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Disposable Voltammetric Determination of Celestine Blue at a Pencil Graphite Electrode

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Research Article

Abstract − The proposed study describes a novel and disposable voltammetric sensor that designed for the sensitive determination of celestine blue (CelsB) using a pencil graphite electrode (PGE). The electrochemical characterization study of the designed sensor was performed by recording the cyclic voltammograms (CVs) and electrochemical impedance (EI) curves in 5.0 mM of $Fe(CN)_6^{3-/4-}$ including 0.10 M of KCl, and compared with the other carbon-based electrodes such as carbon paste (CPE) and glassy carbon (GCE) electrodes. The electrochemical behaviour of CelsB was examined at different carbon-based electrodes including PGE, CPE, and GCE by the cyclic voltammetric (CV) method. The recorded CVs showed that the remarkable response obtained at PGE toward oxidation of CelsB. Moreover, the PGE shows a wide linear range (4.0 − 150 µM) and detects the CelsB with a notable limit of detection (1.21 µM). In addition, the results from the interference studies proved that the PGE enables selective voltammetric determination of CelsB in presence of various species. A feasibility study for CelsB sensor was also tested on tap water and cherry apple juice samples and the recovery values obtained between 96.2 − 103 % with high precision and accuracy indicated that the PGE shows an acceptable and good applicability to real samples.

Keywords − C*elestine blue, electrochemistry, pencil graphite electrode, sensors, voltammetry*

1. Introduction

Dyes have been used as an important component in leather, paper, textile, and pharmaceutical products. As a result, the widespread use of dyestuffs induced soil and water pollution [1-4]. The CelsB which is soluble in water and classified as an essential oxyazine group dye, shows good mediator properties due to its high electron transfer properties (Figure 1) [5]. The CelsB has a non-complex structure, and it is structurally positively charged property [6]. On the other hand, it causes harmful effects on human health [7-9]. It has also been expressed that the extreme use of azo dyes [10] may cause mutagenic, hyperactivity, and carcinogenic impacts in children [11]. According to the information mentioned above, the rapid, selective, and sensitive determinations of CelsB have a great importance on humans and the environment. It may be stated that the electrochemical oxidation and reduction of CelsB proceeds with the exchange of two protons and two electrons via catechol groups [7].

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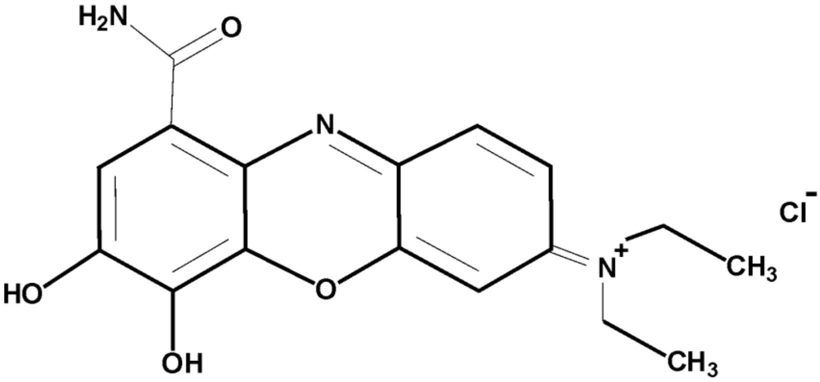

Figure 1. Structure of molecular CelsB [5]

Electrochemical methods are still attractive due to their cheapness, high sensitivity, mobility, selectivity, speedy response, easy instrumentation, ability to be miniaturized properties [12,13]. Various carbon-based electrodes, such as PGE, CPE, and GCE have been widely used in the design of electrochemical sensors [14]. The GCE is expensive and includes hard and time-consuming surface cleaning and polishing procedures. The other commonly used electrode, CPE has a renewable surface and cost-effective, but it also includes hard preparation steps and the same limitations mentioned above [15]. Among these electrodes, the PGE attracts great attention due to its many advantageous properties. These features can be listed as follows; disposability, low-priced, pretty reactive, renewable surface, less toxicity, extensive potential range, well mechanical rigidity, and easily available [16-22].

