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ORIGINAL PAPER

Voltammetric determination of florfenicol by using poly(3-methylthiophene) modified glassy carbon electrode

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Abstract

In this study, poly(3-methylthiophene) modified electrode as a voltammetric sensor was developed for the detection of florfenicol (FF). Firstly, for the modification of glassy carbon electrode (GCE), 3-methylthiophene (3-MTF) was polymerized in acetonitrile (AcN) containing tetrabutylammonium tetrafluoroborate (TBATFB) by cyclic voltammetry (CV) method. Then, in order to determine the florfenicol sensor property of 3-MTF modified GCE, parameters such as electrolyte type and electrolyte pH, scan rate, film thickness, pulse amplitude, and pulse width were investigated by using differential pulse voltammetry method (DPV). When the florfenicol responses of the modified electrode were compared to the unmodified GCE responses, it was found that the florfenicol selectivity, sensitivity, and response stability of the modified electrode were significantly increased. A linear calibration plot was obtained for florfenicol in the concentration range of 0.1–1.0 mM. From the linear calibration curve, the correlation coefficient (R^2 value), determination limit (LOD), and quantitation limit (LOQ) were calculated as 0.999, 0.0399 mM, and 0.1197 mM, respectively. In addition, analytical application of the developed sensor for the determination of florfenicol was carried out in red and chicken meat samples. The recovery efficiency for red and chicken meat samples was obtained from 90.07 to 111.92% by using 3-MTF modified GCE. As a result, an electrochemical sensor was developed for the florfenicol detection which is fast, simple, low cost, 98.72% reproducible, stable, sensitive, and selective.

Keywords Florfenicol · Antibiotic · Cyclic voltammetry · Differential pulse voltammetry · Sensor · 3-Methylthiophene

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Introduction

Antibiotics are used for the treatment, prevention, and control of diseases, as well as for accelerating body development and increasing the efficiency of feed used in animals. They have been used frequently to prevent bacterial infection since the discovery of penicillin in 1941 [1]. A new era in breeding began with the introduction of antibiotics in the feed of livestock in the 1950s. However, foods of animal origin are a suitable medium for many microorganisms with human pathogens to grow. Pathogenic bacteria in meat products can pass to people after consumption and become a cause of disease. In people who consume foods containing drug residues, allergic reactions, toxic symptoms, reproductive disorders, obesity, changes in the intestinal flora (bloody diarrhoea that mimics dysentery), and the development of resistant bacteria can be observed. After use, drugs, metabolites, degradation products, free or bound drugs, or chemicals that accumulate or stored in the tissues and organs of animals or edible products such as meat, milk are all characterized as residuals [2–4]. Drug residues can lead to significant public health adverse effects such as hypersensitivity reactions, cancer, deterioration of the normal intestinal flora, reproductive difficulties, and bacterial resistance [5]. The residuals of antibiotics used in animal breeding cause serious hazards to human health. This seriously risks drug residues in animal-based foods, which are an indispensable source of protein for human consumption. Therefore, the health of people who consume such products is under threat. The risk of antibiotic residues and the use of antibiotics in cultivation cause serious hazards to human health. Drugs taken accumulate in various organs and tissues, primarily kidney and liver. It has been demonstrated by scientific data that drug residues lead to serious public health problems, including children and the elderly, entering the food chain, from mild allergy to carcinogenic, teratogenic, or mutagenic effects, and even death as in penicillins [6–8].

Organizations such as FAO (Food and Agriculture Organization) and WHO (World Health Organization) make it necessary to comply with the legal waiting periods specific to each drug after drug use in order to minimize such health problems. However, the long waiting times required for the drug to be completely removed from the body and the disposal of products such as meat, milk, and eggs that contain residues during this period are economically inconvenient to the grower, and therefore, it makes it difficult to comply with the legal waiting periods. For this purpose, the European Union (EU) has set up the directive-related directives within the scope of "traceability" in order to provide food safety from farm to table and set the necessary limits for foods for many drugs [9].

Analysis of drug and drug residue plays important roles in drug quality control and has a great impact on public health [10–16]. In the literature, it was emphasized that veterinary drugs are found as residues in animal tissues and there are important risks when animal foods containing residues turn into human food as a ring of the food chain. Highly accurate and precise methods have been developed for the analysis of the antibiotics and metabolites used for healing and preserving residues in various tissues and biological fluids of living things and some nutrients such as milk, eggs and honey [17–21]. Due to all these features,

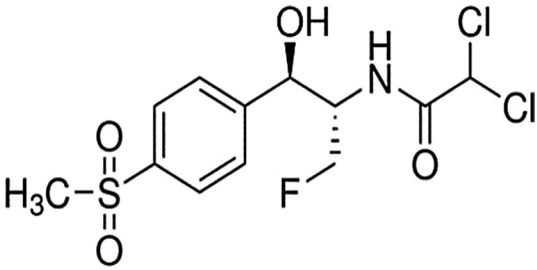
determination of residual antibiotics in foods is very important. For this purpose, there are many methods in the literature for the detection of residuals of the antibiotics in foods. However, most of these methods have disadvantages such as high cost, long time, and complicated processes. Methods such as high-performance liquid chromatography (HPLC) [22–29], high-performance liquid chromatography/mass spectrometry (HPLC/MS) [30], chemiluminescence [31], and liquid chromatography/mass spectrometry LC/MS [32, 33], which are frequently used for the determination of residuals in foods, are highly sensitive but costly and require advanced and specialized equipment [22, 23]. Therefore, a simple, sensitive, and accurate method for the determination of active ingredient is very important in food industry, pharmaceutical, and clinical investigations.

Electrochemical methods developed in recent years have made great progress in overcoming the above-mentioned disadvantages. In addition, electrochemical methods are known for their simplicity, reliability, faster response and are practical and sensitive. It provides more precision with easy portable instrumentation, cheap methodology, and selectivity [34, 35]. In order to prepare electrochemical sensors, conductive or non-conductive polymeric structures are synthesized either electrochemically or chemically. These polymers are very important in that they have conductive, porous, and selective properties. Electrochemically modified electrodes are very useful for environmental, clinical, and biotechnological analyses. They are designed to provide desired selective sites toward analytes. Organic conducting polymers are not only interesting from this point of view but are also important for chemical modification of electrode surfaces for sensitive and selective electrochemical measurements. Numerous polymer modified electrode studies in the field of biosensors and chemical sensors have attracted great attention due to their wide application [35–39].

