

Electroanalysis of Flutamide as an Anticancer Drug at Electrochemically Activated Glassy Carbon Electrode

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Received: 24 October 2022 / Accepted: 16 December 2022 / Published: 27 December 2022

Electrochemical oxidation of a glassy carbon (GC) electrode results in an oxygenated surface, which shows a good ability toward the electrochemical detection of flutamide (FLU). The oxidized electrode (GC_{ox}) can be accomplished easily and efficiently by electrochemical techniques. This procedure is fast, simple, and consists in applying a potential of -0.2 - 2.0 V vs. Ag/AgCl to a GC electrode. Modified electrodes were morphologically characterized by scanning electron microscopy (SEM) and the electrochemical activity of the GC_{ox} electrode was investigated using cyclic voltammetry (CV). Experimental parameters as pH, and scan rate were optimized for the electroanalysis of FLU. Under the optimized conditions, the GC_{ox} electrode showed a linearity from 0.05 to 0.6 mM of FLU. The limits of detection and the limit of quantification were calculated and the relative standard deviation was found to be 4.2%. The stability of the thus modified electrode within a suitable time showed an acceptable precision.

Keywords: Flutamide; Electroanalysis; Cyclic Voltammetry, Glassy Carbon Electrode.

1. INTRODUCTION

Nowadays, continuous follow up of drugs in biological and pharmaceutical formulations is critical for disease surveillance and drug dose quality control. In this context, 4-Nitro-3-(trifluoromethyl)-isobutylanilide, also called as flutamide (FLU, Fig. 1) is used as nonsteroidal antiandrogen drug for the treatment of prostate cancer [1]. Testosterone is one of the most important factors responsible for the increased growth and reproduction of carcinogenic cells in the prostate. This medicine can slow the growth and spread of prostate cancer by suppressing the function of the testosterone hormone [2,3]. Regardless of the advantages, FLU has some side effects, which cause

headaches, reduce blood cells and platelets, and poison some tissues [4,5]. Cirrhosis of the liver is one of the most serious side effects of using FLU as a treatment. Therefore, it is extremely important to find suitable and easy-to-manage methods for measuring FLU in routine analysis [6]. There are various techniques available to detect the FLU, some of which include UV–Vis spectrophotometry, high-performance liquid chromatography (HPLC), photochemistry, polarography, spectrofluorimetry, flow-injection analysis and voltammetric methods [7–12]. Although these methods show good sensitivity and accuracy, they suffer from many drawbacks, for example, the high operational cost; in addition to that, they require the preparation of a specific sample in addition to a highly trained technician. [13,14]. On the other hand, the electrochemical sensors are desirable due to their various advantages, including cost-effectiveness, high selectivity and sensitivity, fast response, and easy handling [15–17]. FLU was firstly analyzed using electrochemical methods on 1989 [18]. The analysis have been achieved using mercury electrode. This report on mercury electrode was followed by several reports on the same electrode but with different approaches [19–21]. Next, the solid electrodes, both bare and modified have been used for this purpose [22–34]. Solid electrodes included polymer modified carbon paste electrode, alone [23] and with silver nanoparticles [24]. Also DNA modified carbon electrodes have been used for the analysis of FLU and for studying the interaction between FLU and DNA in a trial to prop the mechanism of the action of FLU as an anticancer drug [25, 26]. Carbon nanotube and grapheme modified electrodes have been also used for the analysis of FLU [27–29]. In addition, bare and modified gold have been examined for the detection of Flu [30–34].

On the other hand, glassy carbon (GC) electrodes are widely used in electrochemistry due to their unique properties that can be used at high temperatures in addition to many other advantages, including hardness, low density and low electrical resistance [35]. Due to the aforementioned properties as well as their wide potential window, they are commonly applied as electrode materials for electrolysis [36,37]. The importance of this electrode was further heightened by the possibility of establishing electrochemical activation of GC electrodes as one of the widely used pretreatment techniques to activate electrode surfaces. Significant improvements in adsorption properties have been achieved as a result of its activation by various methods. Normally, aromatic cations and neutral species showed no adsorption or weak absorption at bare GC, but they clearly became adsorbents in electroactive GC [38,39]. Electrochemical oxidation is a simple, controllable and reproducible method for processing a GC electrode [40–42]. Most methods usually involve applying a relatively high anodizing voltage in an acidic or neutral aqueous electrolyte using various electrochemistry procedures [43–46]. Electrochemical oxidation of GC can be useful in many applications including electrochemical sensors, as it is generally agreed that electrochemical oxidation of GC activates the electrode surface, leading to faster electron transfer kinetics [47–50] In the current study, we prepared a convenient and rapid method for drug quantification using electrochemical methods, which gave the advantage of simplicity and sensitivity. Therefore, a glassy activated carbon (GCox) electrode was used to determine the concentration of Flo in the process samples.

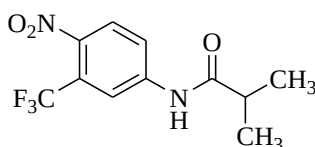


Figure 1. The structure of the studied drug, FLU

2. EXPERIMENTAL

2.1. Materials and Reagents

No further purification was performed on any of the analytical-grade compounds or reagents utilized in this work. A FLU powder was purchased from Sigma–Aldrich. Utilizing deionized water, all of the solutions were made. A series of phosphate buffer solutions (pH 4-10.8) were ready by mixing of (0.1M) NaH_2PO_4 and (0.1M) Na_2HPO_4 and adjusting the solution pH to the required value with (0.1M) H_3PO_4 and/or 0.1M NaOH.

2.2. Apparatus and Electrodes

Using Gamry Instrument, (Potentiostat/Galvanostat/Reference 600TM type), all electrochemical measurements have been carried out. Three electrodes on a traditional electrochemical cell were used for voltammetric investigations, where platinum spiral and the silver/silver chloride (Ag/AgCl/ KCl (sat.)) were served as the counter and reference electrodes, respectively. All potentials will be presented with respect to this reference electrode. GC electrode (3 mm in diameter) was employed as the working electrode. The surface of the GC electrode was mechanically polished with aqueous slurries of successively finer alumina powder with the help of a micro-cloth, and then was washed thoroughly with deionized water followed by sonication in distilled water for 5 minutes. The measurements were carried out at ambient temperature. (25 ± 3 °C).