As far as we know from the literature, there is no study that performed for the electrochemical determination of CelsB using PGE. In this study, the disposable PGE firstly was used for the sensitive and selective voltammetric detection of CelsB. Considering the recovery values obtained from the feasibility test on different samples suggested that the proposed methodology can be applied successfully in the determination of CelsB from daily samples.

2. Materials and Methods

2.1. Apparatus and Chemicals

All electrochemical measurements were performed using a Galvano plot GX203 analyzer originating in Türkiye. Experiments were carried out by choosing RE5B-BASI Ag/AgCl($_{\text{saturated KCl}}$) (Diameter size: 6.0 mm) as the reference electrode, MW1032-BASI Pt wire (Diameter size: 0.50 mm) as the counter electrode, and pencil graphite as the working electrode in the cell of the conventional triple electrode system where the experiment was conducted. All electrochemical measurements were evaluated for the PGE (The used length is 1.0 cm that equals to 0.159 cm^2 of geometric area (A_G), CPE (BASI, Diameter size: 2.87 mm), GCE (BASI, Diameter size: 3.0 mm). A pH meter device (HI-221 Hanna) including a unified glass electrode system was used to regulate Britton-Robinson buffer solutions (BRBS) at different pHs. The pure water was generated from the device of Q7B Elga option. Celestine blue (97%, $C_{17}H_{18}N_3O_4Cl$, 363.80 g mol^{-1}), citric acid, D(+)glucose, tartrazine (Tz), quinoline yellow (QY), and brilliant blue (BB) were purchased from Aldrich. $K_3[Fe(CN)_6]$) and dopamine hydrochloride (DA), were provided from Alfa Aesar. KNO_3, Na_2SO_4, Na_2CO_3, $CaCl_2.2H_2O$, $Mg_2SO_4.7H_2O$, Na_2HPO_4, NaH_2PO_4 $MgCl_2$, KCl, NaCl, CH_3COOH, NaOH, H_3BO_3, H_3PO_4, $K_4[Fe(CN)_6].2H_2O$, L-ascorbic acid (L-AA), fructose, and were provided from Merck company.

2.2. Electrochemical Experiments

The CPE used in the experimental study was prepared by filling the CPE body after obtaining a paste consistency with mineral oil (25%) and graphite powder (75%). Before use, GCE was cleaned with alumina slurry (0.30 μm) and polished. Then, resulted electrode was left in an ultrasonic bath in ethanol and water for 10 minutes to remove the trace of impurities. EI curves of PGE, GCE, and CPE (frequency range of 0.10 – 100000 Hz) were recorded in 5.0 mM of $Fe(CN)_6^{3-/4-}$ solution that contains 0.10 M KCl. Cyclic voltammetric responses of 16 μM CelsB at the mentioned electrodes were recorded in pH 5.0 BRBS containing KCl. The effect of pH and scan rate on electrochemical response of CelsB was examined from the recorded CVs of 50 μM CelsB.

2.3. Real Sample Study

To determine the CelsB in tap water and cherry apple juice samples, known (5 and 10 μM) concentrations of CelsB were spiked into both samples. Afterward, the standard additions were performed from the 5.0 mM standard CelsB solution, and CVs were recorded. Recovery values were calculated for the samples.

3. Results and Discussion

3.1. Characterization Studies

Electrochemical impedance spectroscopy (EIS) is a useful method for the examination of the surface conductivity properties of electrodes. The semicircle part of the curves corresponds to charge transfer resistance (Rct) directly related with the surface conductivity at high frequencies, and the linear part is related with the diffusion [23,24]. The PGE, CPE, and GCE are electrochemically characterized by the recording of the CVs (Figure 2A) and EI curves (Figure 2B) of 5.0 mM of $Fe(CN)_6{}^{3-/4-}$ solution that contains 0.10 M KCl.