In order to determine the active ingredient of drugs, studies on the preparation of new generation electrodes are increasingly common because they are fast, practical, sensitive, and reproducible [40–42]. Kutluay Baytak and Aslanoğlu [40] performed capsaicin determination in pepper samples using carbon nanotube and ruthenium-based modified electrode. Burç et al. [41] developed a polyimide-MWCNT composite membrane-based voltammetric sensor for the fast and high-precision detection of paracetamol. Güngör et al. performed bupivacaine, a local anesthetic, using differential pulse voltammetry using polyimide membrane-based electrodes [42]. Electrodes modified with 3-MTF were used for the determination of inorganic anions [43, 44] and some biologically important compounds [45, 46]. Electrochemical sensor studies are also available for the determination of antibiotics in foods [47–52]. Huet et al. [51] have developed an optical surface plasmon resonance biosensor for the determination of quinolones in eggs, fish, and poultry meat.

Fenicols, a broad spectrum antibiotic group, have effective side effects on human health. Application of antibiotics to animals causes the bactericidal and bacteriostatic components to enter animal tissues and products such as milk, meat, and honey. In this way, antibiotic-resistant bacterial strains, which are potential human health problems, appear [53, 54]. One of the antibiotics used in animals is FF in the fenicols group. FF, the formula of which is shown in Scheme 1, is one of the antibiotics frequently used in

Scheme 1 Molecular formula of florfenicol



cattle breeding and used in the treatment of respiratory diseases that cause great economic losses [55].

Florfenicol (Scheme 1) is a synthetic and long-acting antibacterial drug. It is used only in veterinary field. It is bacteriostatic effective. It is undisputed due to the fact that florfenicol remains ionized at pH levels in the range of 3–9, is poorly dissolved in aqueous solutions, and is well dispersed in tissues due to its lipophilic property, broad spectrum of action, therapeutic efficacy, low toxicity risk, and efficacy in the treatment of respiratory and digestive system infections in animals with food value. It has become one of the important veterinary drugs [55]. As a result of examining the effects of florfenicol on the electrocardiogram, it has been explained that this drug may cause undesirable effects on the cardiovascular system. Monitoring the residues level is an important and critical part of quality control programs. Therefore, determination of the florfenicol residue is very important because of cause a health risk to consumers [53, 54].

In this study, a fast, low-cost, effortlessly prepared, sensitive, stable voltammetric sensor, the preparation of which is shown in Fig. 1, has been developed, which can be used instead of the laborious, complex, costly chromatographic techniques used in the determination of antibiotics. For this firstly, the 3-MTF monomer was polymerized with electrochemical polymerization on GCE by CV method. Electropolymerization of 3-MTF was performed on the surface of a GCE using the cyclic voltammetric method in the potential range of −0.8 to 1.0 V. Using GCE modified by electropolymerization, the most appropriate type of electrolyte and pH of electrolyte, scanning speed, film thickness, pulse amplitude, and pulse width parameters were determined by DPV method. Secondly, it was investigated whether the responses obtained increased linearly with the analyte concentration. Finally, analytical applications have been tested in red and chicken meat samples in order to determine whether the developed sensor can be applied to real samples and whether the matrix effect will cause any passivation or interference effect. Therefore, the developed voltammetric method is very fast, easy to prepare, selective, and sensitive for the determination of residual FF in foodstuffs.

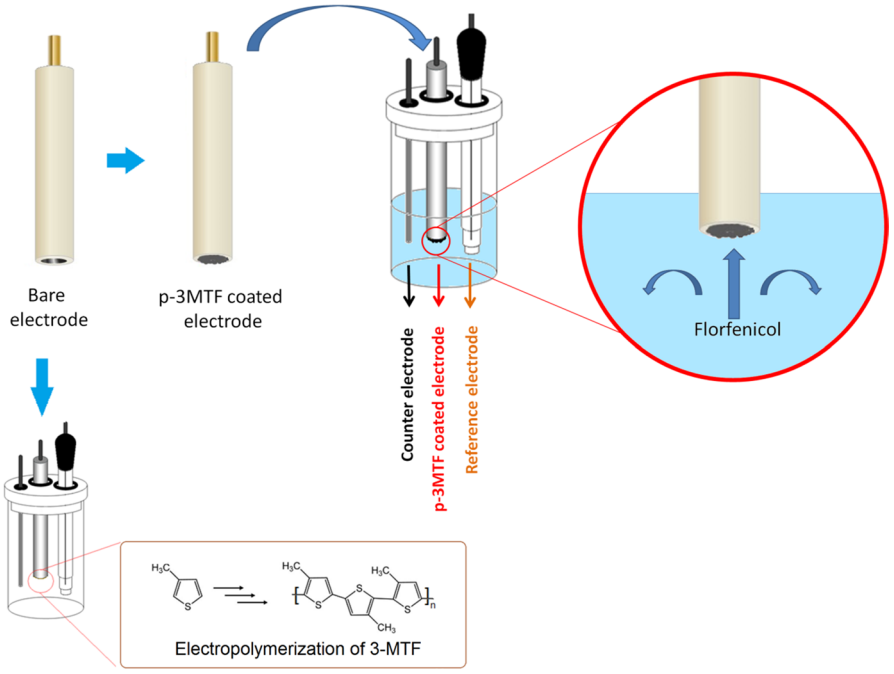


Fig. 1 Preparation of FF sensor

Experimental

Materials and methods

The electrochemical behavior of the FF was investigated using two different voltammetric techniques such as CV and DPV. CV was used for preliminary studies, such as the polymerization of bare GCE with 3-MTF and determining of redox potential of FF. Then, DPV was used for optimization of electrochemical parameters.

