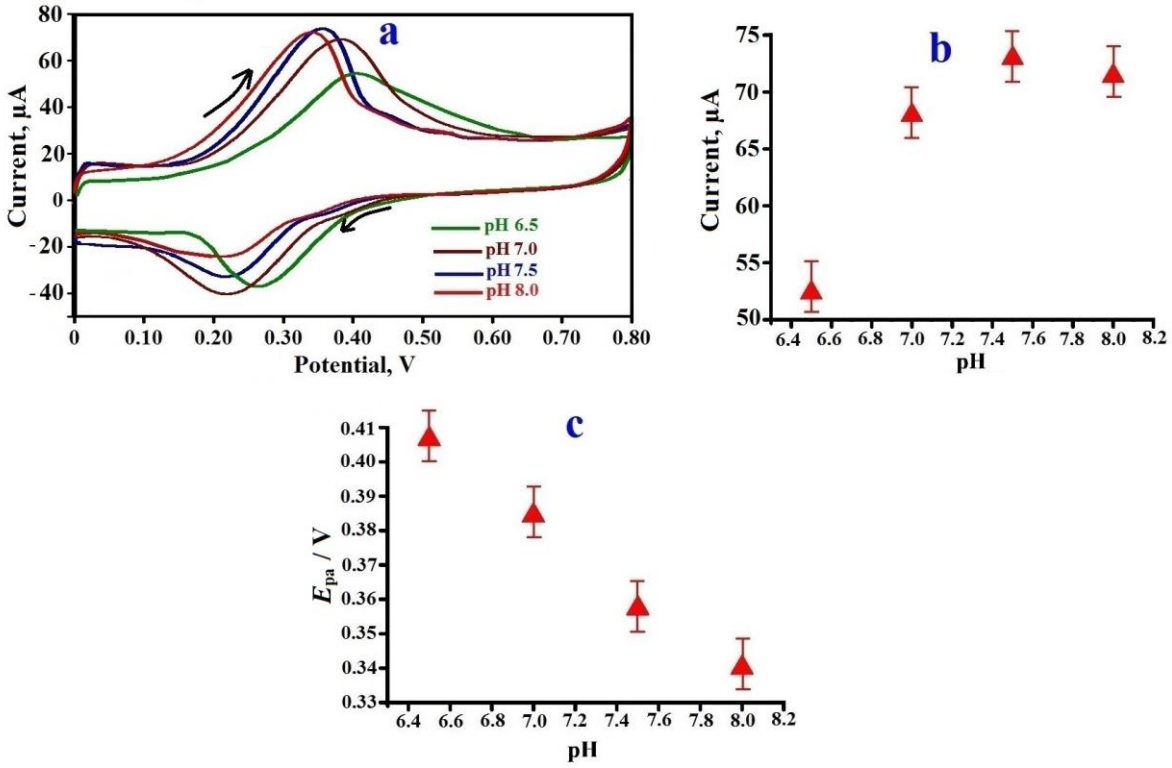


Figure 5: (a) *CVs of 1×10^{-4} M PC at PMMCNTPE in 0.2 M PBS at pH varying from 6.5-8.0, at the scan rate 0.1 V s^{-1},* ***(b)*** *$I_{pa,}$ vs. pH dependence,* ***(c)*** *E_{pa} vs. pH dependence*

Impact of scan rate

Figure 6(a) presents CVs of 1×10^{-4} M PC at PMMCNTPE in 0.2 M PBS of pH 7.5 at various scan rates (ν) ranging from 0.1-0.3 V s^{-1}. The rise in the potential scan rate leads to successive increase in peak current value and at the same time, oxidation peak potential is shifted to more positive potentials. This can also be inferred from the graphical plot of I_{pa} vs. square root of scan rate shown in Figure 6(b), where the linear regression equation is represented as

I_{pa} / µA = 0.3227+ 0.0351 ($v^{1/2}$) (R^2 = 0.9995)

Linearity between I_{pa} and square root of ν indicates that the redox process of PC at the surface of PMMCNTPE is diffusion controlled [40-41]. The graphical plot of log I_{pa} *vs*. log *v* was constructed and shown in Figure 6(c). Good linearity was obtained and the linear fitted equation is expressed as

log (I_{pa} / µA) = 5.3634+ 0.6336 log *v* (R^2 = 0.9959)

The obtained slope from the graph is 0.63, which is very close to the speculative value 0.5 [42]. This suggests that the redox process of PC at PMMCNTPE is a diffusion-controlled process.