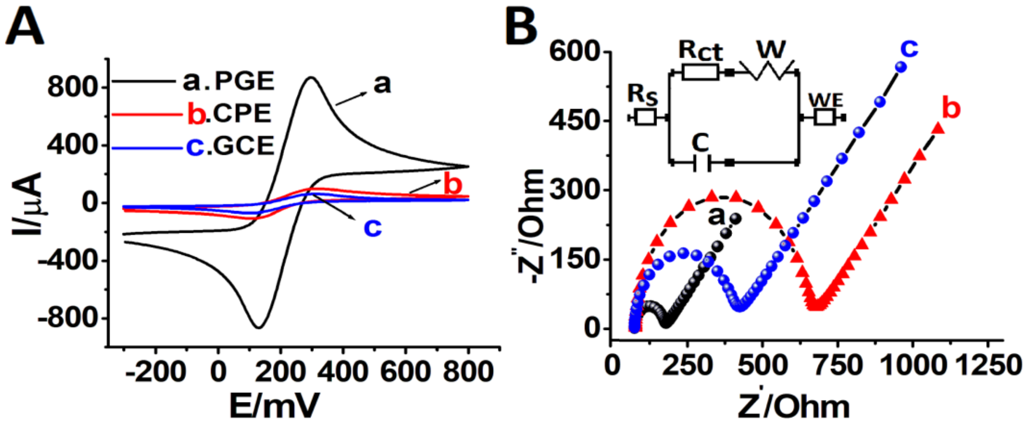

Figure 2. A) CVs and B) EI curves for 5.0 mM of $Fe(CN)_6{}^{3-/4-}$ solution contains 0.10 M KCl at (a) PGE, (b) CPE, and (c) GCE, the inset of Figure B is the electrochemical impedance circuit model: (C: Capacitance for double-layer; R_s: Ohmic resistance; WE: Working electrode ; W: Warburg impedance, (Scan rate (S.rate): 50 mV/s)

As can be seen in Figure 2A, the oxidation (E_a) and reduction (E_c) peak currents of different carbon-originated electrodes (CPE and GCE) are significantly lower than that obtained with PGE (Table 1). The reversibility of the peaks belongs to $Fe(CN)_6^{3-/4-}$ higher (ΔE= 173 mV) than those obtained at CPE and GCE and its surface exhibits better conductivity (R_{ct}= 96 ohm). The PGE shows high voltammetric response and better conductivity among the other electrodes. Because, the PGE has a composite structure including graphite and clay that provides larger electroactive surface. Therefore, this structural property may have improved the electron transfer between PGE and $Fe(CN)_6^{3-/4-}$ [25].

Table 1. CV and EIS responses obtained as a result of the characterization studies of the electrodes

WE	Results from the recorded CVs					Results from the recorded EI curves
	E_a (mV)	E_c (mV)	ΔE (mV)	I_a (μA)	I_c (μA)	R_{ct} (Ohm)
PGE	299	126	173	885	871	96
CPE	325	110	215	94	95	574
GCE	309	100	209	98	97	310

3.2. Investigation of the Electrochemical Behavior of CelsB

The recorded CVs for 16μM CelsB in BRBS (pH 5.0) at the PGE, CPE, and GCE was given in Figure 3. The recorded CVs indicate that the irreversible oxidation of CelsB observed at 746, 800, and 708 mV at the PGE, CPE, and GCE, respectively. Moreover, the highest voltammetric response based on the irreversible oxidation of CelsB obtained with PGE. The best voltammetric response observed at PGE are attributed to the porous composite structure that leads an increase in electroactive surface area of PGE. In other words, the electron transfer between CelsB and PGE on the surface of PGE improved [25]. Therefore, the PGE was selected for the determination of CelsB according to its highest response.

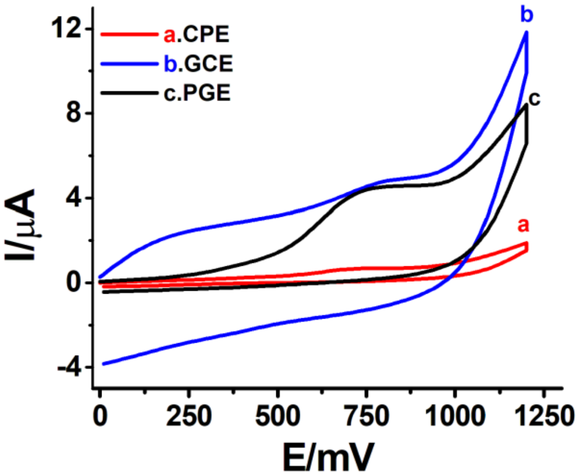

Figure 3. CVs of 16 μM CelsB electrochemical responses at (a) CPE, (b) GCE, and (c) PGE in BRBS (pH 5.0) at S.rate 50 mV/s

3.3. The Effect of pH

The CV method was used to determine the most suitable supporting electrolyte developed for the determination of CelsB. For this aim, CVs of 50μM CelsB in BRBS solutions with different pH values (2.0 − 6.0) were recorded at PGE (Figure 4). Because of the fact that the best electrochemical response was achieved at the pH of 5.0, this supporting electrolyte was chosen for further studies.