3-MTF, TBATFB, Sigma-Aldrich, was used as monomer in electropolymerization; ether, AcN, dimethyl formamide (DMF), H_2SO_4, HNO_3, Tris, Na_2SO_4, Na_2HPO_4, PBS, NaCl, $NaClO_4$, KNO_3, CH_3COONa were purchased from Merck Chemical. "Florkem" drug was purchased at the pharmacy and, after purification, was used as a source of florfenicol.

All voltammetric measurements were performed at room temperature by using bare and 3-MTF modified GCE as the working electrode, an Ag/AgCl/3 M KCl electrode as the reference electrode, and a Pt wire coil as the counter electrode. A Jenway 3010 pH meter was used for pH measurements. DPV and CV experiments were carried out with a BAS 100B (Bioanalytical Systems, Inc.) electrochemical analyzer. The surface of the GCE was prepared prior to modification by polishing with aqueous alumina slurries on a metallographic polishing cloth with a successive reduction in particle size (1–0.3 μm). The remaining particles on the surface were removed in 0.1 M H_2SO_4 in an ultrasonic bath (Branson model 3510) for about 1 min and

dried in air. The pH of the prepared solutions was measured with a Thermo Scientific STAR A-111 pH-meter. The pH meter was calibrated using standard buffers (pH = 4.00, pH = 7.00 and pH = 10.00) from Merck. Weightlab Instrument WSA-224 model scale was used to weigh chemical substances. All aqueous solutions were prepared with distilled water from Millipore brand Elix 20. Aqueous solutions of florfenicol were prepared fresh at the time of experiments in sodium sulfate solution (pH = 4.5).

Preparation of monomer solution

The monomer solution was prepared by dissolving the appropriate amount of 3-MTF monomer in AcN containing 0.1 M TBATFB.

Purification of the FF from the "Florkem" drug

The "Florkem" is a liquid drug. This drug was brought to the form of cream with water; then, it was taken into a separatory funnel. After ethyl acetate was added on it, it was shaken in the shaker for 5 min. Meanwhile, the FF in the water phase switched to the ethyl acetate phase. The water phase was evacuated from the separatory funnel; then, the ethyl acetate phase was removed from the separatory funnel and dry $MgSO_4$ was added thereto. The mixture was then filtered through filter paper, and the residue was washed with ether. Excess solvent was boiled off. The hot solution was allowed to cool (crystallize) under room conditions. The crystals are divided into two as large and powdered and used to collect large FF crystals. The chemical structure of the obtained FF crystals was analyzed by the Fourier transform infrared spectroscopy (FTIR).

The FTIR image of the purified FF (Fig. 2) was compared with the FF image in the literature [56]. According to FTIR spectra in Fig. 2 and FTIR spectra of FF in the literature, we have obtained the florfenicol from the drug proved to be completely pure.

Preparation of standard FF solution

FF antibiotic was obtained by purification from the drug "Florkem" and used. The FF stock solution was prepared by dissolving the appropriate amount of crystals purified in AcN.

Preparation of red and white meat samples

Three different red meat and white meat (chicken meat) samples taken from the market were passed through rondo and cut into small pieces. Then, approximately 3-g samples were taken from red meat and white meat, and they were worked in 3 parallel ways. By mixing 215 mL acetonitrile and 35 mL ultrapure water, a 250 mL solution was prepared and 30 mL of this solution was added to each sample. Then, after the samples were shaken on the shaker for 30 min with their mouths closed,

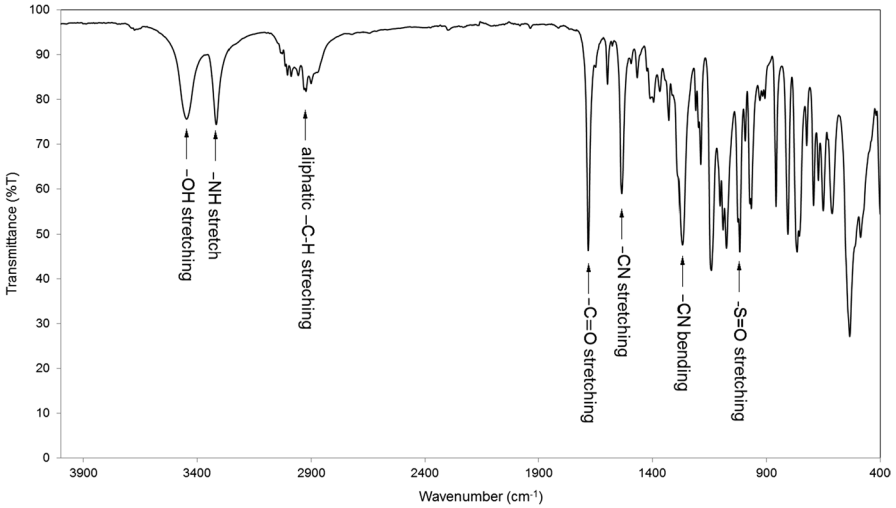


Fig. 2 FTIR spectra of purified FF in this study

they were filtered through filter paper and the filtrate was added to 30 mL by adding AcN-H_2O solution. The 0.5 mL portions taken from this solution were completed to 5.0 mL with a 0.1 M Na_2SO_4 solution, and differential pulse voltammograms were taken at the pre-determined optimum conditions.

Results and discussion

Optimization of the polymerization conditions

Electropolymerization of 3-MTF

3-MTF monomer solution in AcN containing 0.1 M TBATFB was prepared, and the polymer films were synthesized with polymerization of 3-MTF by using CV method in the range of potential (−800 to 1000) mV at different segments (3 and 4) on bare GCE in 0.1 M PBS pH 7.0.

With the electrochemical polymerization of 3-MTF, a conductive and selective film structure is provided on the glassy carbon electrode surface. Electrochemical polymerization of 3-MTF is carried out by a 6-step mechanism [57]. In step 1, oxidation of the 3-MTF monomer and radical cation formation take place. In the second step, two radical cations combine to form a dimeric cation. In step 3, this dimeric cation forms stable dimer by losing two protons. In steps 4–6, polymer formation is shown by oxidizing the dimer and continuing the reaction [57].