2.3. Preparation of GC_{ox} electrode

According to published research, GC was created by activating the glassy carbon electrode in 0.5 M H_2SO_4 [50-52]. This oxidized GC was denoted as GC_{ox} throughout. The activation of the GC electrode was using cyclic voltammetry in 0.5 M H_2SO_4 for certain number of cycles in the potential range – 0.2 to 2 V vs. Ag/AgCl/ KCl (sat.) at a scan rate of 100 mV/sec.

2.4. Instrumentation.

SEM was used to characterize the GC electrodes' morphology both in their unaltered state and after modification using (SEM, JSM-7600F Field Emissions Scanning Electron Microscope). All pHs of the used solutions were measured using pH-meter (Thermo instruments; Orion 2 star).

3. RESULTS AND DISCUSSION

3.1. Surface Characterization

The surface morphology of the GC electrode was studied using SEM. SEM micrographs obtained on the surface of bare GC and GCox electrodes are shown in the figure. 2. Electrochemical oxidation causes the surface to become rough (image b) compared to the smooth surface of the GC (image a) which has not been oxidized. GCox has a few chips on the surface (image b).

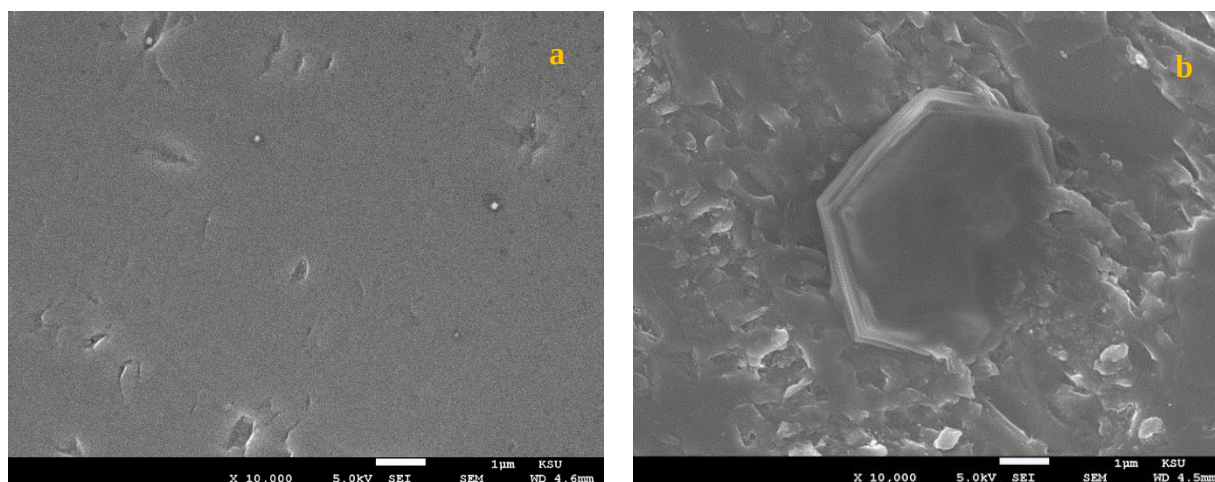


Figure 2. SEM images of bare GC (a) and GC_{ox} (b) electrodes.

3.2. Electrochemical Characterization.

3.2.1. Cyclic Voltammetric Studies.

Figure 3 presents CV results for (0.05 mM FLU) oxidation/reduction at a bare GC (curve. 3a) electrodes in phosphate buffer (PBs) of pH 7 at a scan rate 100 mV/sec. These results show that the electrochemical behaviour of FLU was more efficient on the GCox electrode. These results indicate that GCox catalyzes FLU oxidation due to the larger amount of surface groups resulting from its oxidized structure, which in addition to increasing the sensitivity of the system and the rate of electron transfer between the analyte in solution and the electrode surface led to an increase in the surface area. The peak currents for the oxidation/reduction of Fluo on the GCox electrode were significantly higher than those on the bare GC. It has been reported that the electrochemical oxidation of GC increases the proportion of functional groups having –OH groups on the electrode surface [51, 52]. Generation of functional groups decrease the electron transfer resistance, and consequently increases the electron transfer constant [53, 54].

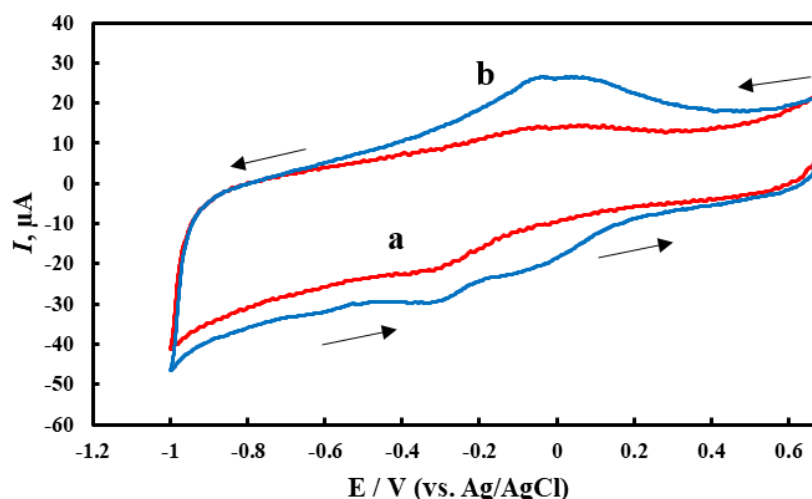


Figure 3. CV for 0.05 mM FLU on (a) bare GC and (b) GC_{ox} (five oxidation cycles) in PBs of pH 7 at scan rate 100 mV/sec.

The effect of the potential cycles used in the preparation of the GC_{ox} electrode on the electrochemical response of FLU is shown in figure. 4, where the CVs obtained at GC_{ox} electrodes, which were attended by different potential cycles, are shown in PBs (pH = 7.0) containing 0.05 mM FLU. The pretreatment of the GC_{ox} electrode gave the largest peak potential and the large current response of FLU. Using more potential cycles for oxidation does not prove the electrochemical behaviour of FLU, rather than it increases the background current and consequently the sensitivity of the determination of FLU. Hence, the modification using ten potential cycles will be used hereafter as the optimum one.

