Heliyon 5 (2019) e02147

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.heliyon.com

Highly sensitive determination of tetracycline in chicken meat and eggs using AuNP/ MWCNT-modified glassy carbon electrodes

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ARTICLE INFO

Keywords:
Analytical chemistry
Tetracycline
Gold nanoparticles
Multiwalled carbon nanotubes
Differential pulse voltammetry

ABSTRACT

Glassy carbon electrodes (GCE) were modified with gold nanoparticles (AuNPs) and multi-walled carbon nanotubes (MWCNTs) by means of sputtering and electrodeposition. The electrodeposited MWCNT on gold coated GCE exhibited the optimum performance as characterized using cyclic voltammetry. The limit of detection and limit of quantitation were found to be 42 ppb and 139 ppb, respectively. The modified electrode was used as working electrode in differential pulse voltammetry to detect tetracycline (TET) residues in the eggs, wings, liver, breast, and thigh, of organic as well as non-organic chicken bought from a local supermarket. The highest concentration in the eggs, wings, liver, breast, and thigh were found to be 5.9 ppm, 2.0 ppm, 1.4 ppm, 1.3 ppm, and 1.2 ppm for organic chicken and 8.70 ppm, 4.8 ppm, 4.3 ppm, 3.3 ppm, and 2.7 ppm for the corresponding parts in non-organic chicken, respectively. The obtained concentrations were remarkably greater compared to the maximum residual limit released by the Codex Alimentarius Commission.

1. Introduction

Chicken meat is one of the most common consumed meat in the world. Eggs are considered to be one of the cheapest sources of animal protein in the market. Chicken meat and eggs are the most common products consumers buy because of their affordability. As of January 2018, the inventory of broiler chicken in the Philippines decreased by 4.07 percent compared to that of 2017 (Philippine Statistics Authority, 2018). To prevent such decrease, chickens are subjected to antibiotic intake, both in oral form or through inoculation, to eliminate death-causing diseases. Antibiotics are usually added to the chicken feed for their growth promoting properties and for disease prevention and treatment. Antibiotics can also be injected to the chicken through the wings and the breast.

Tetracycline (TET) presents an extensive antibacterial spectrum and bacteriostatic activity making it efficient in treating diseases caused by gram-positive and gram-negative bacteria (Masawat and Slater, 2007). Tetracycline is considered to be one of the strongest antibiotics. Overuse of antibiotics prompts bacteria to be resistant to medication, which poses a great threat on human health. In order for safe consumption of food, maximum residue limits (MRLs) for tetracycline were established for specific tissues (Al-Ghamdi et al., 2000). Furthermore, monitoring of certain substances and residues in live animals and animal products is enforced in the European Union (EU) by Directive 96/23/EC and Commission Decision 97/747/EC (Reig and Toldra, 2008).

Due to the possible adverse effects of TET on human health, accurate and precise monitoring of these antibiotics in food is crucial. There are several techniques for the detection of antibiotics residues in food (Andersen et al., 2005; Cinquina et al., 2003; Cooper et al., 1998; Masawat and Slater, 2007; Nakazawa et al., 1999; Sokol and Matisova, 1994; Stubbings et al., 1996; Treetepvijit et al., 2006; Zhao et al., 2004). Among these are chromatographic and electrochemical techniques. Electrochemical techniques such as differential pulse voltammetry (DPV) are more popular due to their low cost, high sensitivity and portability. On the other hand, chromatographic techniques such as high-performance liquid chromatography, are expensive, not well suited for in situ measurements, and require complicated instrumentation.

The performance of electrochemical sensors depends on the design of the working electrode (Calixto et al., 2012; Calixto and Cavalheiro, 2015; Sattayasamitsathit et al., 2007; Taghdisi et al., 2016). The electrode

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https://doi.org/10.1016/j.heliyon.2019.e02147
Received 19 December 2018; Received in revised form 1 May 2019; Accepted 19 July 2019