When CVs of background solutions without 3-MTF (Fig. 3a) and containing 3-MTF (Fig. 3b) are compared, it is understood that 3-MTF at about −0.25 V potential is oxidized and polymerized, and the polymer film becomes thicker as the number of cycles increases.

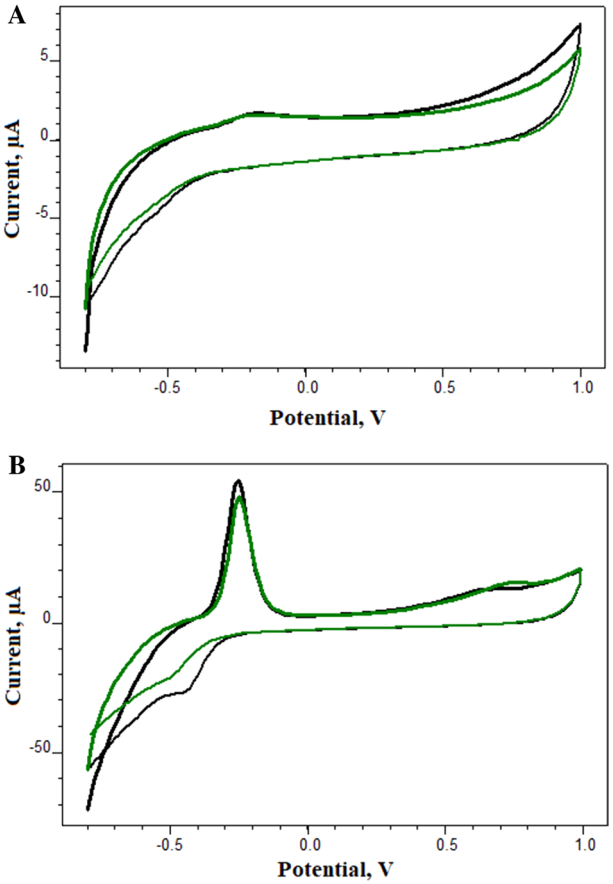


Fig. 3 Cyclic voltammograms of background solution (**a**), of 100 mM 3-MTF in background solution (**b**) on bare GCE

The effect of electrode modification on FF DPV response was examined. Comparing the electrochemical responses of FF on the bare GCE (Fig. 4a) and the *p* (3-MTF) modified GCE electrode (Fig. 4b), it was observed that the FF peak current on the modified electrode increased significantly (Fig. 4a). In addition, it was understood from the voltammograms that the current increased significantly in proportion to the increasing FF concentration. However, as shown in Fig. 4b, the increase in FF concentration on the bare electrode could not be distinguished very well in voltammograms. From here, it has been understood that by using the electrode modified with conductive 3-MTF polymer, a much lower detection limit can be achieved for the FF antibiotic than for the bare electrode.

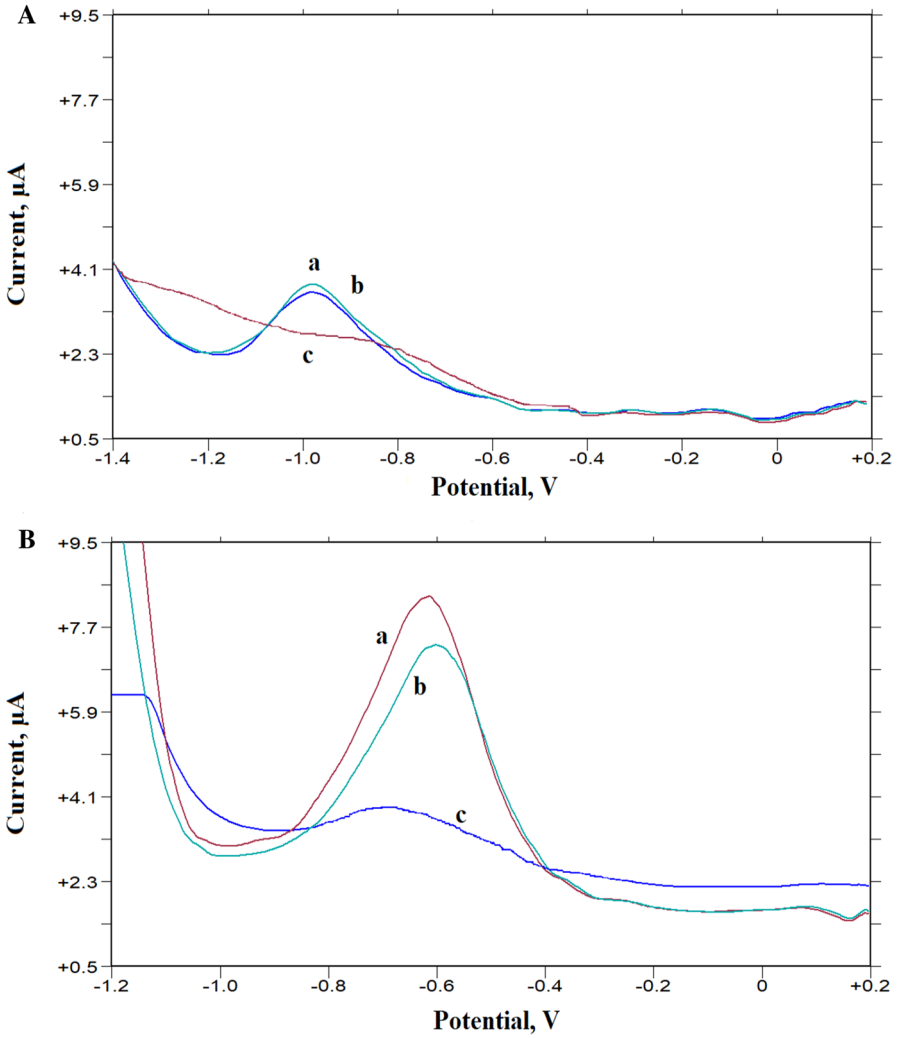


Fig. 4 Cyclic voltammograms of 0.875 mM FF (**a**), 0.491 mM FF (**b**), and background (**c**) on bare GCE (**a**), on *p*(3-MTF) coated GCE (**b**)

The effect of monomer concentration on electropolymerization of 3-MTF

To determine the appropriate monomer concentration, 100, 150, 175, 200, 225, and 250 mM 3-MTF solutions were prepared in AcN, and DPV measurements were taken in 0.491 mM FF solution. Obtained voltammograms are given in Fig. 5 and the concentration–current relationship in Fig. 5 inset. According to the results, it was understood that the most suitable concentration was 200 mM.

