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Electrochemical Determination of Chloramphenicol in Milk and Eye-drop Using Easily Activated Screen Printed Carbon Electrodes

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Abstract
An analytical method that offers fast response with a cheap instrument and simple sample preparation is an ideal technique that is required in scientific analysis. Electrochemical sensing is an analytical method that suits the above criteria to determine various samples using different electrode material. Detection of chloramphenicol in agricultural products and drug samples using cheap electrode materials is highly required due to its wide application in agriculture. In this study a cost-effective activated SPCE was made electrochemically to determine chloramphenicol in eye-drop and pasteurized milk. The activation of the SPCE was straightforward and done by cycling 0.5 M KOH using LSV techniques. Surface imaging, spectroscopy, and electrochemical analyses showed that there is an effective formation of new functional groups during the activation. The activated SPCE gave a higher peak current for Chloramphenicol during the CV and SWV study using PBS pH 6.5 compared to that of the bare one. Utilizing the optimal SWV conditions, a linear calibration curve was obtained in the range of 0.05–100 µM with quite a small detection limit of 20 nM. In addition to the high sensitivity, stability, and remarkable recovery, the excellent reproducibility makes the activated SPCE applicable in real sample analysis.

Keywords: Chloramphenicol; Screen Printed Carbon Electrode; Electrochemical; Stable; Activated.

1. INTRODUCTION

Chloramphenicol (CAP) is an antibiotic specifically used to avoid infections in small wounds, in addition to treating many sicknesses such as cystic fibrosis, conjunctivitis, cholera, typhoid fever, plague, and ear and skin infection [1]. Because of its availability and low price, CAP is administered in animal husbandry though it is banned in the European Union and the United States [2]. Effluents from treated or untreated sewage have diverse types of contaminants from pharmaceutical products and require serious consideration [3]. There is a growing concern that antibiotic tablets should be utilized and applied not only by considering their health beneficial outcomes but also by their effect on producing antibiotic resistant genes [4]. The wide application and usage of CAP in farming and human medication directed the studies for its detection in milk [5-7], honey, [8, 9] urine, [10, 11] feed water [12], and pharmaceutical products [13].

Various analytical strategies have been studied for the determination of CAP, such as Solid-Phase Extraction Based on Molecularly Imprinted Polymer [14], Capillary Electrophoresis [15], Fluorescence [16], Ultra-High Pressure Liquid Chromatography-Tandem Mass Spectrometry [17-18] Liquid Chromatography with tandem mass spectrometry [19], High-Performance liquid chromatography [20] and Gas Chromatography [21], in pure form or in combination with other drugs. Analysis of low concentration of drugs like CAP in biological samples including urine and milk products frequently required analytical techniques that have low detection limits and are applicable to small samples.

Electrochemical techniques are effective and suitable analytical strategies that provide high sensitivity, accuracy, and precision in addition to a wide linear dynamic range, with distinctly low-cost instrumentation [22]. The improvement of screen-printing technology and the serial manufacturing of one-time use cheap SPCEs for sensing of a huge variety of materials is broadly growing [23-24]. The technology used for making screen printed electrodes offers the production of massive numbers of electrodes in a reproducible, low-cost, and disposable format. The opportunity to incorporate chemically functionalized carbon material in the printing process gave a considerable benefit for SPCEs [21]. In this work, the oxidation–reduction behavior of CAP was investigated on electrochemically activated SPCEs. The incorporation of carbonyl group on the SPCEs during activation was found to make

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the SPCE behave more or less like an edge plane graphite electrode or similar to that of CNT modified electrodes [25].

2. EXPERIMENTAL

2.1. Chemicals and Materials

Chloramphenicol, ascorbic acid, uric acid, lactose, glucose, glycine, calcium chloride, magnesium chloride, zinc nitrate hexahydrate, sodium nitrate, potassium nitrate, urea, glacial acetic acid, sodium chloride, and potassium hydroxide were purchased from Sigma-Aldrich. Potassium hydrogen phosphate, potassium dihydrogen phosphate, phosphoric acid, and p-nitrophenol were purchased from BDH. For real sample analyses, commercial pharmaceutical eye drop of chloramphenicol formulation (MBL Pharma, Pakistan) was purchased from a local drug store from Addis Ababa, Ethiopia, and pasteurized milk (Shola milk, Lame Dairy (Shola) PLC, Ethiopia).