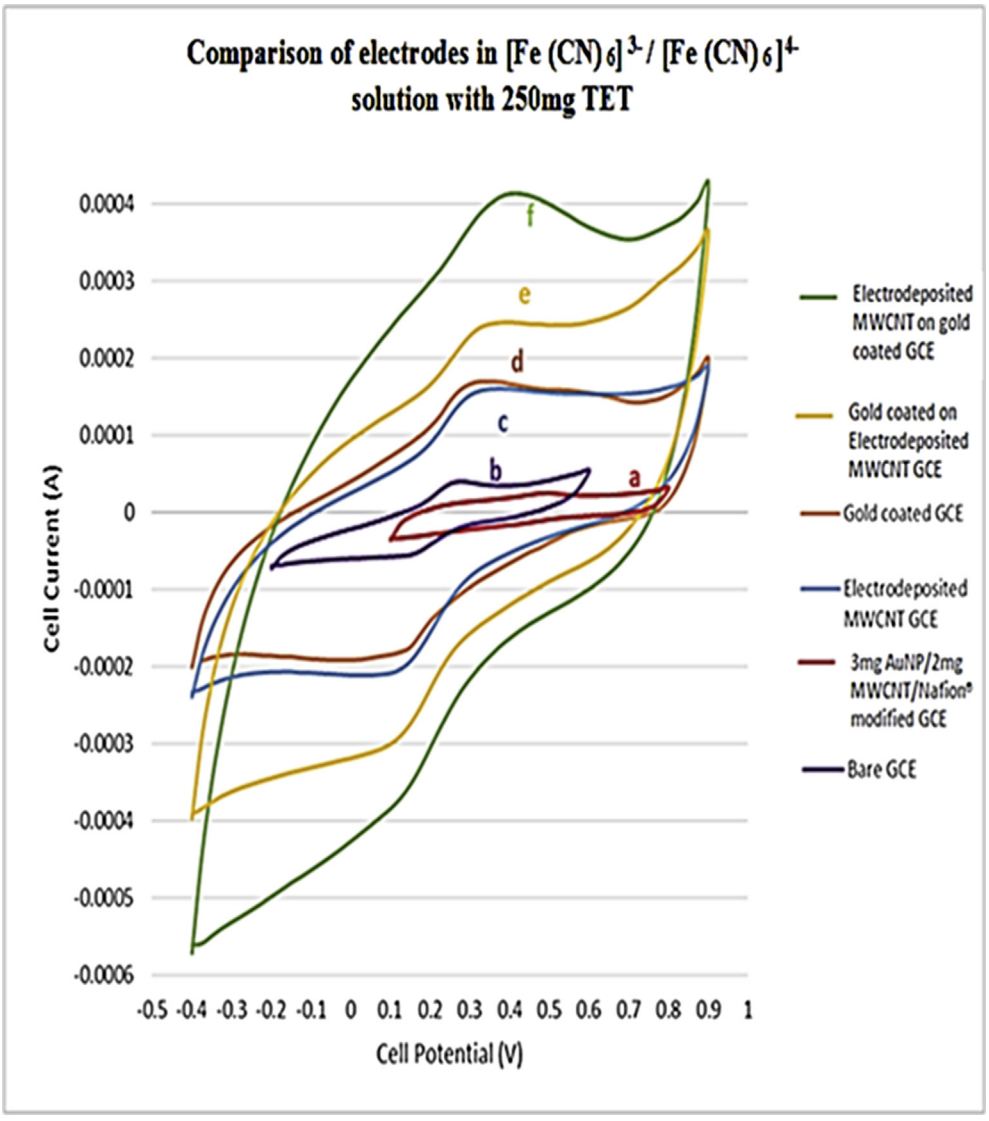


Fig. 1. Cyclic voltammograms obtained in a ferricyanide solution containing 5 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, 100 mM KCl and 250 mg of TET HCl (a) 3 mg AuNP/2 mg MWCNT/Nafion® modified GCE, (b) bare GCE, (c) Electrodeposited MWCNT GCE, (d) gold coated GCE, (e) Gold coated on electrodeposited MWCNT GCE and (f) ElectrodepositedMWCNT on gold coated GCE.