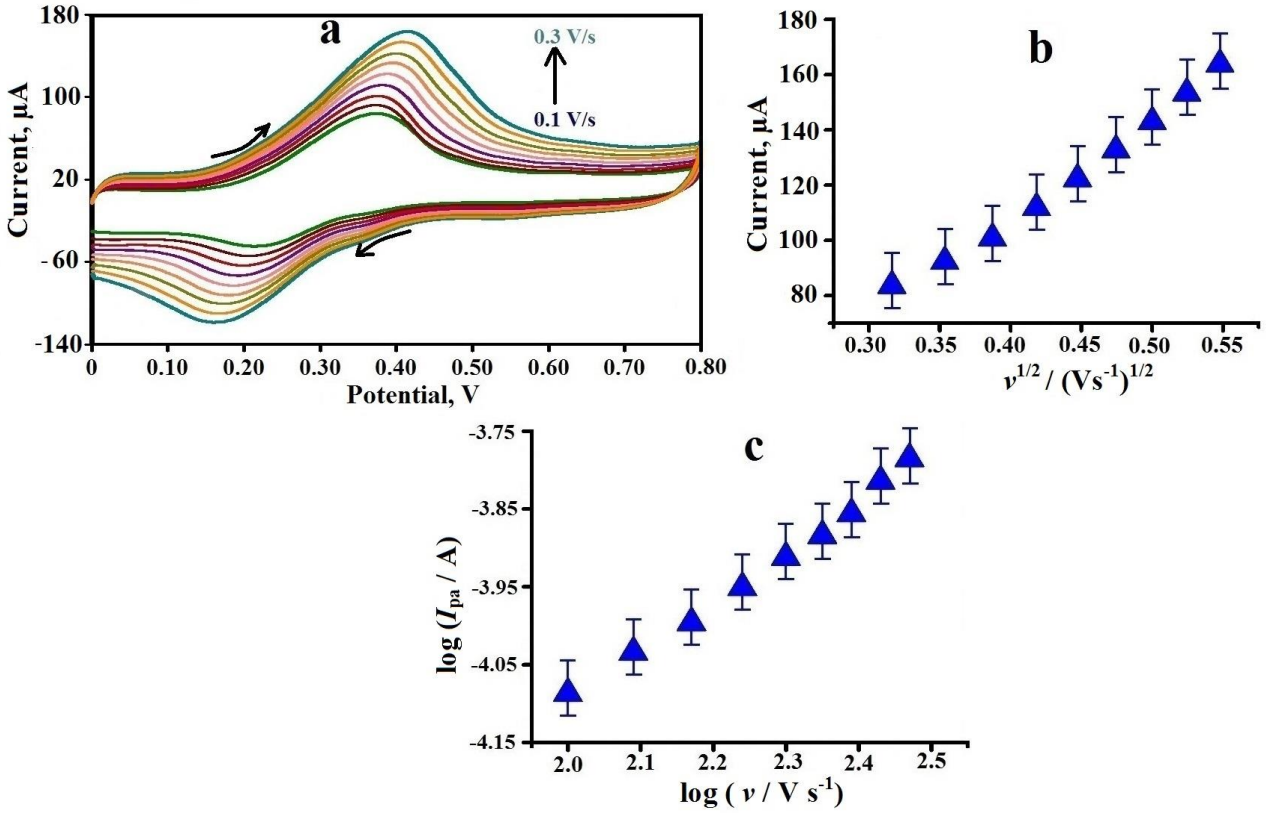


Figure 6: (a) *CVs of 1× 10^{-4} M PC at PMMCNTPE in 0.2 M PBS of pH 7.5, recorded at different scan rates ranging from 0.1-0.3 V s^{-1}* ***(b)*** *I_{pa} vs. square root of scan rate* ***(c)*** *log I_{pa} vs. log v dependence*

Voltammetric determination of PC on PMMCNTPE

The main aim of this study is to develop the sensing electrode based on PMMCNTPE to detect low PC concentrations. Therefore, electro-oxidation of PC at PMMCNTPE in 0.2 M PBS of pH 7.5 was carried out by varying its concentration in the range from 2×10^{-6} M – 1.1×10^{-4} M. Figure 7 displays the graphical plot of I_{pa} *vs*. concentration of PC, specifying that by increasing the concentration of PC peak current also increases, showing the linear relationship between I_{pa} and concentration of PC. The linearity is obtained in the range of 2.0×10^{-6} M – 5.0×10^{-5} M, and the linear fitted equation is expressed as