2.2. Instrumentation

Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV) Square Wave Voltammetry (SWV), and Electrochemical Impedance Spectroscopy (EIS) were performed with a PC-integrated CHI760D electrochemical workstation (CH Instruments, USA). IRTracer-100 Fourier Transform Infrared Spectrophotometer (SHIMADZU) was used for FTIR spectra recoding and JEOL JSM-7401F Field Emission Scanning Electron Microscope was used for imaging. Zensor screen-printed carbon electrodes (ET077-40 Zensor TE100 SPEs - Pack of 40) were purchased from Taiwan with working area 3 mm diameter and made of graphitic carbon powder (working and auxiliary electrodes), Ag/AgCl pellet (reference).

2.3. Activation of SPCE

Fabricated SPCE makes use of an insulating polymer with the printing inks for enhancing the adhesion of the graphite to the substrate. This polymer ink blocks the electrochemically active carbon particles and decreases the electron transfer ability of the electrode; the activation of the SPCE therefore reverses the insulating property of the bare SPCE [26] and in our case, this was performed electrochemically through cycling 0.5 M KOH in the potential range of −1.5 to 1.0 V for 10 cycles at 100 mV s^{-1} scan rate.

2.4. Preparation of Milk Sample

Prior to the determination, the milk that is pasteurized was treated as mentioned in [27]. In brief, 5 ml milk sample that was pasteurized and spiked with varying concentrations of CAP standard solution in 5 mL ethyl acetate. After mixing the sample very well and 10 mins of sonication, the aggregate was centrifuged at 4000 rpm for 5 mins and the supernatant was evaporated. Then the dissolution of the residue was done using 10 mL 0.1 M PBS pH=6.5.

2.5. Chloramphenicol Formulation

50 µL of CAP eye drop was pipetted out and poured right into a 50 mL volumetric flask, then filled with the supporting electrolyte (0.1 M PBS pH 6.5) to a final concentration of 15.5 µM which is in the range of the calibration curve acquired. The solution was then taken and transferred to 25 mL volumetric flasks and spiked with varying concentrations of CAP standard to get the desired concentration.

3. RESULT AND DISCUSSION

3.1. Surface Characterization

From the IR spectrum of the activated SPCE, the absorption bands observed at 3500 cm^{-1}, 1600 cm^{-1}, and 1200 cm^{-1} are due to the formation of hydroxyl and carbonyl containing groups Fig. S1 [28, 29]. The SEM image of the activated SPCE exhibits a greater cracked surface together with massive defects as compared to the bare SPCE. Small ball-like structures with an average length of 56.4 to 86 were nm allocated over the surface of the activated SPCE Fig. S2. This confirms that the electrochemical activation significantly affects the surface morphology of SPCE. The Nyquist plot diameter of the semicircle is quite large on the bare SPCE in contrast to the activated one, suggesting that the surface of the bare SPCE has an insulating property. And the smaller diameter length of the activated SPCE is a piece of evidence for better electrical conductivity of the activated SPCE Fig. S3.

3.2. Electrochemical Property of the Electrodes

Upon scanning from positive to negative potentials, a well-defined irreversible cathodic peak (F1) at −0.59 V and an anodic peak in the reverse scan at −0.069 (F2) were observed. During the second cycle, a new cathodic peak (S1) at −0.036 V was observed. From the redox reaction mechanism of CAP [30], the irreversible cathodic peak at −0.59 V (F1) is a result of the reduction of the nitro functional group in CAP to phenylhydroxylamine, by four-electrons and four-protons transfer mechanisms. Whereas the anodic peak (F2) is due to the oxidation of phenylhydroxylamine to the phenylnitroso group derivative and the cathodic peak (S1) is the reverse reaction of the phenylnitroso group derivative to phenylhydroxylamine Fig. S4. This redox process follows a two-electron and two-proton transfer mechanism. The cyclic voltammograms displayed in Figure 1 shows no

obvious electrochemical response for CAP at the bare SPCE. On the contrary, a well-defined peak was observed for the activated SPCE indicating its high electrocatalytic activity.