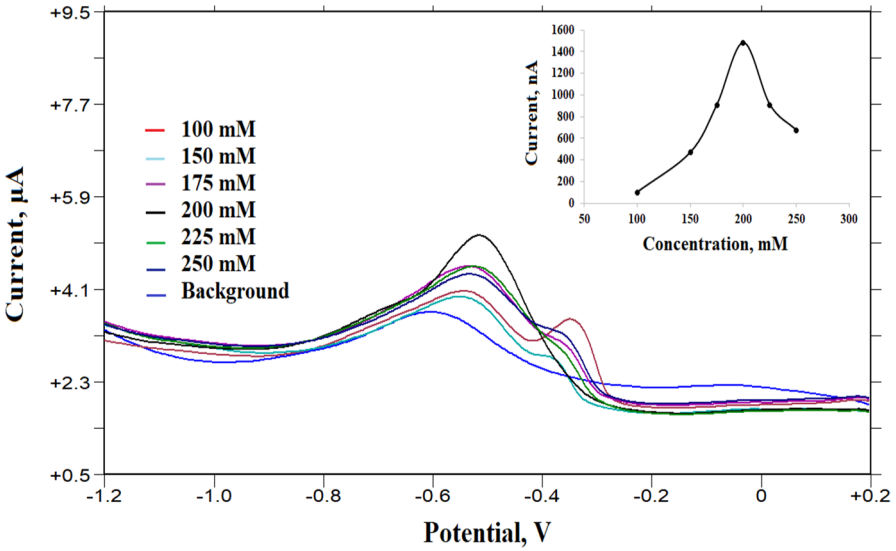


Fig. 5 Effect on FF pulse voltammograms of 3-MTF monomer concentration, the 3-MTFconcentration–current relationship graph (inset)

The effect of segment number on electropolymerization of 3-MTF

In the present work, the film thickness was controlled by adjusting the number of segments during the electropolymerization process using the CV method. Bare GCE was polymerized with five different segments (2, 4, 6, 8, and 10) to determine the optimum polymer film thickness. Segment is half cycle, and as the segment number increased, film thickness increased too. To find the optimum film thickness, we were used different segment numbers in the developing FF sensor. Prepared polymer film-coated GCEs were used for DPV measurement of FF. At the end of this study, as shown in Fig. 6, appropriate polymer thickness was determined as 4 segments.

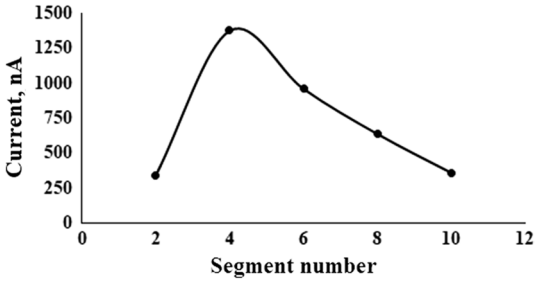


Fig. 6 Effect of the segment number in electropolymerization of 3-MTF on FF DPV response

The effect of the scan rate on electropolymerization of 3-MTF

The effect of the scan rate was investigated in the range of 100–220 mV/s. From Fig. 7, it was clearly observed that best of the DPV response was occurred in the 120 mV/s scan rate.

Electrocatalytic activity of *p* (3-MTF)

Electrocatalytic activity of poly-3-MTF modified GCE electrode, performed in AcN environment of 200 mM 3-MTF, 4 segments thick, with a scan rate of 120 mV/s, 6 mM $K_3[Fe(CN)_6]$, was studied in 1 M KNO_3 using the CV method in the potential range (800 to −200) mV (Fig. 8). As shown in Fig. 8a, CV peaks of bare GCE are stable because the oxidation–reduction reaction of $K_3[Fe(CN)_6]$ is reversible. When compared to the electrocatalytic activity of the modified electrode of bare GCEs in Fig. 8c, the results showed that the electrocatalytic activity of the easily prepared poly-3-MTF modified electrode (Fig. 8b) was quite good.

Optimization of FF analysis parameters

Electroanalytical procedure was developed for determination of FF using DPV. The present study was carried out at experimental conditions pulse width, 50 ms; pulse amplitude, 50 mV; sample width, 20 ms and pulse period, 200 ms, values. The optimization of experimental parameters was done by using DPV method. Differential pulse voltammograms were recorded between 0.0 and + 0.8 V under optimized instrumental parameters.

The effect of electrolyte type and pH

To determine the optimum electrolyte type for the determination of florphenicol, tris, Na_2SO_4, Na_2HPO_4, phosphate-buffered saline buffer (PBS), NaCl, $NaClO_4$, KNO_3, CH_3COONa electrolytes were used. The effect of the electrolyte types on the FF reduction peak current is shown in Fig. 9a. When the voltammograms were examined, it was observed that highest peak current was obtained in Na_2SO_4.