I_{pa} / µA = 0.3035 + 4.0305 M (R^2 = 0.9992)

The limit of detection (LOD) and limit of quantification (LOQ) were calculated by using the equation LOD = 3×S/M and LOQ = 10×S/M, respectively, where S is the standard deviation of the blank and M is the slope of the calibration curve [43]. The calculated LOD and LOQ are 3.85×10^{-8} M and 1.28×10^{-7} M, respectively. A comparison of linear ranges and LOD values for PC determination with those obtained for some other electrodes [44-51] is listed in Table 1 to assess the efficiency of the here fabricated sensor

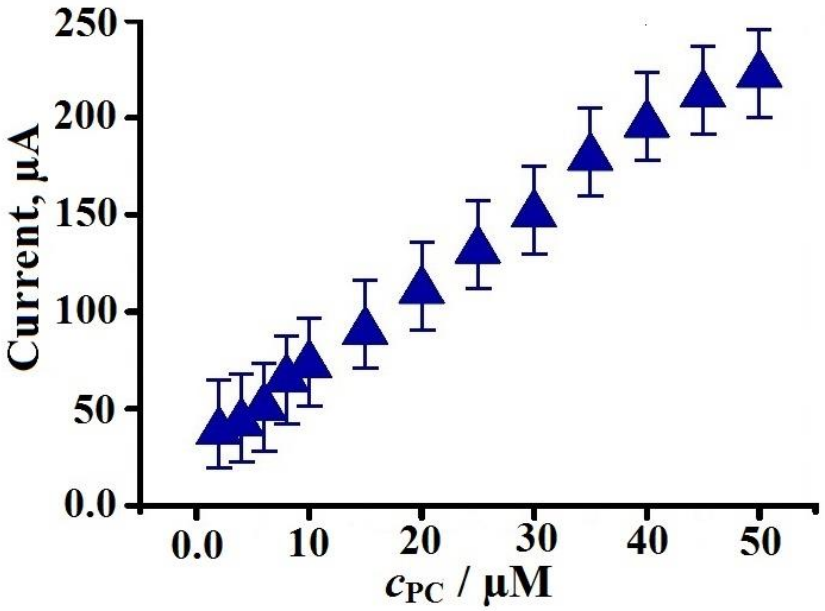


Figure 7. *The graphical plot of I_{pa} vs. concentration of PC*

Table 1. *Comparison of linear ranges and detection limits for PC at different electrodes*

Serial No.	Electrode	Linear working range of PC, µM	Detection limit of PC, µM	References
1	AuNP-PGA/CNT	8.3-140	1.2	[44]
2	AY/nano-TiO_2/GCE	12-120	2.0	[45]
3	PANI-MWCNT	1.0-100	0.25	[46]
4	PEDOT-GCE	1.0-100	0.40	[47]
5	CHCFE-CPE	1.0- 10	0.46	[48]
6	BDDE	50- 83	0.49	[49]
7	Ru-CCE	1.99- 31	0.58	[50]
8	Ni-Al-HCF-GCE	3.0-1500	0.80	[51]
9	PMMCNTPE	2.0 – 50	0.38	Present work

AuNP-PGA/CNT: glutamic acid and gold nanoparticles on a single-walled carbon nanotube film;
PAY: poly(acid yellow 9); GCE: glassy carbon electrode; PANI-MWCNT: polyaniline–multi-walled carbon nanotubes;
PEDOT: poly(3,4-ethylenedioxythiophene); CHCFE-CPE: Cobalt hexacyano ferrate carbon paste electrode;
BDDE: boron doped diamond electrode; Ru-CCE: arene-ruthenium (II) complex carbon ceramic electrode;
Ni-Al-HCF: hexacyanoferate(III) intercalated Ni Al layered double hydroxide.