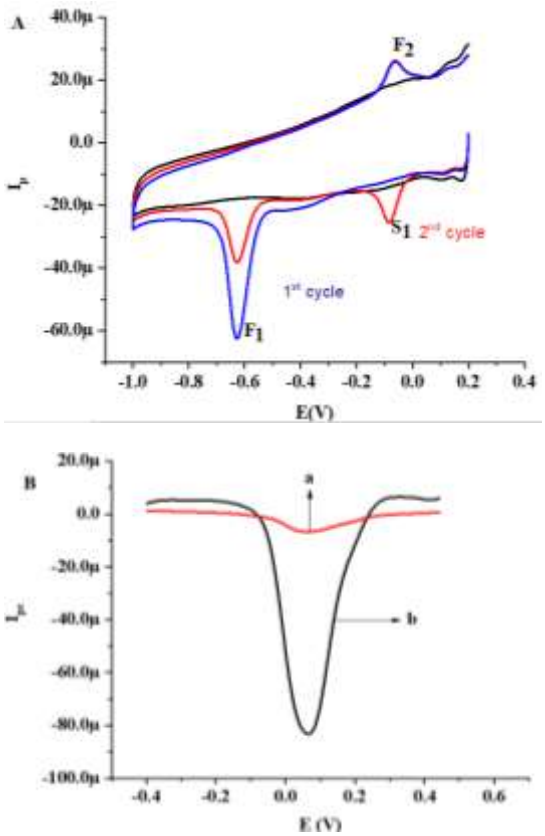

Fig. 1. (A) Cyclic voltammograms of 50 µM CAP at Bare SPCE (black), first cycle (blue), and second cycle at activated-SPCE in 0.1 M PBS at scan rate of 100 mV s^{-1} (B) SWVs of 50 µM CAP in the same solution at bare SPCE (a) and activated-SPCE (b).

3.3. The Effect of pH

The effect of varying the pH on the detection of CAP was investigated in the range of 4.0-8.0, using cyclic voltammetry. It was noted that the peak current of CAP increases with increasing pH from 4.0 to 6.5 which indicates the dependence of the oxidation process on the pH. As displayed in Figure 2, there is a gradual decrease in the peak current after increasing up to pH 6.5; therefore, pH 6.5 was selected as the optimum pH for further analysis. A decrease in the peak current of CAP with increase in pH after 6.5 revealed that the detection of CAP at the activated SPCE is feasible only in a neutral medium.

The peak potential of CAP moves to the negative direction with increase in pH of the electrolyte solution, suggesting the involvement of protons in the redox reaction process. The linear regression equation obtained from the cathodic peak potential vs. pH plot is Epc(V)= −0.05153pH − 0.25276; R^2= 0.99534. The slope 51.53 mV.pH indicates that a reversible redox reaction of CAP at the surface of activated SPCE involves the transfer of an equal number of protons and electrons [30, 31].

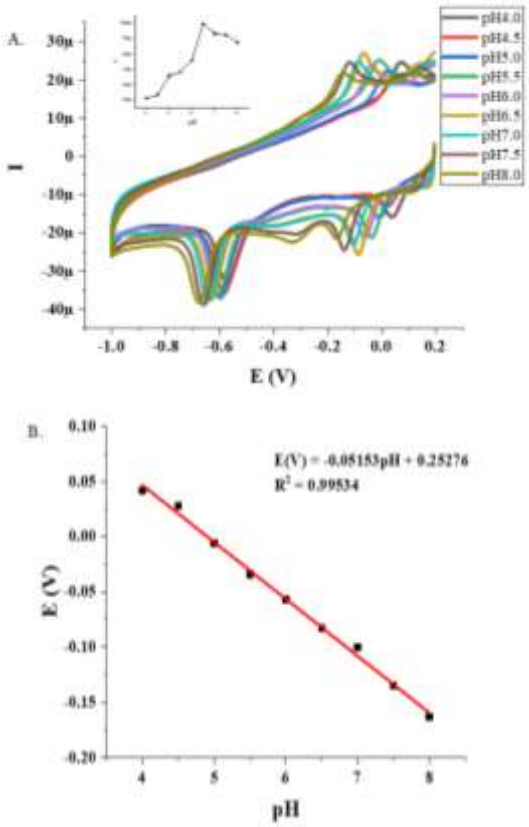

Fig. 2. (A) CV of 50 µM CAP as a function of pH in activated SPCE in PBS of pH 4.0-8.0 with 100 mV s^{-1} scan rate. Inset: plot of peak current vs, pH (B) Plot of peak potentials of 50 µM CAP as a function of pH at activated SPCE in PBS of pH 6.50 with 100 mV s^{-1} scan rate

3.4. The Effect of Scan Rate

The effect of varying the scan rate on the electrochemical property of 50 µM CAP was investigated using cyclic voltammetry (Figure 3) in PBS pH 6.5. Of the three CAP peak currents, the first signal due to the reduction of nitro functional group has a small peak and was not investigated. The plot of the peak current vs. scan rate for the two peak currents are linear in the range 50–275 mV s^{-1} with equations of: I_{pa} (µA) = 0.00285v (mV s^{-1}) +1.175; with R^2 = 0.99342 and I_{pc} (µA) = −0.004887v (mV s^{-1}) + 1.175; with R^2 = 0.99343. There is also a positive peak potential shift with increase in the scan rate. Moreover, the plot of log I_{pc} vs log ν is linear with equation: log I_{pc} (µA) = 0.83171log ν – 0. 84933, R^2 = 0.9919 and gave slope 0.83171 which is close to 1.