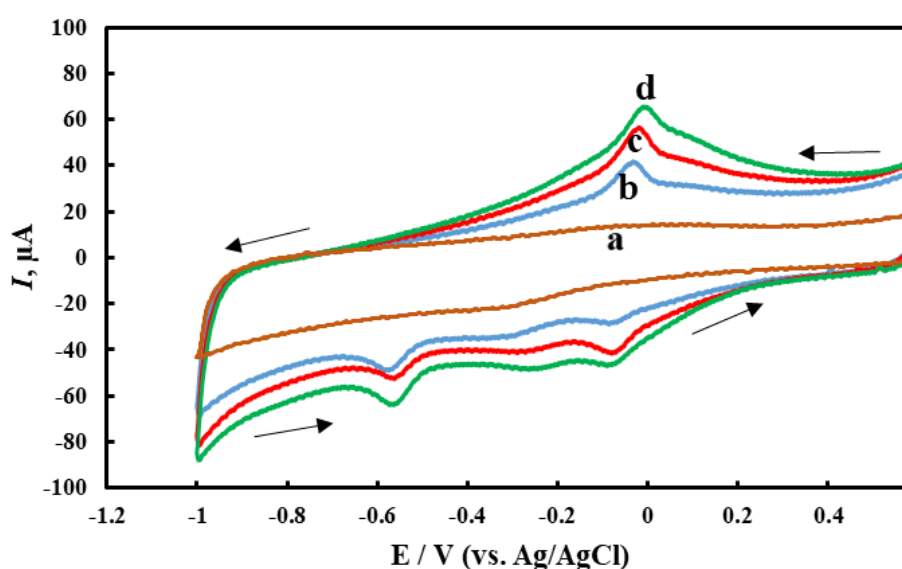


Figure 4. CV for 0.05 mM FLU in PBs of pH 7 at (a) bare GC and GC_{ox} (b), number of potential cycles: one cycle, (c) five cycles and (d) ten cycles. Scan rate 100 mV/sec.

3.2.2. Effect of scan rate.

The effect of scan rate (ν) on the peaks current of FLU oxidation/reduction under the optimum conditions was investigated in the range of 50–500 mV/sec and is shown in (Figure. 5). The anodic peak shifted anodically and the cathodic peaks shifted cathodically with increasing the scan rate, this points to the limitation of the electrode material surface [53-55].

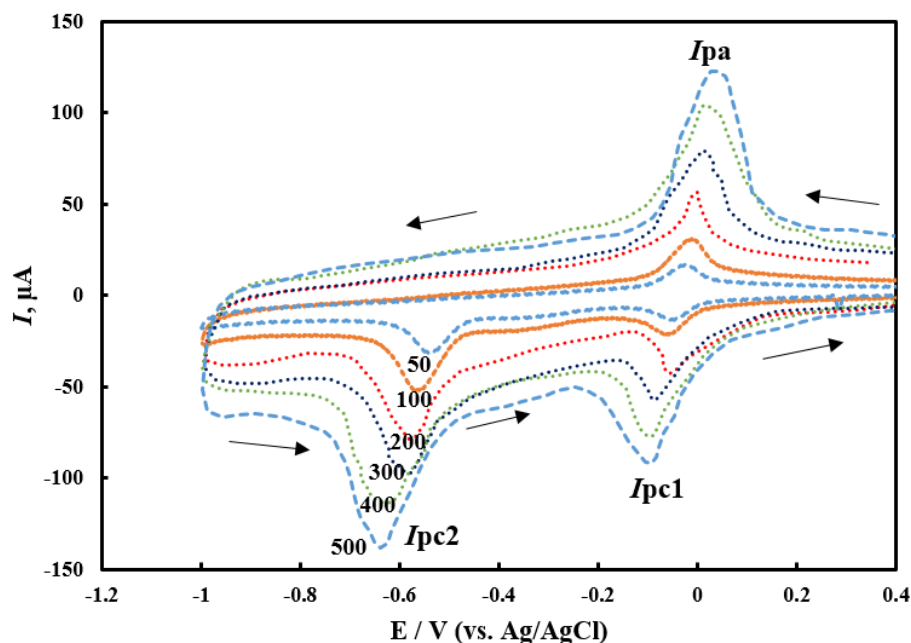


Figure 5. Effect of scan rate on the electrochemical behaviour of 0.05 mM FLU on GC_{ox} after ten oxidation cycles) in PBs of pH 7.0. Scan rate values are from 50–500mV/sec.

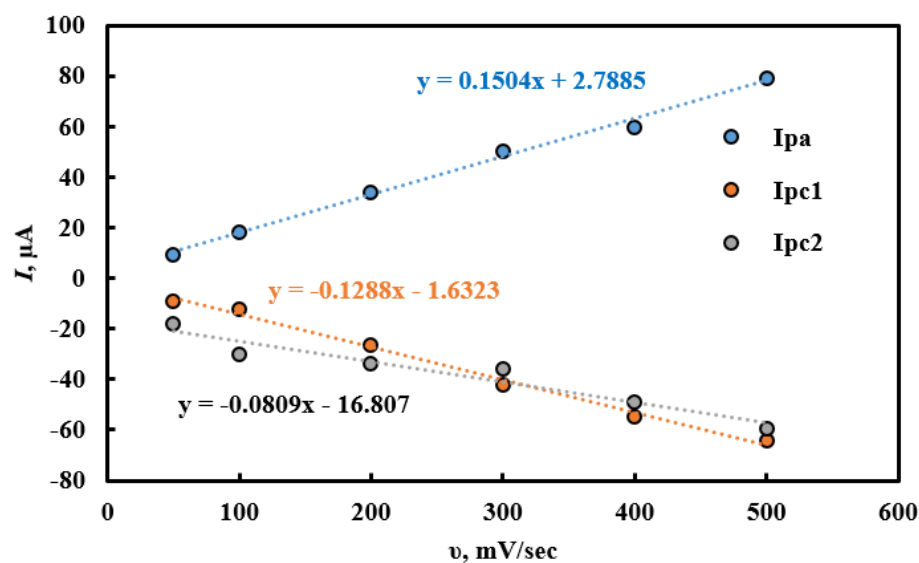


Figure 6. Relation between scan rates and peak currents for 0.05 mM FLU on GC_{ox} after ten oxidation cycles in PBs of pH 7.