surface is usually modified with suitable functional materials to improve its sensitivity. Gold nanoparticles are proven to be excellent for modifying electrodes due to their high conductivity and high stability (Palisoc, et al., 2017a, b; Palisoc et al., 2018). Previous studies (Asadollahi-Baboli and Mani-Varnosfaderani, 2014; Kalambate et al., 2015; Saha et al., 2012; Wang et al., 2011; Wang et al., 2012) reported that electrodes modified with AuNPs showed better limits of detection. Multi-walled carbon nanotubes (MWCNTs) are used in electrode modification due to their remarkable electrochemical properties and numerous electrochemically active sites (Benvidi et al., 2018; Gholivand, 2013; Vega et al., 2007; Wong et al., 2015; Zhan et al., 2016). When AuNP is combined with MWCNT, the performance of the final composite material is improved, since the AuNP/MWCNT composite has the individual properties of both constituent components as well as a synergistic effect (Da Silva et al., 2018). Gold nanoparticles enhance the electron transfer between the heavy metals and the electrode while the high surface-to-volume-ratio of MWCNT enhances the adsorption of heavy metals on the electrode surface. Their combined effect makes the electrode more sensitive in detecting heavy metals.

In this work, glassy carbon electrodes (GCEs) were modified with gold nanoparticles (AuNPs) and multi-walled carbon nanotubes and were used as working electrode in differential pulse voltammetry (DPV) to detect TET in different parts of the chicken as well as in chicken eggs. This was done to determine where the highest concentration of TET residue is present. Both commercially available organic and non-organic chicken were tested. All measurements were done using differential pulse voltammetry with ferricyanide [$(Fe(CN)_6^{3-}/Fe(CN)_6^{4-})$] as the mediator.

2. Methodology

2.1. Apparatus

Cyclic voltammetry (CV) and differential pulse voltammetry measurements were performed using an Autolab PGSTAT128N potentiostat. A three electrode set-up was carried out for both measurements where the working electrode was the electrodeposited MWCNT on gold coated GCE, the reference electrode was an Ag/AgCl electrode and the auxiliary electrode was a platinum wire. The gold was sputtered onto the surface of the electrode using a JOEL JFC 1200 finecoater and a BST8 potientiostat was used for electrodeposition of MWCNT. A JEOL 5310 scanning electron microscope was used to evaluate the morphology of the modified electrodes.