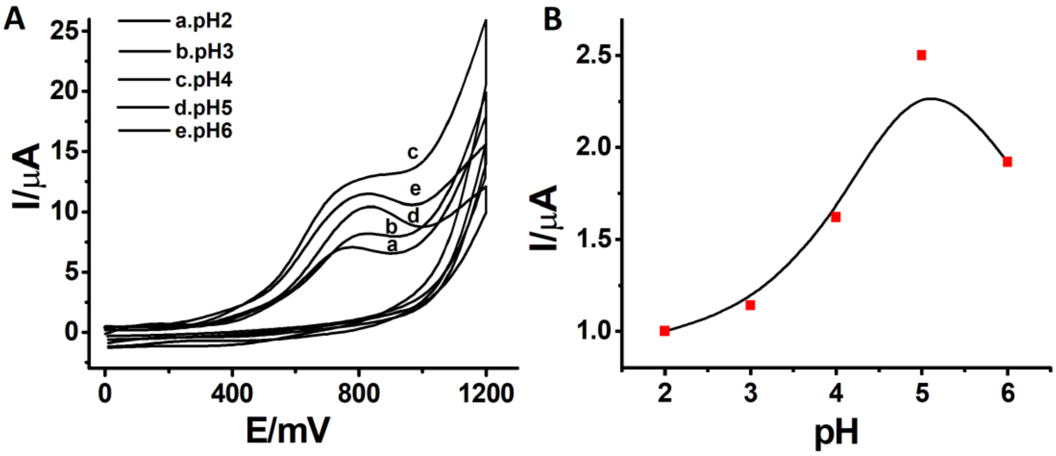

Figure 4. A) The CVs recorded for 50μM CelsB in various pH values (2.0 – 6.0) of BRBS (Potential range: 0 – 1200 mV, S.rate: 50 mV/s) and B) pH versus current graph

3.4. The Influence of Scan Rate

The influence of scan rate on the voltammetric response of CelsB was investigated by recording the CVs 50μM CelsB in BRBS (pH 5.0) at enhanced scan rates ranging from 10 to 600 mV/s (Figure 5). The effect of scan rate on peak current among 10 and 600 mV/s was investigated using the CV method of 50 μM CelsB in pH 5.0 BRBS. As can be understood from the given Figure, the voltammetric response based on the oxidation peak current of CelsB enhances by the increasing of scan rate. In addition, the high linearity (R^2 = 0.9977) between the I_a(μA) vs. square root of scan rate generated from the recorded CVs confirms that the irreversible oxidation of CelsB occurs with a diffusion-controlled process [25-28].