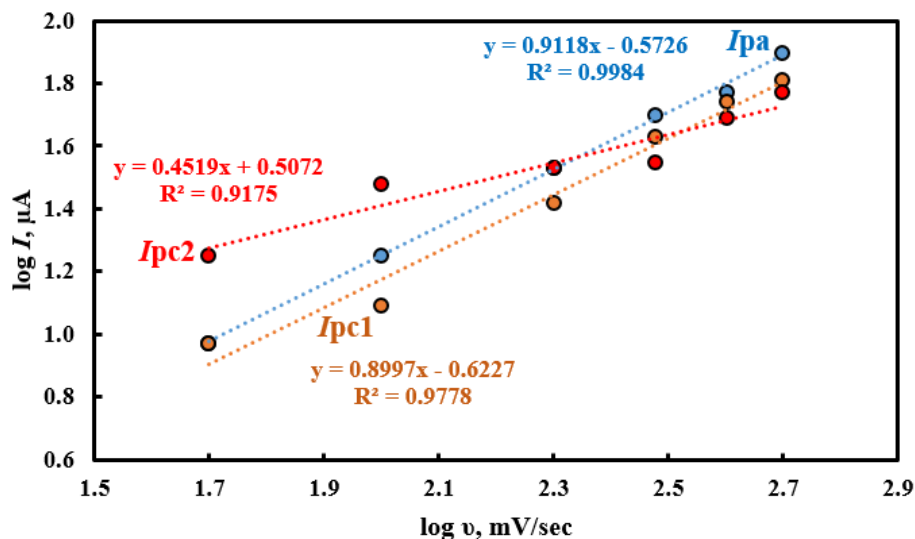
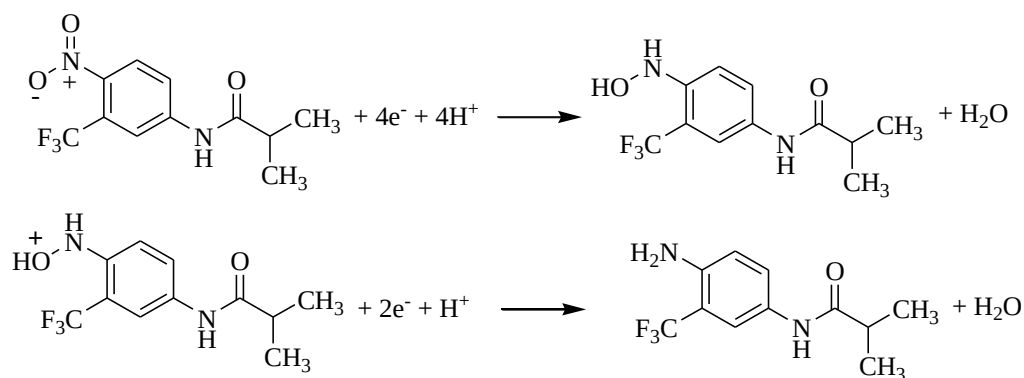


Figure 7. Relation between ($\log i_{pa} - \log v$) for 0.05 mM FLU on GC_{ox} after (ten oxidation cycles) in PBs of pH 7.

The mechanism of oxidation of FLU could be assigned from the effect of the scan rate on the peak current. Linear plots of peak current versus square root of scan ($i_{pa} - v$) points to diffusing electro-active species; whereas adsorption process is revealed from linear dependence of i_p on v . When the scan rate varied from 50 to 500 mV/sec in 0.05 mM FLU, a linear relationship between peak current (i_{pa}) of FLU and v was found, confirmed an adsorption behaviour (Figure.6) [56]. To estimate the contribution of both adsorption and diffusion, a plot of logarithm of peak current ($\log i_{pa}$) versus logarithm of scan rate ($\log v$) [57,58] was given in Fig. 7. A straight line with a slope of 0.91 ($R^2 = 0.998$) for FLU, close to the theoretical value of 1.0 indicates an adsorption-controlled electrode (Figure. 6).

3.2.3. Effect of pH.

The redox behaviour of FLU is expected to depend on the pH value of the PBs as shown in (Scheme 1). Therefore, the effect of pH on the electrochemical response of FLU in the GC_{ox} electrode was investigated in solutions of PBs of different pH (4.0–10.8) at a scan rate of 100 mV/s (Fig. 8). The results showed that the anodic and cathodic potentials of FLU shifted to more negative values with the increase of pH, which indicated that the catalytic oxidation and reduction of FLU on the surface of the GCox electrode included a proton. The relationship gave a slope of 62 mVpH⁻¹, in agreement of literature, which is close to the expected theoretical value of 59 mVpH⁻¹ (Fig. 9) [59]. This indicates that the number of electrons and protons participating in the electrode process is equal, that is, during the reaction, not only electrons but also protons are released from the molecule [60]. The anodic peak at 50 mV acts against the cathodic peak at -50 mV according to the following redox reaction, followed by further reduction of the hydroxylamine group to an amino.



Scheme 1. Electrochemical reduction of flutamide.

Relationship between pH of PBs and the ratio I_{pa}/I_{pc1} was showed that the highest peak current was obtained around pH 7.0 (Figure 10). The peak current of FLU was found to increase while increasing pH up to 7.0, and then decrease with further increasing in pH. This suggest that the optimal pH, that is, the one that shows the highest peak obtained at pH 7.0 (Fig. 10). Therefore, solutions with a pH of 7.0 were used for all subsequent electrochemical studies of FLU. At a pH greater than 7.0, the FLU peaks decreased. The overall electrochemical behaviour for FLU on the oxidized GC was illustrated in Scheme 2.