Therefore, from the result obtained the oxidation-reduction of CAP at the surface of activated SPCE is principally an adsorption controlled process [31].

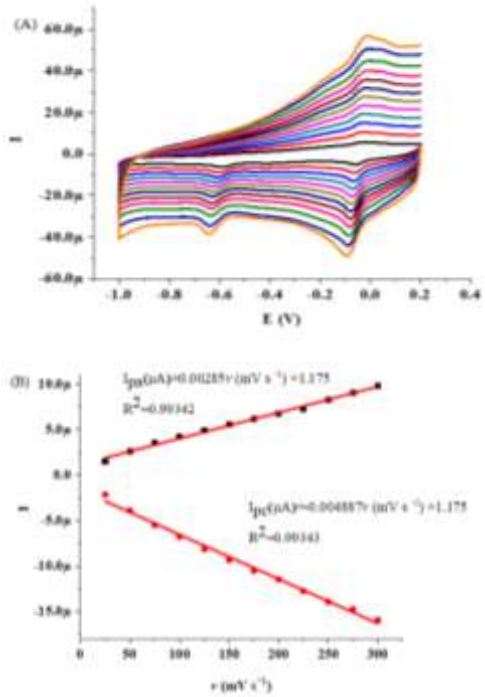

Fig. 3. (A) CVs of 50 µM of CAP at activated SPCE at scan rates of 50–275 mV s^{-1} in PBS pH 6.50 (B) Peak current of CAP vs scan rate

3.5. Optimization of SWV Parameters

The square wave parameters were optimized to obtain the highest peak current signal for determination of CAP. The peak current signal of CAP depends on the values of square wave parameters, and this was studied by varying step potential between 1–15 mV, amplitude between 10–120 mV and frequency between 10–100 Hz ranges. This study was done by varying one parameter while maintaining the other two at constant value. Considering the peak current signals with their peak shape, a step potential of 8 mV, amplitude 90 mV and frequency 30 Hz were selected as the optimized square wave parameters for further analysis.

3.6. The Effect of Accumulation Potential and Time

The effect of varying the accumulation potential on the peak current of CAP was studied in the range 0.0 to −1.0 V with a difference of 0.1 V at an accumulation time of 15 s. The peak current signal increased when the potential was reduced up to −0.8 V, then after the peak current started to decrease (Figure 4 (A)). Therefore, the accumulation potential of −0.8 V was chosen as the optimum potential for further measurements. The effect of accumulation time on the reduction peak current of CAP was also investigated by varying from 15–90 s with a difference of 15 s. As illustrated in Figure 4 (B), the reduction peak current increased with increasing the accumulation time till it reached 60 s, and then a plateau was observed as a result of surface saturation. Therefore, 60 s was selected as the optimal time for the accumulation of CAP at the activated SPCE.

3.7. Interference Study

The influences of potentially interfering substances in the determination of CAP was studied under the optimum conditions. The peak current of a 50 µM CAP was compared with the same CAP solution containing 100 fold concentration of the potential interferents: ascorbic acid, lactose, urea, D-glucose, glycine, *p*-nitrophenol, Zn^{2+}, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Cl^{-} and NO_3^{-} and the result obtained shows that the percent changes in the peak currents were less than 5% for all the studied substances except *p*-nitrophenol. This point out that the activated SPCE exhibited good selectivity and interference from these substances is insignificant, but *p*-nitrophenol must be separated before the determination of CAP.

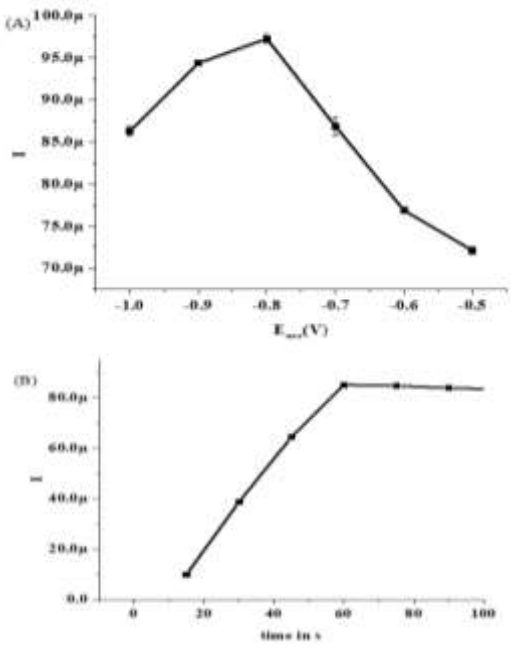

Fig. 4. (A) Current response of 50 µM CAP *vs.* deposition potential (B) Current response of 50 µM CAP *vs.* deposition time.