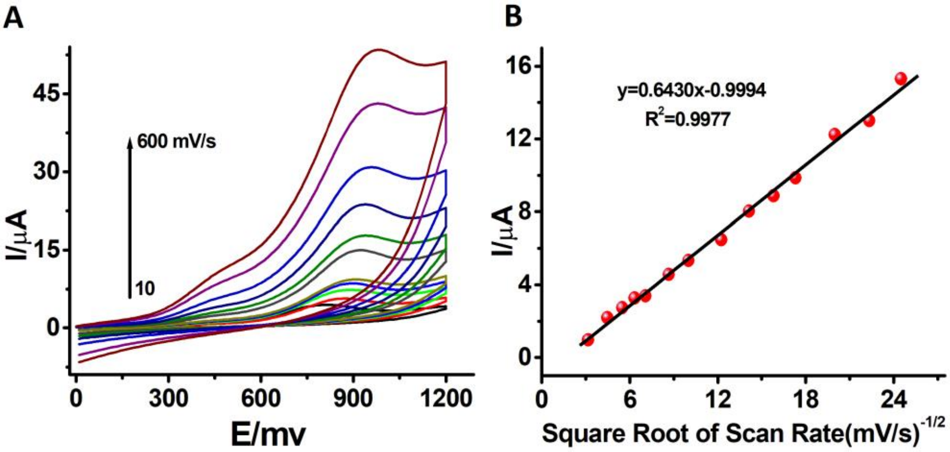

Figure 5. A) CV responses acquired from PGE against 50 μM CelsB at different S.rate (10-600 mV/s) at pH 5 (BRBS) potential range: 0 – 1200 mV, B) the linear variation of the square root of the scan rate versus the oxidation peak currents of CelsB

3.5. The Cyclic Voltammetric Determination of CelsB

The determination of CelsB performed by CV technique. Figures 7 and 8 show the CVs of the increased concentrations of CelsB (0 − 150 μM). The obtained calibration curve generated from the CVs confirmed that the voltammetric response of CelsB goes linearly between 0 − 150 μM. The LOD value was calculated according to the 3×Std/slope and was found to be 1.21 μM (Std is the standard deviation of the minimum CelsB concentration that observes as a measurable signal; the slope was calculated from the calibration plots). The electrochemical performance of the CelsB sensor has been compared with the only study reported in literature (Table 2) (Roushani at al., 2021). In the reported study, screen printed carbon electrode was modified with NiO nanoparticles and synthesized molecularly imprinted polymer of CelsB (CB-MIP/NiO-NPs/SPCE) for the differential pulse voltammetric determination of CelsB. Although the related sensor shows wider linear range (2.0 – 150 µM) and lower LOD (0.35 µM), the method includes significant limitations. Firstly, the SPCE is an expensive electrode material. Secondly, the synthesis of CB-MIP and the preparation of the CB-MIP/NiO-NPs/SPCE include hard and time-consuming procedures. These significant factors limit the practical usability of the designed sensor. On the other hand, the CelsB sensor based on PGE does not include these disadvantages, and provides disposable, low-cost, fast, and practical determination of CelsB. Moreover, there is a limit of study based the electrochemical determination of CelsB [2], the proposed method has the potential to be an example based on practical and low-cost electrochemical determination of CelsB that will contribute to the deficiency in this field.

The reproducibility and repeatability were examined by recording under optimized conditions. The reproducibility was examined five PGEs, and the relative standard deviation (RSD) value was found to be 4.7 %. The intra-day repeatability was researched by 10 times recording the CV responses of 8.0 µM CelsB at the same electrode and the RSD value was calculated as 4.6%. The obtained RSD values lower than 5.0% indicated that the PGE exhibits reproducible and stable intra-day voltammetric responses. Although the PGE shows poor intra-day responses, the disposable and practical use of PGE tolerates this limitation.