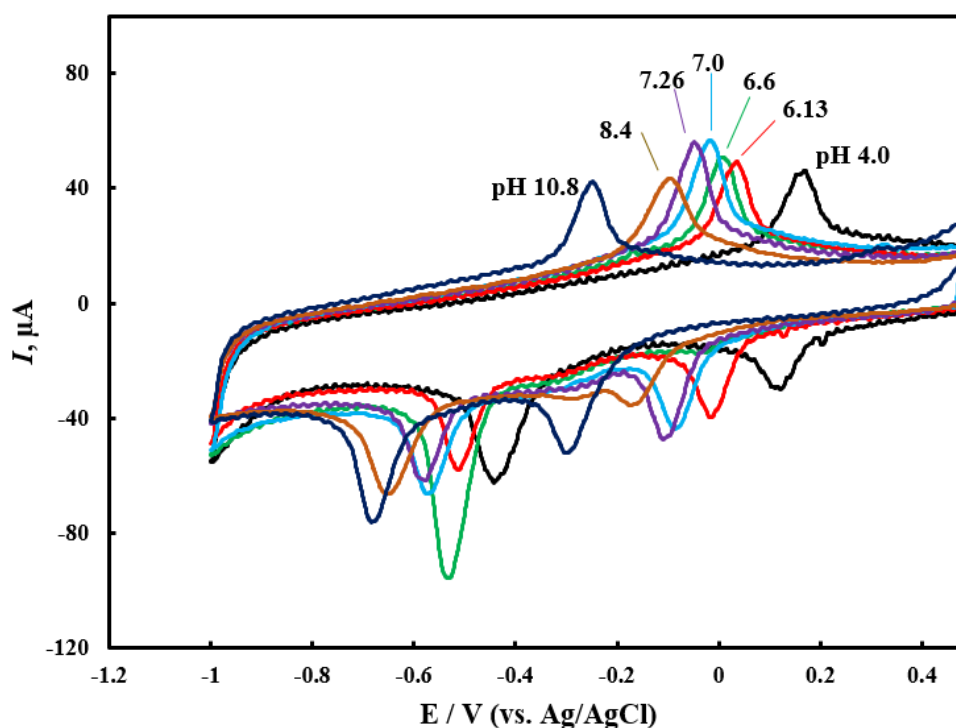


Figure 8. Effect of pH on CV for 0.05 mM FLU on GC_{ox} after (ten oxidation cycles) using PBs.

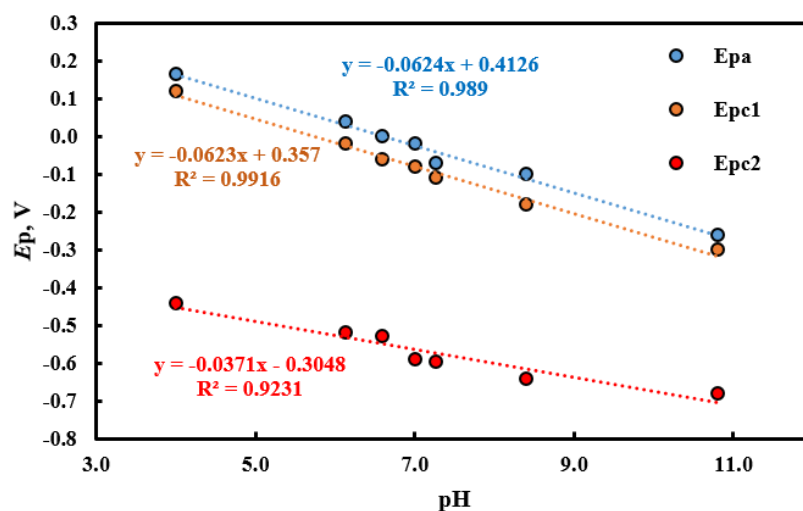


Figure 9. Relation of pH of PBs and peak potential for CV of 0.05 mM FLU on GC_{ox} after (ten oxidation cycles).

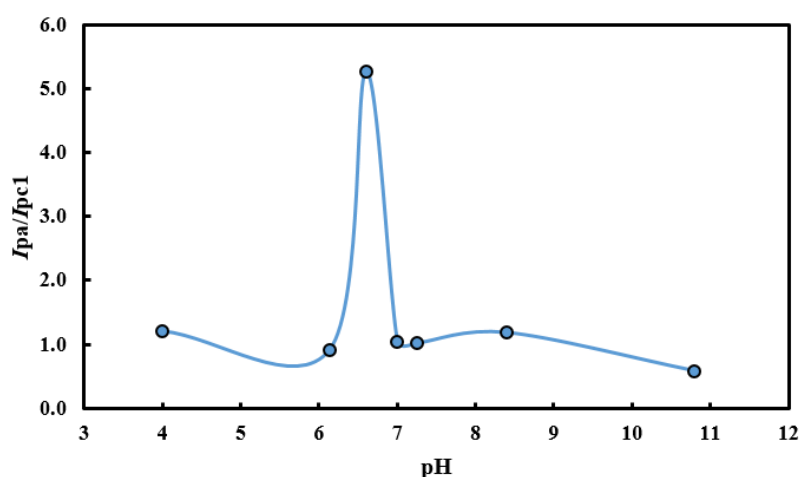


Figure 10. Relation pH of PBs and the ratio I_{pa}/I_{pc1} for CV of 0.05 mM FLU on GC_{ox} after (ten oxidation cycles).