3.8. Determination of CAP by Square Wave Voltammetric Techniqus

The determination of CAP was performed using the optimized square-wave parameters. Figure 5

shows the SW voltammograms of varying concentrations of CAP in 0.1 M PBS pH 6.5 obtained at the activated-SPCE. The peak current versus concentration plot for CAP is linear within 0.05 to 100 µM range, (Figure 5 (B)) with a linear equation: Ip(µA)= −1.68[CAP](µM) – 3.6 and R^2= 0.99517. The calculated values for quantification and detection limits for the blank measurements (n = 6) were found to be 0.067 µA and 0.02 µA, respectively.

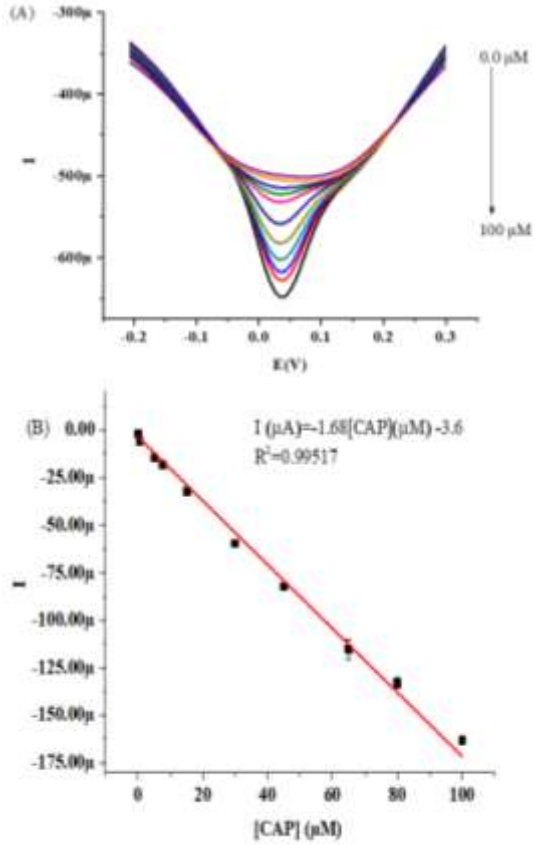

Fig. 5. (A) SWVs for varying concentrations of CAP: 0.0, 0.05, 0.5, 5.0, 7.5, 15, 30, 45, 65, 80 and 100 µM in 0.1 M PBS pH 6.50 at activated SPCE (B) the plot of peak current *vs*. CAP concentration

As shown in the Table 1, the developed electrode has a wider linear range and better sensitivity compared to all modified electrodes except that of graphene oxide hierarchical zinc oxide nanocomposite modified glassy carbon electrode.

3.9. Analytical Application

The practical applicability of the developed sensor was demonstrated by analyzing CAP-eye drop from commercial pharmaceutical products (Table 2) and pasteurized milk sample (Table 3) from the local market. The experimentally detected value of CAP-eye drop was compared with its label, and the result obtained was in good agreement with the described composition. Moreover, the accuracy and reliability of the proposed method was checked by adding CAP standard to both the pharmaceutical product and pasteurized milk sample and an increase in peak current was observed. The percent recovery values were calculated and the results lie between 93.6% and 104.2%, indicating that the effect of the sample matrix is not significant and hence the activated SPCE has excellent potential to be used in real sample analysis.

Table 1. Comparison of the performance of the proposed method with other electrochemical sensors used for the determination of CAP.

Electrodes	Method	Linear Range (µM)	LOD (µM)	Ref.
[a]Gr/CuPc/GCE	DPV	0.01-20	0.027	[31]
[b]EPC/GCE	SWV	0.01-1 and 1-4	0.0029	[30]
[c]GO/ZnO/GCE	DPV	0.2–7.2	0.01	[33]
[d]Z-800/rGO/GCE	DPV	1-180	0.25	[34]
[e]MoS2-IL/GO/GCE	DPV	0.1–400	0.047	[35]
[f] rGO/PdNPs/GCE	DPV	0.05-100	50	[36]
[g]Mn_2O_3 TNS/SPCE	DPV	0.015–1.28 and 1.35–566.3	4.26	[37]
Activated SPCE	SWV	0.05-100	0.02	This Work

[a]Graphene/Copper Phthalocyanine Nanocompositse, [b]exfoliated porous carbon, [c]graphene oxide hierarchical zinc oxide nanocomposite, [d]zeolitic imidazolate framework reduced graphene oxide, [e]de-layered molybdenum disulfide/graphene oxide nanocomposites, [f]palladium nanoparticles decorated reduced graphene oxide, [g]manganese(III) oxide tiny nanostructures screen printed carbon electrodes.