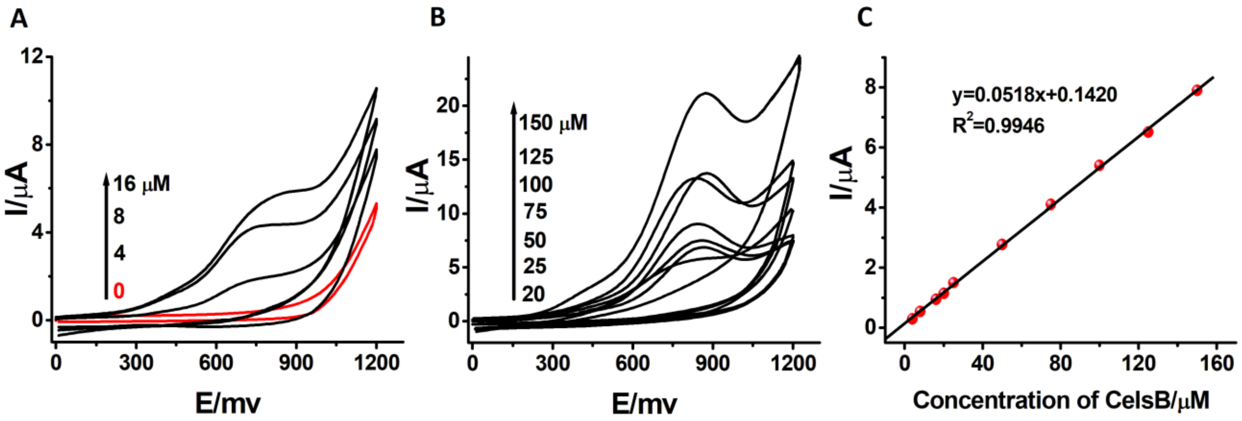

Figure 6. A) CVs from 0 to 16 µM CelsB B) CVs from 20 µM to 150 µM CelsB (BRBS pH5.0; S. rate: 50 mV/s) C) Calibration curve of CVs acquired from CelsB at increasing concentrations

Table 2. The performance comparison between electrochemical CelsB sensors

WE	Method	E_a(mV)	Linear response range (µM)	LOD (µM)	Real sample	Reference
PGE	CV	+746	4.0 − 150	1.21	Cherry apple juice, tap water	This work
CB-MIP/NiO-NPs/SPCE	DPV	-100	2.0 – 150	0.37	Waste water from textile, industry	[2]

3.6. The Selectivity to CelsB

The influence of some possible kinds of molecules and ions on the voltammetric response of 50 µM CelsB was tested under the optimized conditions. Table 3 shows that the influence of 25-fold Fructose, Na^+, Ca^{2+}, K^+, Mg^{2+}, NO_3^-, 10-fold SO_4^{2-}, CO_3^{2-}, 1-fold Tz, Qy, BB, Citric acid, and 0.01-fold L-AA on CelsB was found to be negligible according to the tolerance limit of 10%. According to all these results, it was found that the proposed method can be applied for selective determination of CelsB in real samples including the mentioned species.

Table 3. Influence of some possible kinds of interferences (n=3)

Interference	The amount of interference (fold)	% Alteration in voltammetric response	±SD
L-AA	0.01	+ 1.72	0.11
Citric acid	1	+ 8.15	1.13
Fructose	25	+ 5.76	0.54
Glucose	50	+ 0.90	1.74
Tz	1	− 0.80	0.16
QY	1	− 5.43	0.25
BB	1	+ 8.72	0.65
Na^+	25	+ 2.79	0.78
Ca^{2+}	25	+ 3.43	0.86
K^+	25	+ 6.34	1.50
Mg^{2+}	25	+ 8.33	1.10
NO^{3-}	25	+ 6.30	1.50
SO_4^{2-}	10	+ 8.10	0.78
CO_3^{2-}	10	+ 2.60	0.56

3.7. The Application on Real Samples

The feasibility of the method was examined in cherry apple juice and tap water samples by using the standard addition-CV techniques together. Each sample was enriched with 5 and 10 µM of CelsB and the additions from standard solution were performed and the CVs were recorded. The percentage values for the recovery of CelsB were calculated from the calibration curves that generated from the recorded CVs (Table 4). The high percentages of recovery (96.2 – 103%) found from the feasibility studies proved the high applicability of the proposed sensor on real samples.

Table 4. Results of recovery applications for the detection of CelsB using the standard addition management in real samples (n=3)

Sample	Adding (µM)	Found (µM)	RSD (%)	Recovery (%)
Tap water	5	5.05	3.09	102
	10	10.22	3.08	102.20
Cherry apple juice	5	4.81	2.60	96.20
	10	10.30	4.85	103

4. Conclusion

As a result, a novel and disposable sensor based on cyclic voltammetric determination of CelsB was performed at PGE for the first time. The proposed methodology provides fast, practical, and low-cost electrochemical determination of CelsB without including time-consuming and hard, cleaning, polishing modification, and steps. The CelsB sensor designed on PGE shows wide linear range (4.0 – 150 µM) and low LOD (1.21 µM) for the voltammetric determination of CelsB. Moreover, the proposed methodology exhibits good repeatability and reproducibility, and provides determination of CelsB in high precision and accuracy from real samples. In summary, considering that the studies upon the electrochemical detection of CelsB in the literature are quite limited, it is hoped that this study will add diversity to the existing studies in terms of cost, speed, and practicality.

Author Contributions

The author read and approved the final version of the paper.

Conflicts of Interest

The author declares no conflict of interest.