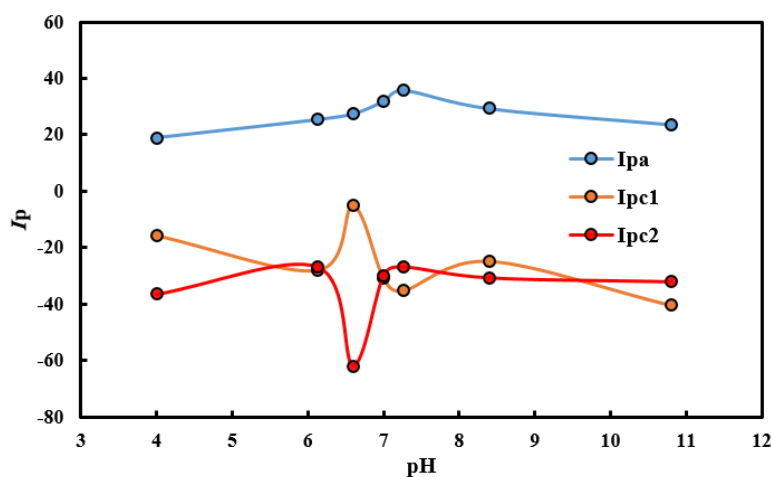
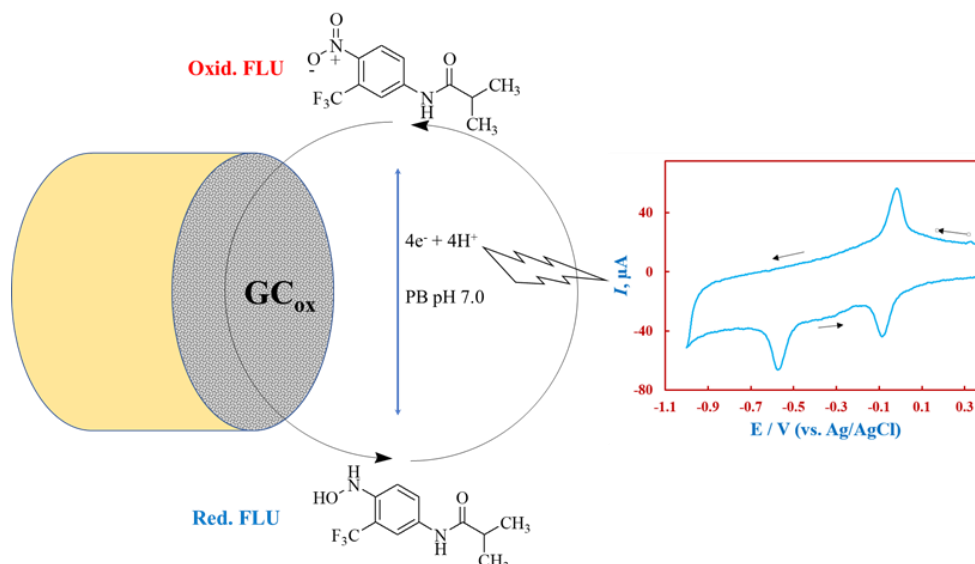


Figure 11. Relation pH of PBs and peak current for CV of 0.05 mM FLU on GC_{ox} after (five ten oxidation cycles).



Scheme 2. The overall steps for electrochemical behaviour of FLU on GC_{ox}.

3.3. Electroanalysis of FLU

Figure 12 shows cyclic voltammograms for GC_{ox} electrode using several FLU concentrations (0.05 mM - 0.6 mM). Peak currents for FLU oxidation and reduction were measured on the GC_{ox} electrode, and they were inversely related to the amount of electroactive species present in the PBs solution, which happens as more molecules arrive at the electrode-solution interface. These findings showed that the peak currents increased as FLU levels rose. Figure 13 depicts the linear calibration curves for FLU that were produced in PBs (pH 7.0) over a broad concentration range. Two regions are obtained, i.e., the linear ranges from 0.05 to 0.3 mM and from 0.3 to 0.6 mM with a good correlation coefficient ($R^2 \approx 0.995$) were obtained for the FLU determination. As mentioned on the elucidation of the mechanism of the electrochemical process, the electrochemical response of FLU is adsorption-controlled process.

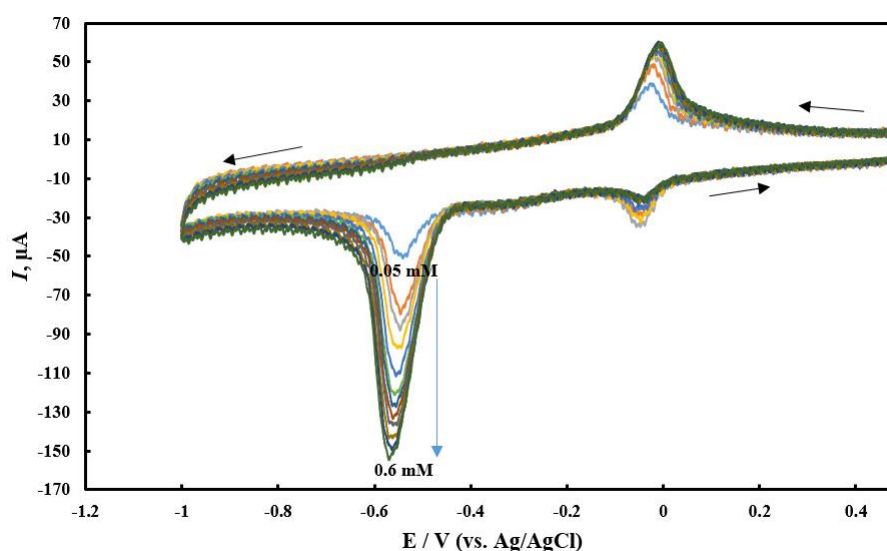
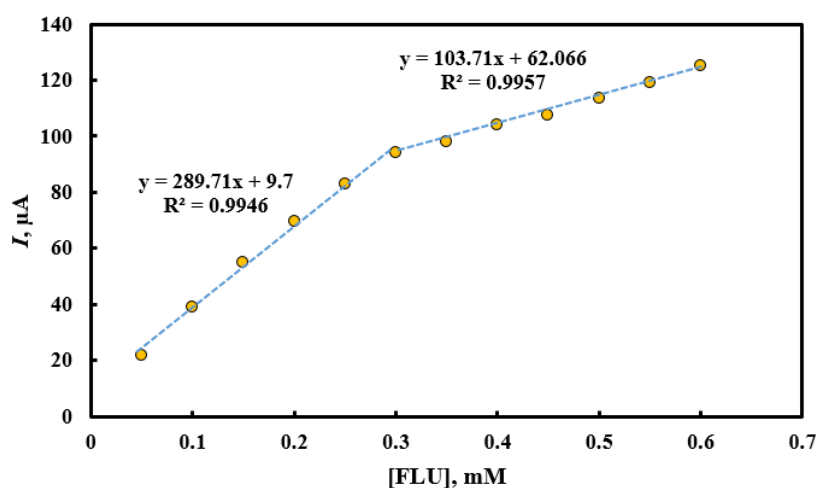


Figure 12. Effect of concentration of CV for FLU on GC_{ox} after (ten oxidation cycles) using PBs of pH 7.0

Table 1. Electroanalysis variables for voltammetrically determining FLU using GC_{ox}