Table 2. Recovery of CAP spiked in CAP-eye drop sample (n=3).

Added (µM)	Found (µM) (±sd)	Recovery (%)
0	15.12±0.26	--
10	26.18±0.32	104.2

Table 3. Detection of CAP in milk products (n=3).

Added (µM)	Found (µM) (±sd)	Recovery (%)
10	9.34±0.065	93.6
20	20.46±0.13	102.3
50	51.55±0.21	103.1

4. CONCLUSION

CAP is an important antibiotic drug that is widely used for both human medication and in animal farms. In the present study, pasteurized milk from the local market and CAP-eye drop samples were

analyzed using the activated SPCE that was prepared electrochemically in a simple way. The SWV study of CAP sample in PBS pH=6.5 gave an excellent result on the activated SPCE compared to the bare one. The cost-effectiveness of the electrode material, simpler electrode modification and working with smaller sample size is another additional advantage of using the SPCE. The developed electrode also shows excellent analytical characteristics such as high sensitivity, repeatability, reproducibility, and stability. The activated SPCE was used to test complex matrixes of pasteurized milk and CAP-eye drop and successful recoveries were obtained for the added CAP standard, which indicate the capability of the system for real sample analysis.

Data Availability

The Microsoft Word data used to support the findings of this study are included within the article and supplementary material.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper."

Supplementary Materials

Picture of IR, SEM, EIS, mechanism of CAP redox reaction, and scheme for activation

REFERENCES

[1] W.F. Bansode. K.R. Singh. and P. Shukla. Chloramphenicol Toxicity: A Review. *J. Med. Med. Sci*. 2 (13) (2011) 1313-1316.

[2] A.Y. Adel. CHLORAMPHENICOL: Relation of Structure to Activity and Toxicity. *Ann. Rev. Pharmacol. Toxicol*. 128 (1998) 83-100.

[3] C.M. Roberts. Antibiotic toxicity, interactions and resistance development. *Periodontology* 2000. 28 (2002) 280–297.

[4] S. Goel. Antibiotics in the Environment: A Review. ACS Symposium Series Emerging Micro-Pollutants in the Environment: Occurrence, *Fate and Distribution*. (2015) 19–42.

[5] P.A. Guy. D. Royer. P. Mottier. E. Gremaud. A. Perisset. and R.H. Stadler. Quantitative determination of chloramphenicol in milk powders by isotope dilution liquid chromatography coupled to tandem mass spectrometry. *J. Chromatogr. A*. 1054 (2004) 365–371.

[6] L.K. Sørensen. T.H. Elbæk. and H. Hansen. Determination of Chloramphenicol in Bovine Milk by Liquid Chromatography/Tandem Mass Spectrometry. *J. AOAC Int*. 86 (2003) 703–706.

[7] X. Wu. X. Tian. L. Xu. J. Li. X. Li. and Y. Wang. Determination of Aflatoxin M1 and Chloramphenicol in Milk Based on Background Fluorescence Quenching Immunochromatographic Assay. *Biomed Res. Int*. (2017) 1–7.

[8] S.-I. Kawano. H.-Y. Hao. Y. Hashi. and J.-M. Lin. Analysis of chloramphenicol in honey by on-line pretreatment liquid chromatography–tandem mass spectrometry. *Chin. Chem. Lett*. 26 (2015) 36–38.

[9] F. Barreto. C. Ribeiro. R.B. Hoff. and T.D. Costa. Determination and confirmation of chloramphenicol in honey, fish and prawns by liquid chromatography–tandem mass spectrometry with minimum sample preparation: validation according to 2002/657/EC Directive. *Food Addit Contama* A. 29 (2012) 550–558.

[10] A. Aresta. D. Bianchi. C. Calvano. and C. Zambonin. Solid phase microextraction—Liquid chromatography (SPME-LC) determination of chloramphenicol in urine and environmental water samples. *J. Pharm. Biomed. Anal.* 53 (2010) 440–444.

[11] A. Gantverg. I. Shishani. and M. Hoffman. Determination of chloramphenicol in animal tissues and urine. *Analytica Chimica Acta*. 483 (2003) 125–135.

[12] M. Rejtharová. and L. Rejthar. Determination of chloramphenicol in urine, feed water, milk and honey samples using molecular imprinted polymer clean-up. *J. Chromatogr. A.* 1216 (2009) 8246–8253.