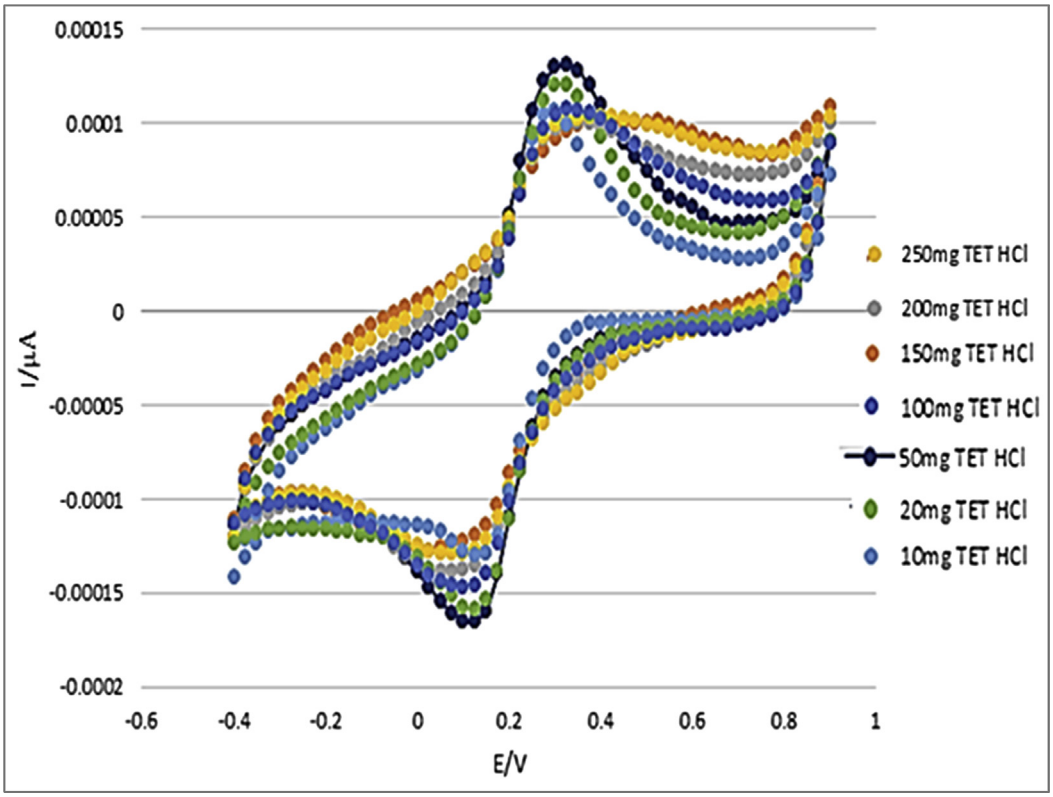


Fig. 2. CV obtained using a ferricyanide buffer solution containing 5 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and 100 mM KCl of the electrodeposited MWCNT on gold coated GCE detecting different concentrations of TET HCl.

2.2. Chemicals and reagents

Gold nanoparticles, ethanol, methanol, 0.3 μm and 0.05 μm of alumina slurry, nitric acid, MWCNT, potassium chloride (KCl), potassium ferricyanide ($K_3[Fe(CN)_6]$), citric acid monohydrate ($C_6H_8O_7$), disodium hydrogen phosphate dehydrate (Na_2HPO_4), ethylenediaminetetraacetic acid (EDTA), Tris-HCl, tetracycline chloride, acetonitrile (CH_3CN) were all sourced from Sigma Aldrich (Sigma-Aldrich Pte Ltd, Singapore). Distilled as well as deionized water were also used in the study.

2.3. Modification of the electrode

A GCE was polished using 0.30-micron and 0.05-micron alumina slurry sequentially; after which, it was rinsed with deionized water until the surface of the GCE was homogeneously flat and displayed a mirror-like surface. The GCE was then ultrasonically rinsed further in ethanol for 15 min and dried at room temperature. Gold was sputtered onto the GCE using a JOEL JFC 1200 fine coater and MWCNT was electro-deposited using a BST8 potientiostat.

2.4. Preparation of solutions

The ferricyanide solution was made up of 0.005M of potassium ferricyanide ($K_3[Fe(CN)_6]$) and 0.1 M of potassium chloride (KCl). The solution was used as an electrochemical indicator to generate electron flow between the analyte solution and the working electrode. It was used for the CV characterization and DPV to detect TET. The measurements done for CV was at a potential range of −0.5 V–1.0 V at a scan rate of 0.09 V/s while DPV measurements were at a potential range of −0.3–0.5V with a modulation amplitude of 0.05V.

2.5. Preparation of samples

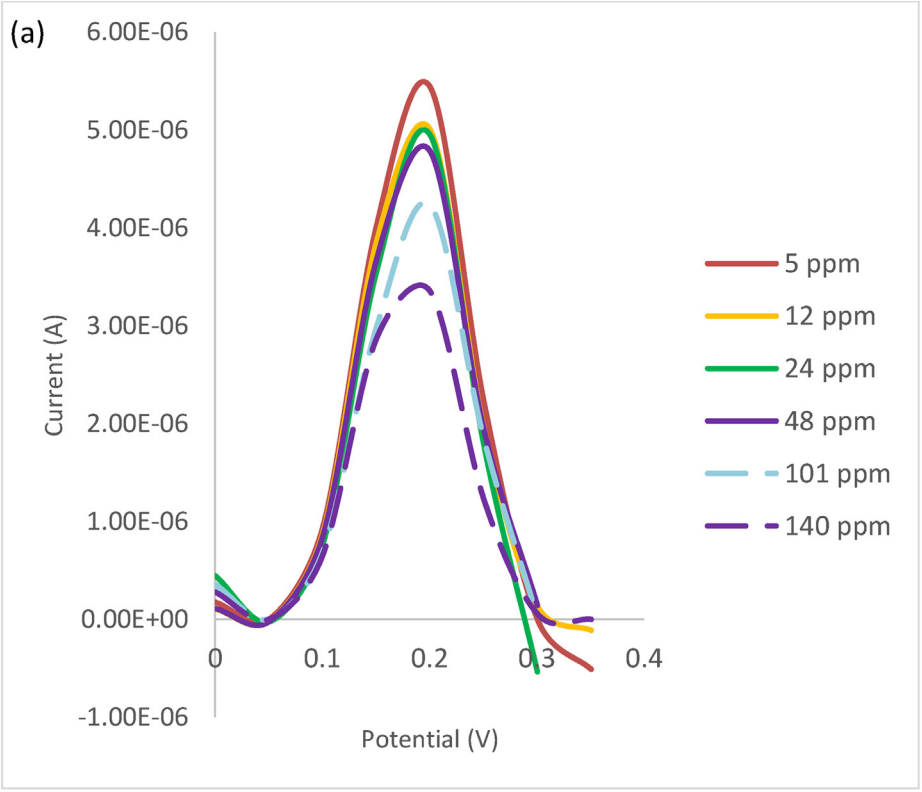
Organic and non-organic dressed chicken were purchased from a local supermarket. The breast, wings, and thigh parts were all filleted. All the samples, including the liver were minced separately using a food processor and then weighed using the BOSCH SAE200 electronic balance to get 2.5 g of each. The samples were centrifuged with Na_2-EDTA-McIlavaine buffer (15g of disodium hydrogen phosphate dihydrate, 13g of citric acid monohydrate, and 3.72g of EDTA dissolved in 1L of distilled water). The supernatant was then collected then placed in an activated solid phase extraction cartridge (SPE) cartridge using deionized water and methanol. The cartridge was then washed with deionized water and the TET was eluted using 10mL of methanol.