Repeatability, reproducibility and stability

The repeatability of PMMCNTPE was scrutinized by four repetitive measurements with the same electrode, resulting with the RSD of 2.2 %. The reproducibility of PMMCNTPE was inspected by four repetitive measurements with different PMMCNTPE electrodes, what-resulted in the RSD of 3.5 %. Both the repeatability and reproducibility exposed RSD less than 4 %, indicating thus good repeatability and reproducibility of the proposed sensor. The stability of the designed sensor was assessed by 30 successive potential cycles. The percentage degradation was calculated by using the following formula

$$\text{Degradation, \%} = (I_{pn} / I_{p1})100$$

where I_{pn} and I_{p1} are the last and first anodic peak current, respectively [52]. The calculated percentage degradation is 94 %. This suggests that the modified electrode retained its activity even after 30 cycles. Good stability, excellent reproducibility and acceptable repeatability confirm the excellent performance of the proposed sensor.

Voltammetric response of PC at PMMCNTPE by DPV technique

The voltammetric response of PC at PMMCNTPE was also recorded *via* differential pulse voltammetry (DPV) technique. Figure 8 depicts differential pulse voltammograms (DPVs) of the electro-oxidation of 1×10^{-4} M PC in 0.2 M PBS of pH 7.5 at the sweep rate 0.1 V s^{-1} on the surfaces of PMMCNTPE and BCNTPE. At the surface of the PMMCNTPE, an enhanced current sensitivity was observed for the electro-oxidation of PC, while for BCNTPE in identical conditions, inferior voltammetric response was obtained. The peak current of 71.9 µA at peak potential of 0.268 V was obtained for the electrochemical oxidation of PC at PMMCNTPE. Thus, good electro-catalytic activity towards the electro-oxidation of PC at PMMCNTPE is confirmed *via* DPV approach too.

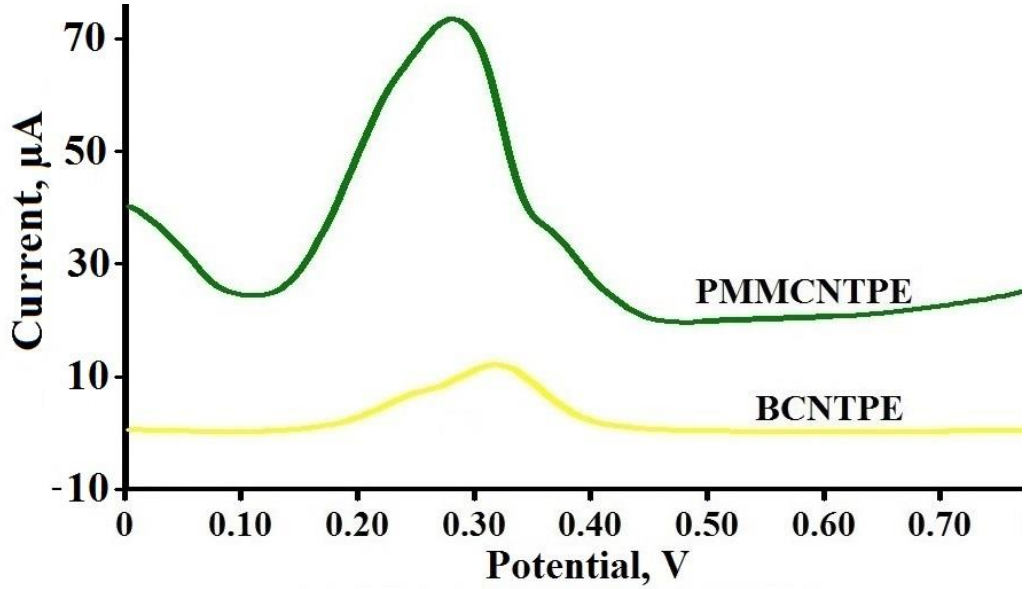


Figure 8. *DPVs recorded for 1.0×10^{-4} M PC at BCNTPE and PMMCNTPE in 0.2 M PBS of pH 7.5, at the sweep rate 0.1 V s^{-1}.*

Interference study

The selectivity of the designed PMMCNTPE sensor was examined by carrying out the interference study through CV and DPV methods. Folic acid (FA) and dopamine (DA) are commonly coexisting with PC in biological samples. Thus, the simultaneous detection of PC, FA, and DA was performed. Figure 9(a) shows CVs of PMMCNTPE in 0.2 M PBS of pH 7.5 with simultaneous presence of PC (1×10^{-4} M), DA (1×10^{-4} M) and FA (1×10^{-4} M). Figure 9(b) shows CVs for the concentration of PC varied in the range of 1×10^{-4} -3.5 $\times10^{-4}$ M and concentrations of DA and FA kept constant (1×10^{-4} M). In all cases, the scan rate 0.1 V s^{-1} was performed within the potential window -0.2 V to 1.0 V. Three well-separated and sharp peaks for DA, PC, and FA were gained in CVs of Figures 9(a) and (b). Furthermore, by increase of PC concentration from 1×10^{-4} to 3.5 $\times10^{-4}$ M, peak current of PC also increases, what can clearly be observed in Figure 9(b) and is also shown by plotting the graph of I_{pa} *vs.* concentration of PC in Figure 9(c). All these above-mentioned results suggest that good selectivity of the designed sensor has been achieved *via* CV technique.