Parameter	Value
The media used	Phosphate buffer
The used electrode	Oxidized glassy carbon (GC _{ox})
Method of modification	Electrochemically oxidation
pH	7.0
Scan rate, mV/sec	100
Linear range, mM	0.05-0.6
^a slopes	289.7, 103.7
^a intercepts	9.7, 62.1
^b SD, mM	0.021
^b RSD, %	4.2
Correlation coefficient (R ²)	0.995
SD of slope	5.63
SD of intercept	1.39
LOD, mM	0.016
LOQ, mM	0.048

^a: $I, \mu A = a [FLU, mM] \pm b$ ^b: Number of replicates (n = 6)**Figure 13.** Calibration curve for FLU determination using GC_{ox} after (ten oxidation cycles) using PBs of pH 7.0

The adsorption of FLU on the electrode surface block some part of the electrode and thus the electrochemical active surface area decreases and consequently the current response at large FLU concentration decreases and this is reflected on a lower sensitivity "small slope at large FLU concentrations". The standard deviation (SD) for the determination of FLU, after six replicates (n = 6), was found to be 0.021 mM and the relative standard deviation (RSD), was equalled 4.2% using 0.5 mM FLU concentration. In addition, the limits of detection (LOD) and quantification (LOQ) were calculated and found to be 0.016 and 0.048 mM, respectively. Using activated glassy carbon (GC_{ox}), all of the analytical parameters for voltammetrically determining FLU were reported in Table (1). It was clear from the comparison with the previous studies [7-11], see Table 2, reported on other modified electrodes and techniques that the LOD for estimating FLU using the developed method is acceptable.

Table 2. Comparison between the developed method and some previously published works for determination of FLU

The used technique	Remakes	LOD	Ref.
DPV	Modified pencil graphite electrode with SDS	0.034 mM	[7]
SWV	Chitosan/gold collapse gel (GS-Au CG)	0.0048 MM	[8]
SWV	Modified hallow fiber pencil graphite electrode	0.029 mM	[9]
Spectrophotometry	First flow-injection (FI)	0.47 μ M	[10]
DPV	Nano-structure GFL-Ho ³⁺ /NiO NSs	0.057 mM	[11]
CV	Oxidized glassy carbon electrode	0.016 mM	PM

DPV: differential pulse voltammetry, SWV: square wave voltammetry, CV: cyclic voltammetry, PM: present method

4. CONCLUSIONS

The electrochemical behaviour of FLU at the surface of GC_{ox} electrode was studied. The dependence of the electrochemical behaviour on pH, concentration and scan rate were investigated by cyclic voltammetry technique. In comparison to the bare GC electrode, the modified electrode exhibits outstanding electrocatalytic activity and significantly increases the peak current. The GC_{ox} electrode offers good operational characteristics including simplicity, cost-effectiveness, sensitivity, reproducibility and fast response. According to the findings, the GC_{ox} electrode is an appropriate sensor for identifying FLU with a good acceptable limit of detection compared with the previously published procedures.

References

- Y.M. Temerk, H.S. Ibrahim and W. Schuhmann, *Electroanalysis*, 28 (2016) 379.
- Z. Rezaeifar, G.H. Rounaghi, Z.Es' haghgi and M. Chamsaz, *Mater. Sci. Eng.*, 91 (2018) 18.
- A. Mehrabi, M. Rahimnejad, M. Mohammadi and M. Pourali, *J. Appl. Electrochem.*, 51 (2021) 606.
- R. Karthik, M. Govindasamy, S. M. Chen, T.W. Chen, A. Elangovan, V. Muthuraj and M. C. Yu, *RSC Adv.*, 7 (2017) 25709.
- L.J. Núñez-Vergara, D. Farias, S. Bollo and J.A. Squella, *Bioelectrochem.*, 53 (2001) 110.
- F. Ahmadi, J.B. Raoof, R. Ojani, M. Baghayeri, M.M. Lakouraj and H. Tashakkorian, *Chin. J. Catal.*, 36 (2015) 445.
- A.A. Ensaf, E. Khoddami, B. Rezaei, *J. Iran. Chem. Soc.*, 13 (2016) 1690.
- B. Mutharani, P. Ranganathan and S. M. Chen, *Int. J. Biol. Macromol.*, 124 (2019) 770,.
- A.A. El-Shanawany, S.M. El-Adl, D.S. El Haleem and S. El Wanees, *Annalen der Chemschen Forshung*, 2 (2014) 40.
- P.D. Tzanavaras and D.G. Themelis, *J. Pharm. Biomed. Anal.*, 43 (2007) 1824.
- Z. Fathi, S. Jahani and M.M. Foroughi, *Monatsh. Chem.*, 152 (2021) 766.
- P.K. Brahman, R.A. Dar, S. Tiwari and K.S. Pitre, *Colloids Surf., A*, 396 (2012) 15,.
- J.S. Farias, H. Zanin, A.S. Caldas, C.C. Dos Santos, F.S. Damos and R. de Cássia Silva Luz, *J. Electron. Mater.*, 46 (2017) 5628.
- M. Wang, M. Hu, B. Hu, C. Guo, Y. Song, Q. Jia and S. Fang, *Biosens. Bioelectron.*, 135 (2019) 29.
- K. Pecková, M. Průchová, J. C. Moreira, J. Barek, J. Fischer and V. Vyskočil, *Collect. Czech. Chem. Commun.*, 76 (2012) 1823.
- R. Zokhtareh M. Rahimnejad, *Electroanalysis*, 30 (2018) 927.