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References

[1] V. Aruna Janani, D. Gokul, N. Dhivya, A. Nesarani, K. Mukilan, A. Suresh Kumar, M. Vignesh Kumar, *Optimization studies on methyl orange (MO) dye adsorption using activated carbon nanoadsorbent of ocimum basilicum linn leaves*, Journal of Nanomaterials 2023 (2023) Article ID 7969512 14 pages.

[2] M. Roushani, Z. Saedi, Z. Mirzaei Karazan, A. Azadbakhat, *Electrochemical detection of celestine blue based on screen printed carbon electrode modified with molecular imprinted polymer and NiO nanoparticles*, Analytical and Bioanalytical Chemistry Research 8 (4) (2021) 493–504.

[3] K. G. Akpomie, J. Conradie, *Biosorption and regeneration potentials of magnetite nanoparticle loaded solanum tuberosum peel for celestine blue dye*, International Journal of Phytoremediation 23 (4) (2021) 347–361.

[4] P. S. Ganesh, G. Shimoga, S. H. Lee, S. Y. Kim, E. E. Ebenso, *Interference free simultaneous detection of dihydroxy benzene isomers at cost-effective and reliable celestine blue modified glassy carbon electrode*, ChemistrySelect 6 (9) (2021) 2379–2386.

[5] Y. Chen, Y. Zhong, J. X. Ye, Y. Lei, A. L. Liu, *Facile label-free electrochemical dna biosensor for detection of osteosarcoma-related survivin gene*, Biosensors 12 (9) (2022) 747 11 pages.

[6] A. Valipour, M. Roushani, *TiO_2 nanoparticles doped with celestine blue as a label in a sandwich immunoassay for the hepatitis C virus core antigen using a screen printed electrode*, Microchimica Acta 184 (2017) 2015–2022.

[7] A. Noorbakhsh, M. Khakpoor, M. Rafieniya, E. Sharifi, M. Mehrasa, *Highly sensitive electrochemical hydrogen peroxide sensor based on iron oxide-reduced graphene oxide-chitosan modified with DNA-celestine blue*, Electroanalysis 29 (4) (2017) 1113–1123.

[8] E. Hamidi-Asl, J. B. Raoof, A. S. Meibodi, Z. H. Bazgir, *Celestine blue as a new indicator in electrochemical DNA biosensors,* Science China Chemistry 59 (1) (2016) 128–134.

[9] N. Abbasi, S. A. Khan, T. A. Khan, *Response surface methodology mediated process optimization of celestine blue B uptake by novel custard apple seeds activated carbon/FeMoO4 nanocomposite*, Journal of Water Process Engineering 43 (2021) Article ID 102267 14 pages.

[10] M. S. Saad, L. Balasubramaniam, M. D. H. Wirzal, N. S. Abd Halim, M. R. Bilad, N. A. H. Md Nordin, F. N. Ramli, *Integrated membrane–electrocoagulation system for removal of celestine blue dyes in wastewater*, Membranes 10 (8) (2020) 184 12 pages.

[11] K. Pliuta, A. Chebotarev, A. Pliuta, D. Snigur, *Voltammetric determination of allura red AC onto carbone-paste electrode modified by silica with embedded cetylpyridinium chloride*, Electroanalysis 33 (4) (2021) 987–992.

[12] E. Murugan, A. Poongan, A. Dhamodharan, *Electrochemical sensing of acetaminophen, phenylephrine hydrochloride and cytosine in drugs and blood serum samples using β-$AgVO_3$/ZrO_2@g-C_3N_4 composite coated GC electrode*, Journal of Molecular Liquids 348 (2022) 118447 11 pages.

[13] T. Erşan, D. G. Dilgin, E. Kumrulu, U. Kumrulu, Y. Dilgin, (2023). *Voltammetric determination of favipiravir used as an antiviral drug for the treatment of COVID-19 at pencil graphite electrode*, Electroanalysis 35 (4) 11 pages.

[14] N. Sedhu, J. J. Kumar, P. Sivaguru, V. Raj, *Electrochemical detection of riboflavin in pharmaceutical and food samples using in situ electropolymerized glycine coated pencil graphite electrode*, Journal of Electroanalytical Chemistry 928 (2023) 117037 9 pages.