Voltammograms were taken to determine the pH of the Na_2SO_4 solution selected as the working electrolyte. It was worked on poly-3-MTF modified GCE, which was

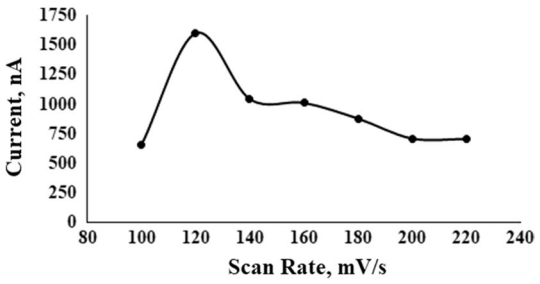


Fig. 7 Effect of scan rate on electropolymerization of 3-MTF

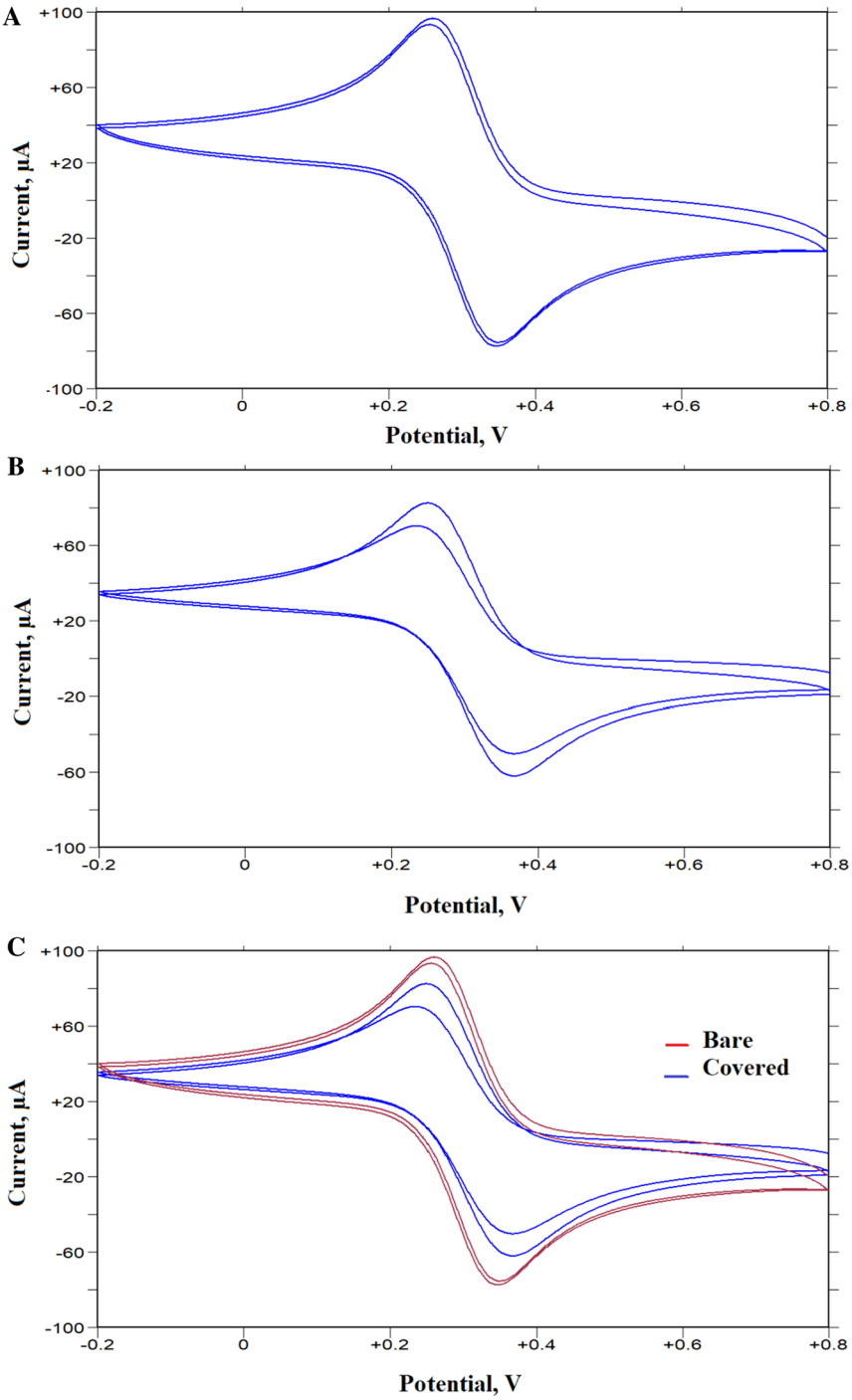


Fig. 8 Cyclic voltammograms of 6 mM $K_3[Fe(CN)_6]$ in 1 M KNO_3 **a** on bare GCE, **b** on 3-MTF Modified GCE **c** on bare and 3-MTF modified GCE overlap

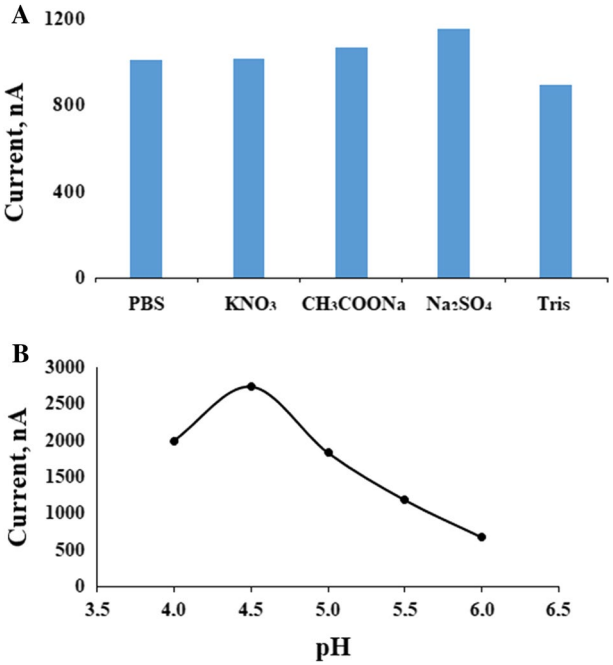


Fig. 9 Effect of the electrolyte type (**a**), electrolyte (Na_2SO_4) pH (**b**) on FF electrochemical signal

obtained under optimum conditions, at pH values of 4.00, 4.50, 5.00, 5.50, and 6.00, and Fig. 9b shows that the most suitable electrolyte pH is 4.50.

The effect of scan rate

The influence of scan rate on the peak current of FF in Na_2SO_4 at pH 4.50 was studied by DPV in the range of 20–100 mV/s (Fig. 10). The results indicated that the peak current was increased up to 60 mV/s and then decreased. Therefore, it was decided to use a scan rate of 60 mV / s in subsequent studies.