Simultaneous detection of PC, DA, and FA was also performed by means of DPV technique. DPV of simultaneous detection of PC (1×10^{-4} M), DA (1×10^{-4} M) and FA (1×10^{-4} M) in 0.2 M PBS of pH 7.5 is displayed in Figure 10(a), where distinct peaks for DA, FA and particularly for PC can be observed. Figure 10(b) depicts DPVs for the variation of PC concentration from 1×10^{-4} to 3.5 $\times10^{-4}$ M without changing the concentration of DA and FA equal to 1×10^{-4} M for each. The graphical plot of I_{pa} *vs.* concentration of PC shown in Figure 10(c) implies that for the increasing concentration of PC, peak

current also increases. This approves that the fabricated sensor detects PC in the presence of interference compounds DA and FA.

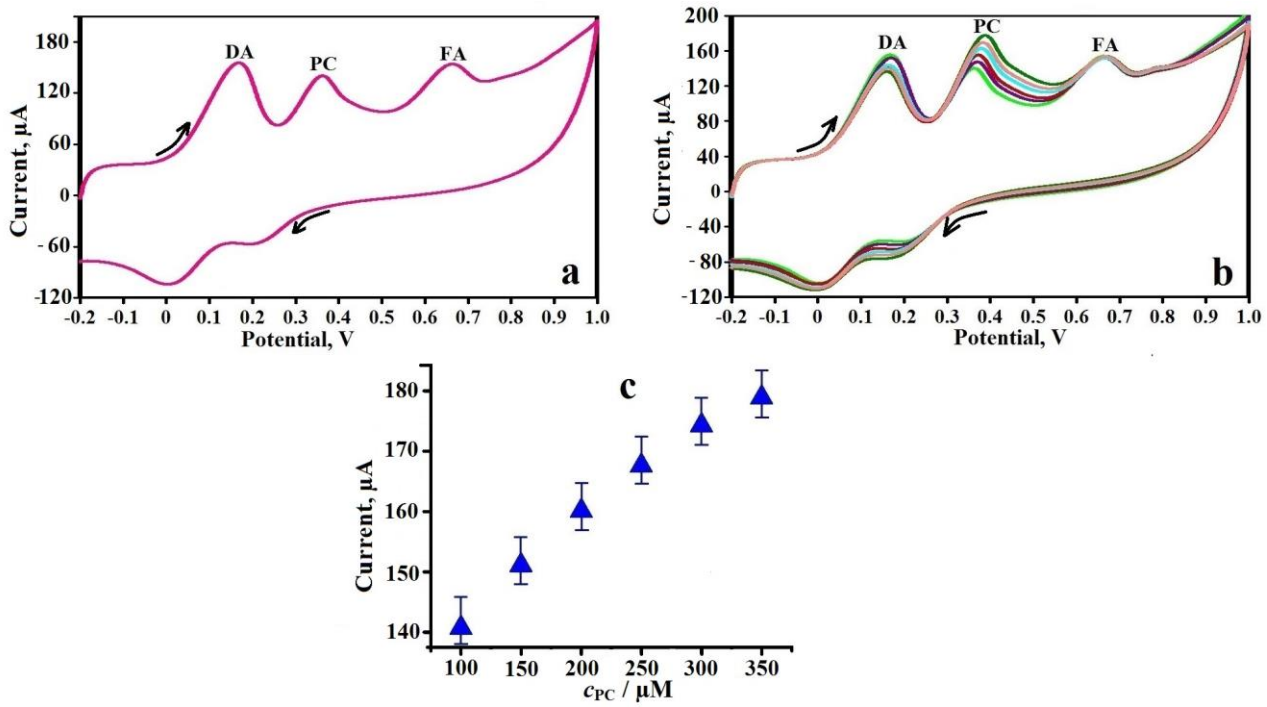


Figure 9. *CV at PMMCNTPE in 0.2 M PBS of pH 7.5, recorded at the scan rate 0.1 Vs^{-1} in presence of:* ***(a)*** *PC (1×10^{-4} M), DA (1×10^{-4} M) and FA (1×10^{-4} M), (b) DA (1×10^{-4} M), FA (1×10^{-4} M), and PC of varying concentration from 1×10^{-4}-3.5 ×10^{-4} M,* ***(c)*** *I_{pa} vs. concentration of PC.*