[13] T.A. Hamoudi. and W.A. Bashir. Spectrophotometric Determination of Chloramphenicol in Pharmaceutical *Preparations. J. Educ. Sci*. 27 (2018) 19–35.

[14] Y. Xie. Q. Hu. M. Zhao. Y. Cheng. Y. Guo. H. Qian. and W. Yao. Simultaneous Determination of Erythromycin, Tetracycline, and Chloramphenicol Residue in Raw Milk by Molecularly Imprinted Polymer Mixed with Solid-Phase Extraction. *Food Anal. Methods*. 11 (2017) 374–381.

[15] B.W. Blais. A. Cunningham. and H. Yamazaki. Novel immunofluorescence capillary electrophoresis assay system for the determination of chloramphenicol in milk. *Food Agric. Immunol*. 6 (1994) 409–417.

[16] H. Tsai. H.C. Hu. C.C. Hsieh. Y.H. Lu. C.H. Chen. and C.B. Fuh. Fluorescence studies of the interaction between chloramphenicol and nitrogen-doped graphene quantum dots and determination of chloramphenicol in chicken *feed. J. Chin. Chem. Soc*. 67 (2019) 152–159.

[17] X.-D. Pan. P.-G. Wu. W. Jiang. and B.-J. Ma. Determination of chloramphenicol, thiamphenicol, and florfenicol in fish muscle by matrix solid-phase dispersion extraction (MSPD) and ultra-high pressure liquid chromatography tandem mass spectrometry. *Food Control*. 52 (2015) 34–38.

[18] E. Alechaga. E. Moyano. and M.T. Galceran. Ultra-high performance liquid chromatography-tandem mass spectrometry for the analysis of phenicol drugs and florfenicol-amine in foods. *Analyst*. 137 (2012) 2486.

[19] A. Forti. G. Campana. A. Simonella. M. Multari. and G. Scortichini. Determination of chloramphenicol in honey by liquid chromatography–tandem mass spectrometry. *Analytica Chimica. Acta*. 529 (2005) 257–263.

[20] M. Ashton. HPLC Determination of Chloramphenicol, Chloramphenicol Monosuccinate and Chloramphenicol Glucuronide in Biological Matrices. *J. Liq. Chromatogr*. 12 (1989) 1719–1732.

[21] H.-Y. Shen. and H.-L. Jiang. Screening, determination and confirmation of chloramphenicol in seafood, meat and honey using ELISA, HPLC–UVD, GC–ECD, GC–MS–EI–SIM and GCMS–NCI–SIM methods. *Analytica Chimica Acta*. 535 (2005) 33–41.

[22] T. Menanteau. E. Levillain. and T. Breton. Electrografting via Diazonium Chemistry: From Multilayer to Monolayer Using Radical Scavenger. *Chem. Mater*. 25 (2013) 2905–2909.

[23] C.A. Richard. N.B. Philip. L. Jacek. Electrochemistry of Carbon Electrodes. *Adv. Electrochem. Sci. Eng*. (2015) 19-35.

[24] H. Beitollahi. S.Z. Mohammadi. M. Safaei. and S. Tajik. Applications of electrochemical sensors and biosensors based on modified screen-printed electrodes: a review. *Anal. Method*s. 12 (2020) 1547–1560.

[25] H.M. Mohamed. Screen-printed disposable electrodes: Pharmaceutical applications and recent developments. *Trends Analyt Chem*. 82 (2016) 1–11.

[26] A. Ambrosi. R. Antiochia. L. Campanella. R. Dragone. and I. Lavagnini. Electrochemical determination of pharmaceuticals in spiked water samples. *J. Hazard. Mater*. 122 (2005) 219–225.

[27] T. Gan. J. Li. H. Li. Y. Liu. and Z. Xu. Synthesis of Au nanorod-embedded and graphene oxide-wrapped microporous ZIF-8 with high electrocatalytic activity for the sensing of pesticides. *Nanoscale*. 11 (2019) 7839–7849.

[28] M.M. Athar. and M. Zaib. Electrochemical Evaluation of Phanerocheaete Chrysosporium Based Carbon Paste Electrode with Potassium Ferricyanide Redox System. *Int. J. Electrochem. Sci*. 10 (2015) 6690 – 6702.

[29] B.V.M. Zanoni. V.L.I. Rosa. R.C. Pesquero. and R.N. Stradiotto. Electrochemical Behavior of a Nitrobenzenesulfonyl Derivative of Aniline in Aqueous Solution. *J. Braz. Chem. Soc*. 8 (1997) 223-227.