It also appears to give a fast and distinct signal with 3-MTF modified GCE for FF even at different scan rates of 20, 40, 60, 80, and 100 mV/s. It is seen that the determination time of the prepared electrode is quite low.

The effect of FF concentrations

DPV voltammograms of different concentrations (0.1, 0.3, 0.6, 0.8, and 1.0 mM) of FF under the optimal experimental conditions are shown in Fig. 11. The peak currents increased with the increment of the concentration of FF. The electrochemical performance and selectivity of the present modified electrode provide a sensitive determination of FF in the linear range of 0.1–1.0 mM with 0.0399 mM limit of detection. Limit of detection was calculated with LOD = 3S/m equation

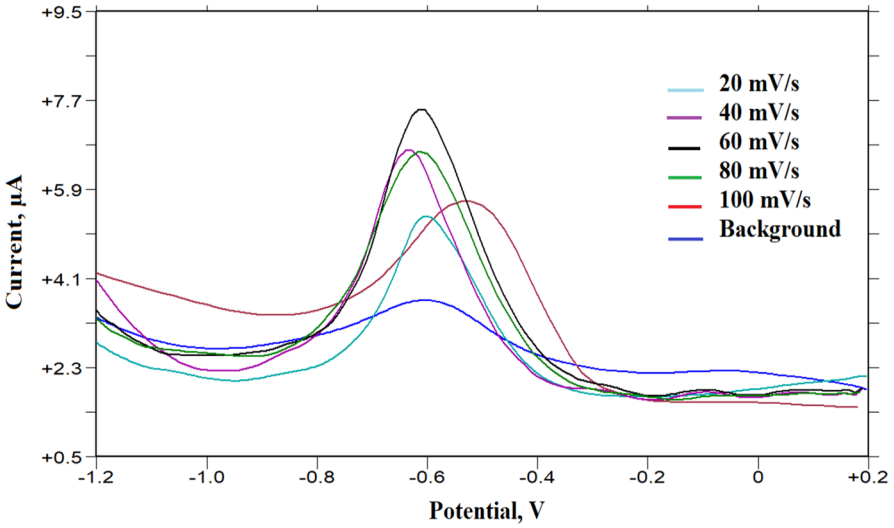


Fig. 10 DPV voltammograms of 0.491 mM FF in Na_2SO_4 at different scanning rates on 3-MTF modified GCE

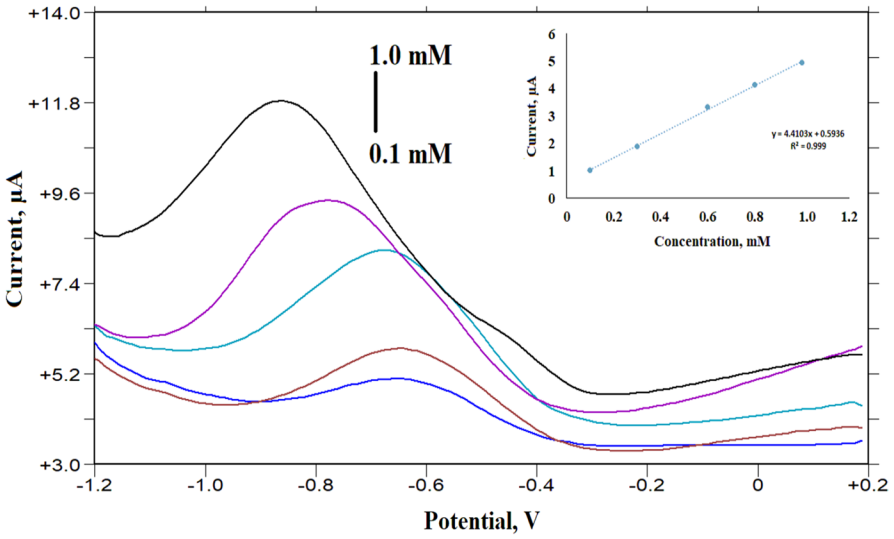


Fig. 11 Differential pulse voltammograms of 0.1, 0.3, 0.6, 0.8, and 1.0 mM FF, calibration curve (inset)

from the calibration curve (Fig. 11 inset) coefficients (S is the standard; m is the slope of the calibration curve).

The developed electrochemical sensor has linear response to FF in the range of the detection limit of 0.0399 mM and correlation coefficient of 0.999.

The effect of reproducibility

To test the stability of the method developed for FF determination, the electrode was modified 10 times and voltammograms were taken by immersed in 0.1 M Na_2SO_4 containing 0.5 mM FF (Fig. 12). The reproducibility of the voltammetric responses obtained with ten measurements by using modified electrode shows that stability of present method is very good. On the other hand, given the standard deviation (0.06) and % relative standard deviation, %RSD, (1.28) calculated from the bar graph in Fig. 12 (inset), the method proved to be reproducible, highly stable, and highly accurate (98.72%).

Florfenicol determination in red and chicken meat samples

The applicability to the real sample of the development sensor was investigated by determination of FF in two different type meat samples (red meat samples purchased from three different markets and three different brands of chicken meat samples). Just prior to analysis, appropriate amounts were taken from the solution mentioned above and analyzed by diluting two fold. The standard addition method was used for analysis of the meat samples, and then, recovery efficiencies were calculated using from peak current values (Tables 1, 2).