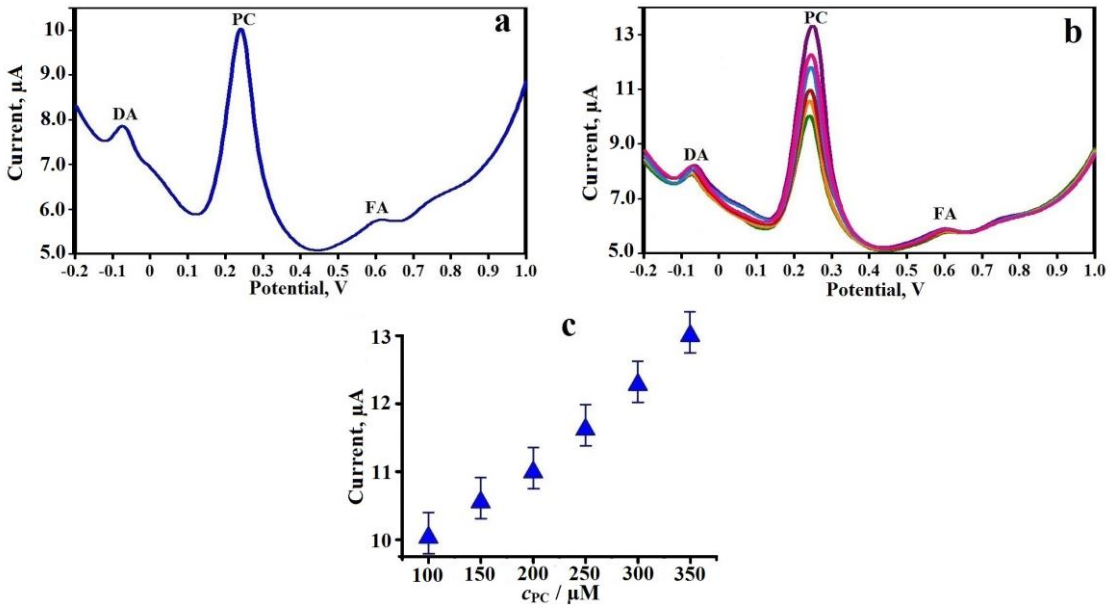


Figure 10. *DPVs of PMMCNTPE in 0.2 M PBS of pH 7.5, recorded at the scan rate 0.1 V s^{-1} for simultaneous detection of PC, DA and FA at: (a) PC (1×10^{-4} M), DA (1×10^{-4} M) and FA (1×10^{-4} M)* ***(b)*** *DA (1×10^{-4} M), FA (1×10^{-4} M) and PC varied from 1×10^{-4}-3.5 ×10^{-4} M,* ***(c)*** *Graphical plot of I_{pa} vs. concentration of PC*

Real sample analysis

The workability of the constructed PMMCNTPE sensor for the analysis of PC was assessed by detecting PC in some pharmaceutical formulations, such as paracetamol and Dolo tablets that were

procured from the local drugstore. The tablets were weighed and ground into a fine powder using the pestle in a mortar. Solutions were prepared from powdered tablets and analyzed by CV technique. The CVs were documented in 0.2 M PBS of pH 7.5 at the sweep rate of 0.1 V s^{-1}. A good recovery ranges from 95 to 103 % was accomplished by the developed method.

Conclusions

In this study, PMMCNTPE was prepared as electrochemical sensor which could serve for a sensitive and selective determination of PC. The fabricated PMMCNTPE disclosed good electro-catalytic activity towards the oxidation of PC with CV and DPV techniques. The PMMCNTPE sensor boosted the analytical sensitivity of PC by yielding low detection limit of 3.8×10^{-8} M. The sensor unveiled an excellent stability, repeatability, and reproducibility. In addition, the fabricated sensor was implemented to the simultaneous detection of PC, DA, and FA, showing significant selectivity. The sensing performance of the developed sensor was successfully applied for the determination of PC in some pharmaceutical formulations. This implies that routine analysis of PC can be established following the proposed technique. This simple and quick method provides benefits like low cost, short analysis time and good detection limit.