[30] N. Sebastian. W.-C. Yu. and D. Balram. Electrochemical detection of an antibiotic drug chloramphenicol based on a graphene oxide/hierarchical zinc oxide nanocomposite. *Inorg. Chem. Front*. 6 (2019) 82–93.

[31] L. Xiao. R. Xu. Q. Yuan. and F. Wang. Highly sensitive electrochemical sensor for chloramphenicol based on MOF derived exfoliated porous carbon. *Talanta*. 167 (2017) 39–43.

[32] B. Uslu. B.D. Topal. and S.A. Ozkan. Electroanalytical investigation and determination of pefloxacin in pharmaceuticals and serum at boron-doped diamond and glassy carbon electrodes. *Talanta*. 74 (2015) 1191–1200.

[33] Y.-M. Xia. W. Zhang. M.-Y. Li. M. Xia. L.-J. Zou. and W.-W. Gao. Effective Electrochemical Determination of Chloramphenicol and Florfenicol Based on Graphene/Copper Phthalocyanine Nanocomposites Modified Glassy Carbon Electrode. *J. Electrochem. Soc*. 166 (2019) B654-B663.

[34] K. Kor. and K. Zarei. Electrochemical determination of chloramphenicol on glassy carbon electrode modified with multi-walled carbon nanotube–cetyltrimethylammonium bromide–poly(diphenylamine). *J. Electroanal. Chem.* 733 (2014) 39–46.

[35] Y. Yuan. X. Xu. J. Xia. F. Zhang. Z. Wang. and Q. Liu. A hybrid material composed of reduced graphene oxide and porous carbon prepared by carbonization of a zeolitic imidazolate framework (type ZIF-8) for voltammetric determination of chloramphenicol. *Microchimica Acta*. 186 (2019) 1-8.

[36] T. Sun. H. Pan. Y. Mei. P. Zhang. D. Zeng. X. Liu. S. Rong. and D. Chang. Electrochemical sensor sensitive detection of chloramphenicol based on ionic-liquid-assisted synthesis of de-layered molybdenum disulfide/graphene oxide nanocomposites. *J. Appl. Electrochem*. 49 (2018) 261–270.

[37] W. Yi. Z. Li. C. Dong. H.-W. Li. and J. Li. Electrochemical detection of chloramphenicol using palladium nanoparticles decorated reduced graphene oxide. *Microchem. J.* 148 (2019) 774–783.

تعیین کلرامفنیکل در شیر و قطره چشمی با استفاده از الکترود کربن صفحه چاپی فعال‌شده

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چکیده

یک روش تجزیه ای که ارائه دهنده ی یک پاسخ سریع به همراه یک دستگاه ارزان قیمت و روش آماده سازی راحتی باشد، مطلوب تجزیه های علمی می باشد. حسگرهای الکتروشیمیایی که این شرایط را برای نمونه های مختلف توسط مواد مختلف الکترود فراهم می کند، مناسب می باشند. شناسایی کلرامفنیکل در محصولات کشاورزی و نمونه های دارویی با استفاده از مواد الکترودی ارزان قیمت به دلیل کاربرد وسیعشان در کشاورزی بسیار مورد نیاز است. در این مطالعه یک SPCE فعال مقرون به صرفه به طریق الکتروشیمیایی تهیه و برای تعیین کلرامفنیکل در قطره چشمی و شیر پاستوریزه بکار رفت. فعالسازی SPCE یک راست با استفاده از تکنیک LSV چرخه ای در حضور KOH ۰٫۵ M صورت گرفت. تصویر برداری سطح، مطالعات اسپکتروسکوپی و تجزیه های الکتروشیمیایی بیانگر تشکیل موثر گروه های عاملی جدید در طی فرایند فعالسازی بود. SPCE فعال شده پیک جریان بالایی را برای کلرامفنیکل در خلال مطالعات CV و SWV با استفاده از محلول بافر فسفات pH=۶٫۵ در مقایسه با الکترود بدون پوشش از خود نشان داد. در شرایط بهینه یک منحنی کالیبراسیون خطی در رنج ۱۰۰ μM– ۰٫۰۵ با حد تشخیص کوچکی در حد ۲۰ μM بدست آمد. علاوه بر حساسیت بالا، پایداری و بازیابی خوب، تکرارپذیری عالی نیز الکترود پیشنهادی برای تجزیه نمونه های حقیقی از خود نشان داده است.

واژه‌های کلیدی

کلرامفنیکل؛ الکترود کربن صفحه چاپی؛ الکتروشیمیایی؛ پایدار؛ فعال‌شده.