The determination of FF in red and chicken meat samples was carried out using DPV method. The recovery efficiencies were obtained for the FF determination in red and chicken meat samples using the *p*(3-MTF)/GCE in 0.1 M Na_2SO_4, pH 4.5. Developed sensor was successfully applied to the red and chicken meat samples, and

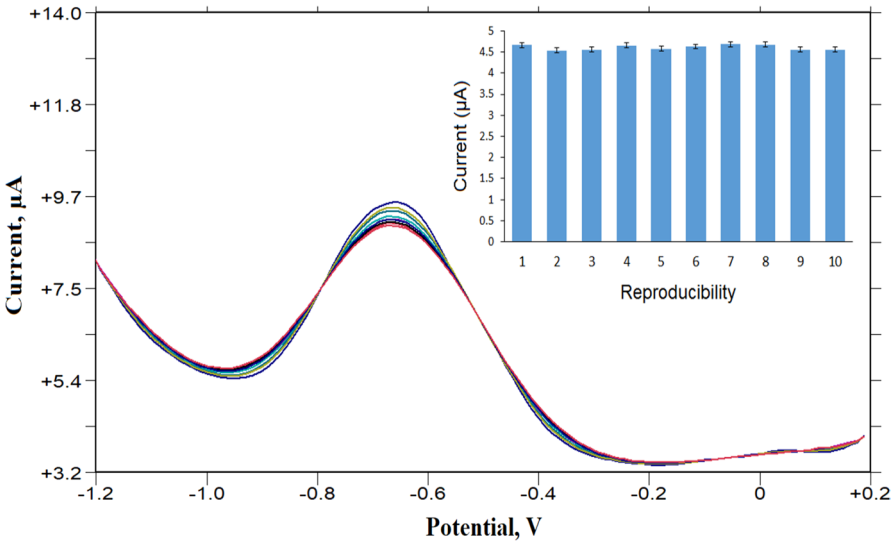


Fig. 12 Reproducibility Current (µA) of differential pulse voltammetric response, the bar graph (inset) of 0.6 mM FF oxidation on *p*(3-MTF)/GCE in Na_2SO_4, pH 4.5 ($n = 10$)

Table 1 Average peak currents and recovery yields of red meat samples

Sample	Original found in sample (mM)	Standard added (mM)	Total found (mM)	*R* (%)
Red meat 1	Below detection limit	0.8	0.87 ± 0.001	109.23
Red meat 2	Below detection limit	0.8	0.84 ± 0.050	105.17
Red meat 3	Below detection limit	0.8	0.90 ± 0.044	111.92

Table 2 Average peak currents and recovery yields of chicken meat samples

Sample	Original found in sample (mM)	Standard added (mM)	Total found (mM)	*R* (%)
Chicken meat 1	Below detection limit	0.8	0.81 ± 0.015	100.73
Chicken meat 2	Below detection limit	0.8	0.81 ± 0.018	100.73
Chicken meat 3	Below detection limit	0.8	0.72 ± 0.026	90.07

Table 3 Comparison of FF detection methods with the literature

Methods	Electrode/modifier sensors	Linear range, M	LOD, M	Ref
CV	(MIP)/Pt–Pd NPs-N-rGO/GCE	5.0×10^{-8}–8.0×10^{-6}	1.0×10^{-9}	[69]
CV	Gr/CuPc/GCE	1.0×10^{-6}–3.0×10^{-5}	7.5×10^{-7}	[70]
GC	–	1.49×10^{-6}–1.63×10^{-6}	4.59×10^{-9}–1.36×10^{-8}	[62]
HPLC	–	139.6×10^{-6}–1396×10^{-6}	4.18×10^{-6}–6.98×10^{-6}	[71]
DPV	3-MTF/GCE	1.0×10^{-4}–1.0×10^{-3}	3.99×10^{-5}	This study

(MIP)/Pt–Pd NPs-N-rGO/GCE: Pt–Pd bimetallic nanoparticles- porous N doped – graphene/glassy carbon electrode

Gr/CuPc/GCE Graphene/copper phthalocyanine/glassy carbon electrode, *GC* Gas Chromatography

recovery efficiencies were calculated in the range of 105.17–111.92% (Table 1) for red meat and in the range of 90.07 to 100.73 for chicken meat (Table 2).

Many studies have been carried out about determination of florfenicol in recent years. Dumont et al. [50] conducted a surface plasma resonance biosensor study to simultaneously identify thiamfenicol, florfenicol, florfenicol amine, and chloramfenicol residues in shrimps, and simultaneous determination of the same antibiotics has been carried out by liquid chromatography–tandem mass spectrometry method [58]. On the other hand, FF determination was performed by using many methods for the determination of phenol. Among them, methods such as HPLC [59–61], GC–MS [62], HPLC–MS/MS [63–66], spectroscopy [67], ELIZA [68] attract attention. For high-sensitivity determination of chloramfenicol by electrochemical method [2], an electrochemical sensor has been developed to detect thiamfenicol residue in milk using electrodes modified with carbon nanotubes and gold nanoparticles [48].

However, there are a limited number of studies in the literature regarding the determination of florfenicol by voltammetric method (Table 3). We have developed

a new electrochemical FF sensor using the poly-3-MTF modified GCE to cover this gap in the literature.

For the first time at 2019 year, Xia Y.M et al. have determined FF with an electrochemical sensor through the nanocomposites modified electrode. They managed to develop a highly effective electrochemical sensor based on graphene (Gr)/copper phthalocyanine (CuPc) nanocomposites. It was designed and obtained. They collected Gr/CuPc nanocomposites on the glassy carbon electrode surface and investigated the transformation of Gr/CuPc/GCE to chloramfenicol (CAP) and florfenicol by cyclic voltammetry and differential pulse voltammetry methods [70]. In another study at 2019 year, toxicity assessment was made. The antibacterial activity of FF has been shown to be completely eliminated after electrocatalytic dechlorination process [72].

Polythiophene and its derivatives are among the most used conductive polymers because of their high electrical conductivity, chemical and mechanical stability, and workability in doped conditions [73]. In this study, *poly* 3-MTF was used to modify the electrode in the development of the FF sensor.

Conclusion

GCE was successfully modified with electropolymerization of 3-MTF. The optimum conditions for the determination of FF were found as Na_2SO_4 pH 4.5 and 60 mV/s scan rate. Under the optimum conditions, the peak current was linearly related to the concentration of FF in the range of 0.1–1.0 mM. The detection limit was found to be 0.0399 mM and correlation coefficient 0.999. Developed electrochemical sensor for FF was used successfully for determination of FF because of the easy preparation, chemical stability, selectivity, good reproducibility, low cost, rapidly response properties of poly(3-MTF) membrane.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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