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References

[1] F. R. Lichtenberg, *International Journal of Health Care Finance and Economics* **5** (2005) 47-73.
[2] A. K. Wagner, J. D. Quick, D. Ross-Degnan, *BMC Health Services Research* **14** (2014) 1-6.
[3] M. A. Mallah, S. H. Sherazi, M. I. Bhanger, S. A. Mahesar, M. A. Bajeer, *Spectrochimica Acta Part A* **141** (2015) 64-70.
[4] H. Beitollahi, F. Garkani-Nejad, S. Tajik, M. R. Ganjali, *Iranian Journal of Pharmaceutical Research* **18** (2019) 80-90.
[5] R. N. Goyal, V. K. Gupta, M. Oyama, N. Bachheti, *Electrochemistry Communications* **7** (2005) 803-807.
[6] T. Skeika, M. Ferreira de Faria, N. Nagata, C. A. Pessoa, *Journal of the Brazilian Chemical Society* **19** (2008) 762-768.
[7] S.J. Richard Prabakar, S.S. Narayanan, *Talanta* **72** (2007) 1818-1827.
[8] A. U. Alam, Y. Qin, M. M. R. Howlader, N.-X. Hu, M. J. Deen, *Sensors and Actuators B* **254** (2018) 896–909.
[9] S. F. Mbokou, M. Pontié, B. Razafimandimby, J. Bouchara, E. Njanja, I. Tonle Kenfack, *Analytical and Bioanalytical Chemistry* **408** (2016) 5895-5903
[10] R. T. Kachoosangi, G. G. Wildgoose, R. G. Compton, *Analytica Chimica Acta* **618** (2008) 54–60.
[11] A. M. Larson, J. Polson, R. J. Fontana, T. J. Davern, E. Lalani, L. S. Hynan, J. S. Reisch, F. V. Schiødt, G. Ostapowicz, A. O. Shakil, W. M. Lee, *Hepatology* **42** (2005) 1364–1372.
[12] M. Mazer, J. Perrone, *Journal of Medical Toxicology* **4** (2008) 2-6.
[13] N. T. Anh Thu, H. V. Duc, N. H. Phong, N. D. Cuong , N. T Vuong Hoan , D. Q. Khieu, *Journal of Nanomaterials* (2018) 1-15.
[14] B. D Blair, J. P. Crago, C. J. Hedman, R. D. Klaper, *Chemosphere* **93** (2013) 2116–2123.
[15] M. E. Bosch, A. J. Sánchez, F. S. Rojas, C. B. Ojeda, *Journal of Pharmaceutical and Biomedical Analysis* **42** (2006) 291–321.
[16] M. K. Srivastava, S. Ahmad, D. Singh, I. C. Shukla, *Analyst* **110** (1985) 735–737.
[17] K. G. Kumar, R. Letha, *Journal of Pharmaceutical and Biomedical Analysis* **15** (1997) 1725–1728.
[18] G. Burgot, F. Auffret, J.-L. Burgot, *Analytica Chimica Acta* **343** (1997) 125–128.
[19] W. Lohmann, U. Karst, *Analytical and Bioanalytical Chemistry* **386** (2006) 1701-1708.
[20] H.-G. Lou, H. Yuan, Z.-R. Ruan, B. Jiang, *Journal of Chromatography B* **878** (2010) 682-688.
[21] I. Baranowska, B. Kowalski, *Water, Air and Soil Pollution* **211** (2010) 417-425.