Egg samples for both organic and non-organic eggs, also purchased from a local supermarket, were prepared by transferring each egg to a beaker with 50 mL of distilled water then mixed until homogenized. Twenty grams (20g) of the homogenized mixture in a 50 mL beaker was weighed then transferred to a 50 mL volumetric flask and absolute ethanol was added to the mark. This was then transferred to centrifuge tubes and the supernatants were collected after the centrifuge process.

3. Results and discussion

3.1. Optimization

Five (5) GCEs were modified with AuNPs and MWCNTs and characterized to determine the best electrode by evaluating their figures of merit via cyclic voltammetry. The addition of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ as the mediator enabled the modified GCEs to have a reversible voltammogram for all modifications. Fig. 1 shows the cyclic voltammograms of the modified electrodes with $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ as the mediator for 250 mg of TET HCl. The gold-coated GCE which was subsequently modified with electrodeposited-MWCNT showed the highest anodic peak current. It was even higher than the gold-coated on MWCNT-deposited electrode. This proves that the MWCNT, inspite of being hybridized by AuNPs, is the major enhancer of conductivity than the AuNPs. This can be attributed for the very high aspect ratio of the MWCNT enabling the modified GCE



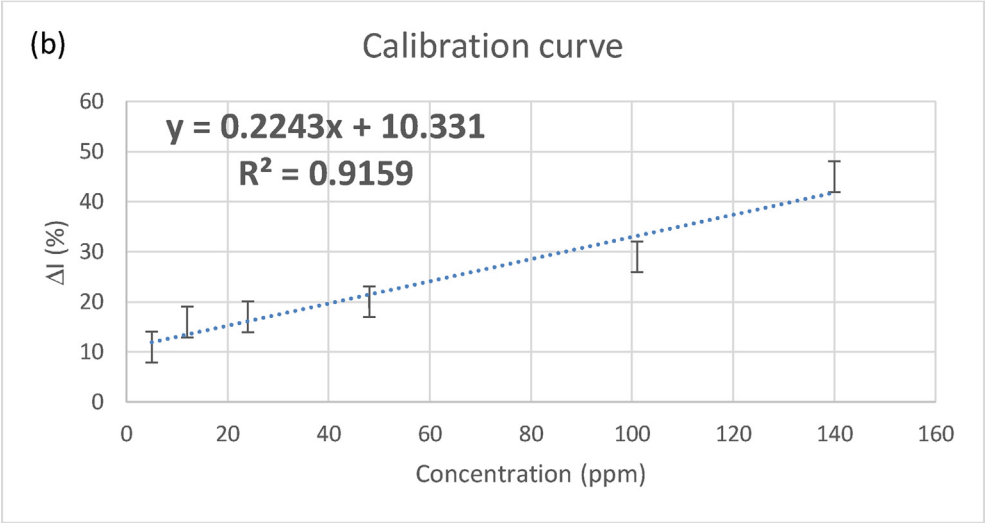


Fig. 3. (a) Differential pulse voltammograms TET concentrations. The modulation amplitude was 50 mV, step potential was 50 mV, and the modulation period was 0.2 s. (b) TET HCl DPV calibration curve with Pearson coefficient of 0.9159.

to have better conductivity. The chosen working electrode was the gold-coated GCE which was subsequently modified with electrodeposited-MWCNT because this obtained the highest anodic peak current.