[15] S. Karakaya, *Development of an amperometric hydrazine sensor at a disposable poly (alizarin red S) modified pencil graphite electrode*, Monatshefte für Chemie-Chemical Monthly 150 (2019) 1911–1920.

[16] E. Pradeepa, Y. A. Nayaka, N. R. Manjushree, *Sensitive and selective determination of vanillin in the presence of dopamine and uric acid using low-cost and trouble-free pencil graphite electrode modified with methyl orange*, Materials Chemistry and Physics 296 (2023) 127180 14 pages.

[17] L. A. Zambrano-Intriago, C. G. Amorim, A. N. Araújo, D. Gritsok, J. M. Rodríguez-Díaz, M. C. Montenegro, *Development of an inexpensive and rapidly preparable enzymatic pencil graphite biosensor for monitoring of glyphosate in waters*, Science of The Total Environment 855 (2023). 158865 12 pages.

[18] N. M. Omar, E. M. Mabrouk, A. Y. El-Etre, A. I. Ali, A. M. Beltagi, *Development of a disposable pencil graphite electrode modified with poly 1,5-diaminonaphthalene for voltammetric determination of flufenamic acid*, Journal of The Electrochemical Society 170 (8) (2023) 087501 10 pages.

[19] G. Önal, A. Levent, *Electrochemical evaluation and determination of vindesine used in cancer chemotherapy at disposable pencil graphite electrode by voltammetric method*, Monatshefte für Chemie-Chemical Monthly 154 (2) (2023) 205–213.

[20] N. Ghaffari, K. Pokpas, E. Iwuoha, N. Jahed, *Sensitive electrochemical determination of bisphenol a using a disposable, electrodeposited antimony-graphene nanocomposite pencil graphite electrode (PGE) and differential pulse voltammetry (DPV),* Analytical Letters 57 (6) (2023) 1008–1025.

[21] F. Akter, D. C. Kabiraz, M. M. Islam, S. Ahmed, M. A. Hanif, Y. S. Kim, *Disposable pencil lead as an electrochemical transducer for monitoring catechol in river and tap water*, Coatings 13 (5) (2023) 913 12 pages.

[22] R. M. Carvalho, E. R. Pedão, F. M. R. Guerbas, M. P. Tronchini, V. S. Ferreira, J. M. Petroni, B. G. Lucca, *Electrochemical study and forensic electroanalysis of fungicide benzovindiflupyr using disposable graphite pencil electrode*, Talanta 252 (2023) 123873 7 pages.

[23] A. Afkhami, A. Bahiraei, T. Madrakian, *Gold nanoparticle/multi-walled carbon nanotube modified glassy carbon electrode as a sensitive voltammetric sensor for the determination of diclofenac sodium*, Materials Science and Engineering: C 59 (2016) 168–176.

[24] M. Minakshi, K. Wickramaarachchi, *Electrochemical aspects of supercapacitors in perspective: from electrochemical configurations to electrode materials processing*, Progress in Solid State Chemistry 69 (2023) 100390 10 pages.

[25] S. Karakaya, B. Kartal, Y. Dilgin, *Development and application of a sensitive, disposable and low-cost electrochemical sensing platform for an antimalarial drug: amodiaquine based on poly (calcein)-modified pencil graphite electrode,* International Journal of Environmental Analytical Chemistry 102 (17) (2020) 5136–5149.

[26] S. Karakaya, Y. Dilgin, *The application of multi-walled carbon nanotubes modified pencil graphite electrode for voltammetric determination of favipiravir used in COVID-19 treatment*, Monatshefte für Chemie-Chemical Monthly 154 (2023) 729–739.

[27] S. Ayaz, Y. Dilgin, *Flow injection amperometric determination of hydrazine based on its electrocatalytic oxidation at pyrocatechol violet modified pencil graphite electrode*, Electrochimica Acta 258 (2017) 1086–1095.

[28] A. Wilson, B. Sajeevan, M. G. Gopika, A. Babu, K. M. Sreedhar, B. Saraswathyamma, *Electrochemical quantification of vanillin using hydrazine derivative modified pencil graphite electrode*, Materials Today: Proceedings 80 (2023) 558–563.