[22] G. M. Hadad, S. Emara, W. M. Mahmoud, *Talanta* **79** (2009) 1360-1367.
[23] M. G. Gioia, P. Andreatta, S. Boschetti, R. Gatti, *Journal of Pharmaceutical and Biomedical Analysis* **48** (2008) 331-339.
[24] S. Zhao, W. Bai, H. Yuan, D. Xiao, *Analytica Chimica Acta* **559** (2006) 195-199.
[25] W. Ruengsitagoon, S. Liawruangrath, A. Townshend, *Talanta* **69** (2006) 976-983.
[26] Y.Z. Fang, D.J. Long, J.N. Ye, *Analytica Chimica Acta* **342** (1997) 13-21.
[27] Sirajuddin, A. R. Khaskheli, A. Shah, M. I. Bhanger, A. Niaz, S. Mahesar, *Spectrochimica Acta Part A: Molecular and Bimolecular Spectroscopy* **68** (2007) 747-751.
[28] N. Al-Zoubi, J. E. Koundourellis, S. Malamataris, *Journal of Pharmaceutical and Biomedical Analysis* **29** (2002) 459-467.
[29] D. Šatinský, I. Neto, P. Solich, H. Sklenárová, M. Conceição, B. S. M. Montenegro, A. N. Araújo, *Journal of Separation Science* **27** (2004) 529-536.
[30] M. Shalash, A. Salhin, B. Saad, I. A. Rahman, *Journal of Liquid Chromatography and Related Technologies* **36** (2013) 155-166.
[31] M. S. M. Quintino, K. Araki, H. E. Toma, L. Angnes, *Electroanalysis* **14** (2002) 1629-1634.
[32] H. Beitollahi, F. G. Nejad, *Electroanalysis* **28** (2016) 2237-2244.
[33] H. Beitollahi, J. B. Raoof, H. Karimi-Maleh, R. Hosseinzadeh, *Journal of Solid State Electrochemistry* **16** (2012) 1701-1707.
[34] H. Beitollahi, K. Movlaee, M. R. Ganjali, P. Norouzi, *Journal of Electroanalytical Chemistry* **799** (2017) 576- 582.
[35] H. Beitollahi, S. Nekooei, M. Torkzadeh-Mahani, *Talanta* **188** (2018) 701-707.
[36] V. K. Gupta, T. A. Saleh, *Environmental Science and Pollution Research* **20** (2013) 2828-2843.
[37] K. Giribabu, Y. Haldorai, M. Rethinasabapathy, S.-C. Jang, R. Suresh, W.-S. Cho, Y.-K. Han, C. Roh, Y.-S. Huh, V. Narayanan, *Current Applied Physics* 17 (2017) 1114-1119.
[38] C. Raril, J. G Manjunatha, Biomedical Journal of Science and Technical Research 9 (2018) 7149-7154.
[39] M. Baccarin, F. A. Santos, F. C. Vicentini, V. Zucolotto, B. C. Janegitz, O. Fatibello-Filho, *Journal of Electroanalytical Chemistry* **799** (2017) 436-443.
[40] N. Karikalan, R. Karthik, S.-M. Chen, M. Velmurugan, C. Karuppiah, *Journal of Colloids and Interface Science* **483** (2016) 109-117.
[41] T. T. Minh, N. H. Phong, H. V. Duc, D. Q. Khieu, *Journal of Materials Science* **53** (2018) 2453-2471.
[42] A. Wong, A. M. Santos, O. Fatibello-Filho, *Diamonds and Related Materials* **85** (2018) 68-73.
[43] M. M. Charithra, J. G. Manjunatha, *Materials Science for Energy Technologies* **2** (2019) 365-371.
[44] M.-P.N. Bui, C. A. Li, K. N. Han, X.-H. Pham, G.H. Seong, *Sensors and Actuators B* **174** (2012) 318-324.
[45] S. Ashok Kumar, C. Tang, S. Chen, *Talanta* **76** (2008) 997-1005.
[46] M. Li, L. Jing, *Electrochimica Acta* **52** (2007) 3250-3257.
[47] S. Mehretie, S. Admassie, T. Hunde, M. Tessema, T. Solomon, *Talanta* **85** (2011) 1376-1382.
[48] R. C. Saini, L. Gebresilassie, T. Hunde, M. Tirfu, R. Pal, *International Journal of Chemistry and Pharmaceutial Sciences* **4** (2016) 122-129.
[49] B. C. Lourenção, R. A. Medeiros, R. C. Rocha-Filho, L. H. Mazo, O. Fatibello-Filho, *Talanta* **78** (2009) 748-752.
[50] S. Machado, G. N. Calaça, J. P. da Silva, M. P. de Araujo, R. T. Boeré, C. A. Pessôa, K. Wohnrath, *Journal of Electrochemical Society* **164** (2017) B314-B320.
[51] K. Asadpour-Zeynali, R. Amini, *Electroanalysis* **29** (2017) 635-642.
[52] J. G. Manjunatha, *Sensing and Bio-Sensing Research* **16** (2017) 79-84.