The cyclic voltammograms of the electrodeposited MWCNT on gold coated GCE are shown in Fig. 2. The tetracycline concentration was varied using a ferricyanide buffer of 5 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and 100 mM KCl. Reversibility is observed in all voltammograms with the 10mg and 200mg TET HCl concentrations having the best reversibility of ~ unity.

3.2. Differential pulse voltammetry

Fig. 3a shows the differential pulse voltammograms of different TET concentrations in a ferricyanide solution containing 5 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and 100 mM KCl. It can be seen that as the TET concentration increases the anodic peak current decreases. This can be attributed to the response of the ferricyanide solution on the surface of the electrode. The increase in the TET concentration hinders the ferricyanide solution to react with the electrode surface (Benvidi et al., 2018).

Fig. 3b shows the calibration curve which was obtained using the electrodeposited MWCNT on gold coated GCE. Six concentration points were gathered for the calibration curve. The highest peak was obtained from the lowest concentration of TET HCl and as the concentration increases the anodic peak decreases.

Table 1
Comparison between the LOD of this study and other related investigations.

Nature of sensor	Voltammetric technique	Antibiotic detection	Limit of detection (ppm)	Source
Reduced graphene oxide and magnetite nanoparticles	DPV	TET	0.26	[26]
A novel M-shaped electrochemical apt sensor	DPV	TET	0.45	[12]
Bismuth film electrode	DPV	TET	1.2	[13]
Screen printed gold electrode	DPV	TET	0.96	[20]
CPE GO/MWCNT-COOH (Modified carbon paste electrode)	DPV	TET	0.36	[28]
Gold microelectrode	CV	TET	0.20	[19]
Graphite-polyurethane composite electrode (GPU)	DPV	TET	2.80	[14]
Graphite-polyurethane composite electrode (GPU)	DPV	TET	2.60	[15]
MWCNT-GCE	HPLC-EF	Oxy-tetracycline	0.44	[24]
UV-irradiated DNA film modified GCE	DPV	TET	0.27	[25]
Electrodeposited MWCNT on gold coated GCE	DPV	TET	0.042	This work

Table 2
Concentrations of TET in parts and eggs of organic and non-organic chicken.

	Organic chicken (ppm)	Non-organic chicken (ppm)
Thighs	1.20	2.7
Breasts	1.30	3.3
Liver	1.40	4.3
Wings	2.00	4.8
Eggs	5.90	8.70

3.3. Limit of detection and limit of quantitation

The limit of detection (LOD) was obtained by using the concentration point values of the calibration curve shown in Fig. 3b. Table 1 shows the comparison of the LODs from different works and this work. Compared to the other works listed on the table, this study using the electrodeposited MWCNT on gold coated GCE yielded the lowest LOD of 42 ppb which is well below the MRL values for chicken parts which range from 0.2 to 0.6 ppm. This complies with one of the requirements of EU that in case the residue has a maximum residue limit, the screening method must be capable to detect the residue below this limit (Reig and Toldra, 2008). The limit of quantitation (LOQ) was also computed and the obtained value was at 139 ppb. This means that the lowest detectable limit of the optimum fabricated electrode without bias was 139 ppb.

3.4. Real sampling

Table 2 shows the concentration in parts per million (ppm) of TET in the organic chicken part samples. The concentration of TET was highest in the wings and least in the thighs. This can be ascribed to the possibility that inoculation of tetracycline was still done on the inside part of the wings, although in smaller quantities. The muscle tissues showed lower concentration of TET. Muscle tissues in poultry tend to have the least concentration of antibiotics since they do not process toxins like the liver and they are not directly inoculated unlike the inside of chicken wings. Furthermore, breasts tend to have more tetracyline concentration than thighs showing that not all tissue muscles incorporate antibiotics at the same concentration in agreement with other studies (Marangon and Busani, 2006; Shalaby and Salama, 2011). The chicken parts contain tetracycline residues that are above 2 ppm, which are much higher that those of maximum residual limit (MRL) values. The table also shows that although the chicken samples were labeled as “organic”, tetracycline was still present in their tissues. The TET concentration in the organic chicken samples was significantly less than that in non-organic samples though. It can be inferred that organic poultry raisers in the Philippines still mix antibiotics, though in less amount, in chicken feeds and water for disease prevention.