17. H. Ezoji M. Rahimnejad, *Int. J. Sci. Eng. Res.*, 7 (2016) 246.
18. A. Snyckerski, *J. Pharm. Biomed. Anal.* 7 (1989) 1513.
19. A. Álvarez-Lueje, C. Peña, L. J. Núñez-Vergara, and J. A. Squella, *Electroanalysis* 10 (1998) 1043.
18. E. Hammam, H. S. El-Desoky, K. Y. El-Baradie, and A. M. Beltagi, *Can. J. Chem.* 82 (2004) 1386.
20. K. Pecková, M. Průchová, J.C. Moreira, J. Barek, J. Fischer, and V. Vyskočil, *Collect. Czech. Chem. Commun.* 76 (2011) 1811.
21. P. K. Brahman, R. A. Dar, S. Tiwari, and K. S. Pitre, *Colloids Surf. A* 396 (2012) 8.
22. F. Ahmadi, J. B. Raoof, R. Ojani, M. Baghayeri, M. M. Lakouraj, H. Tashakkorian, *Cuihua Xuebao Chin. J. Catalysis* 36 (2015) 439.
23. Y. Temerk, H. Ibrahim, *J. Electroanal. Chem.* 736 (2015) 1.
24. P. K. Brahman, R. A. Dar, and K. S. Pitre, *Arab. J. Chem.* 9 (2016) S1884.
25. A. A. Ensafi, E. Khoddami, and B. Rezaei, *J. Iran. Chem. Soc.* 13 (2016) 1683.
26. Y. M. Temerk, H. Ibrahim, and W. Schuhmann, *Electroanalysis* 28 (2016) 372.
27. P. K. Brahman, L. Suresh, K. R. Reddy, J. S. Bondili, *RSC Adv.* 7 (2017) 37898.
28. J. S. Farias, H. Zanin, A. S. Caldas, C. C. dos Santos, F. S. Damos, R. de Cássia Silva Luz, *J. Electron. Mater.* 46 (2017) 5619.
29. R. Karthik, M. Govindasamy, S. M. Chen, T. W. Chen, J. Vinoth Kumar, A. Elangovan, V. Muthuraj, M.C. Yu, *RSC Adv.* 7 (2017) 25702.
30. Z. Rezaeifar, G. H. Rounaghi, Z. Es'haghi, M. Chamsaz, *Mater. Sci. Eng. C* 91 (2018) 10.
31. B. Mutharani, P. Ranganathan, and S. M. Chen, *Int. J. Biol. Macromol.* 124 (2019) 759.
32. A. Mehrabi, M. Rahimnejad, M. Mohammadi, and M. Pourali, *Biocatal. Agric. Biotechnol.* 22 (2019) 101375.
33. S. Sakthinathan, T. Kokulnathan, S. M. Chen, R. Karthik, P. Tamizhdurai, T. W. Chiu and K. Shanthi, *J Electrochem Soc* 166 (2019) B68.
34. M. Akilarasan, S. Maheshwaran, T. W. Chen, S. M. Chen, E. Tamilalagan, M. Ajmal Ali, W. A. Al-onazi, and A. M. Al-Mohaimed, *Microchem. J.* 159 (2020) 105509.
35. P.J. Harris, *Crit. Rev. Solid State Mater. Sci.*, 30 (2005) 253.
36. A.F. Craievich, *Mater. Res. Bull.*, 11 (1976) 1255.
37. G.M. Jenkins and K. Kawamura, *Nature*, 231 (1971) 176.
38. K. Shi and K.K. Shiu, *J. Electroanal. Chem.*, 574 (2004) 70.
39. K. Shi and K.K. Shiu, *Electrochim. Acta*, 51 (2006) 2638.
40. R.L. McCreery, *J. Electroanal. Chem.*, 13 (1991) 374.
41. K. Shi, K. Hu, S. Wang, C.Y. Lau and K.K. Shiu, *Electrochim. Acta*, 52 (2007) 5913.
42. M. Musameh, N.S. Lawrence and J. Wang, *Electrochem. Commun.*, 7 (2005) 18.
43. T. Ito, L. Sun and R.M. Crooks, *Electrochem. Solid-State Lett.*, 6 (2002) C4.
44. C.M. Liu, H.B. Cao, Y.P. Li, H.B. Xu and Y. Zhang, *Carbon*, 14 (2006) 2924.
45. D.A.L. Almeida, E.F. Antunes, V.Q. da Silva, M.R. Baldan and N.G. Ferreira, *J. Solid State Electrochem.*, 17 (2013) 1984.
46. P. Chen and R.K. McCreery, *Anal. Chem.*, 68 (1996) 3965.
47. Y. Yi, G. Weinberg, M. Prenzel, M. Greiner, S. Heumann, S. Becker and R. Schlögl, *Catal. Today*, 295 (2017) 40.
48. M. Morita, R. Arizono, N. Yoshimoto and M. Egashira, *J. Appl. Electrochem.*, 44 (2014) 453.
49. M.I. Awad, M.E. Al-Hazemi and Z. T. Al-thagafi, *Int. J. Electrochem. Sci.*, 17 (2022) Article Number 220448.
50. Z.T. Althagafi, J.T. Althakafi, B. A. Al Jahdaly and M. I. Awad, *J. Sensors* 2020, , Article ID 8873930.
51. M. A. Kassem, M. I. Awad, M. Morad, B. A. Aljahdali, R. A. Pashameah, H. Alessa, G. I. Mohammed, A. Sayqa, *Int. J. Electrochem. Sci.*, 17 (2022) Article Number: 220441.
52. Mohamed I Awad, Ali Sayqal, Rami Adel Pashameah, A Hameed, Moataz Morad, Hussain Alessa, Reem Kamal Shah, Mohammed A Kassem, *Int. J. Electrochem. Sci.*, 16 (2021) Article number:

150864.

53. P. Sharma, S. Radhakrishnan, S. S. Jayaseelan, B. –S. Kim, *Electroanalysis*, 28 (2016) 2626.
54. V. Vinothkumar, A. Sangili, S. –M. Chen, P. Veerakumar, *New J. Chem.*, 44 (2020) 2821.
55. A. T. E. Vilian, P. Puthiaraj, C. H. Kwak, S. –K. Hwang, Y. S. Huh, W. –S. Ahn, Y. –K. Han, *ACS Appl. Mater. Interfaces* 2016, 8, 12740–12747.
56. R.N. Goyal, V.K. Gupta, M. Oyama and N. Bachheti, *Electrochem. Commun.*, 8 (2006) 70.
57. A.A. Ramadan and H. Mandil, *Anal. Biochem.*, 404 (2010) 7.
58. X.Y. Liu, *Bull. Korean Chem. Soc.*, 31 (2010) 1186.
59. S. Kubendhiran, R. Sakthivel, S. –M. Chen, B. Mutharani, T. –W. Chen, *Anal. Chem.*, 90 (2018) 6283.
60. P.S. Dorraji and F. Jalali, *Sens. Actuators, B*, 200 (2014) 258.

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