Table 2 also shows the TET concentration in eggs of both organic and non-organic chicken. The TET concentration in the eggs of non-organic chicken is remarkably higher than that in the eggs of organic chicken. This can be attributed to the higher tetracycline administered to the non-organic chicken where the eggs came from. Although the TET concentration in the organic chicken eggs are less, it is still above the MRL set by the CODEX Alimentarius European Commission (CAC/MRL, 2015). This shows that the eggs are falsely labeled as “organic”.

The summary of the TET concentration of the different tissues as well as eggs of both organic and non-organic chicken is shown in Fig. 4. The trend of TET concentration is similar for both organic and non-organic where the eggs have the highest concentration, followed by the wings, then the liver, and lastly by the muscle tissues. The breast has more TET concentration than the thigh. This may be explained by the fact that the breast muscle tissue is more fibrous providing more space for the TET to lodge in whereas the thigh has less fibrous tissues. Also, TET is injected in the wings and the breast is closer to the wings than the thighs.

4. Conclusions

Glassy carbon electrodes modified with gold nanoparticles and multi-walled carbon nanotubes were successfully fabricated and were used as

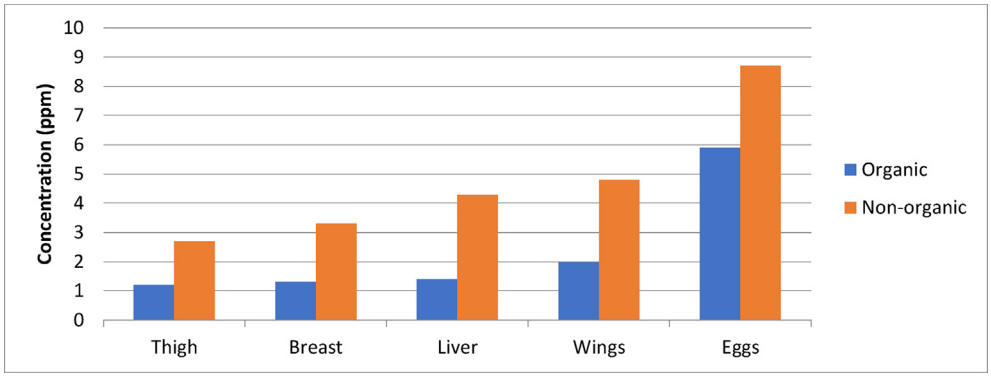


Fig. 4. TET concentration of different tissue parts and eggs of organic and non-organic chicken.

working electrode in differential pulse voltammetry to detect TET. Multi-walled carbon nanotubes electrodeposited onto gold-coated GCE exhibited the highest anodic peak current for TET in ferricyanide solution. With this, the MWCNT electrodeposited onto gold-coated GCE was chosen as the modified electrode for TET residue detection in this study. The limit of detection of the fabricated MWCNT/AuNP GCE was found to be 42 ppb and the limit of quantitation was 139 ppb. Hence, taking all the figures of merit into consideration, the fabricated modified electrodes in this study can be considered as highly sensitive and effective as they can detect TET concentration using DPV with LOD well below the maximum residual limit set by CODEX Alimentarius European Commission for poultry products.

The fabricated electrodes were tested to measure TET in organic and non-organic chicken parts. The trend was similar in both chicken categories in that the eggs contained the greatest TET concentration, followed by the wings, then the liver and lastly, the muscle tissues. It was also observed that not all muscle tissues incorporate antibiotics at the same concentrations in agreement with previous works. The breast hold more antibiotics than the thigh. The non-organic eggs and chicken parts had more TET concentration than those of the organic chicken which exhibited TET concentration higher than the MRL prescribed by CODEX Alimentarius European Commission for poultry products. This showed that the chicken products were not categorically "organic".

Declarations

Author contribution statement

Shirley Palisoc, Michelle Natividad: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Aubrey Alzona, Pietro De Leon, Lotis Racines: Performed the experiments; Analyzed and interpreted the data.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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