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Studies on detection of tetracycline in honey using screen printed electrode with buffer electrolytes

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Abstract
The main objective of this work is to study the electrochemical oxidation using buffer electrolytes for detecting tetracycline in honey. The three electrode system was used to conduct the optimization studies of different buffers (citric acid (CA), sulphuric acid (SA) and hydrochloric acid (HA)) at pH ranging from 2 to 6 using CV. SA buffer at pH 4 provided the maximum peak current of 1.529 mA at 1.399 V and was optimized for further studies. The detection of TCHC at concentration ranging from 10 µl/l to 100 µl/l was studied by both CV and DPV with a screen printed electrode. From the calibration curve of CV and DPV at different concentration of TCHC, it was observed that DPV shown a better detection with correlation coefficient of 0.9709. Under the optimized conditions, the response of DPV was used to detect the TCHC concentration in honey. The limit of detection was found to be 0.77 µl/l with a percentage recovery ranging between 74 and 116.7%.

Keywords: tetracycline, sulphuric acid, cyclic voltammetry, differential pulse voltammetry, buffer pH

1. Introduction
Honey is a natural sweetener consisting of carbohydrates, enzymes, amino acids, polyphenols, vitamins and minerals in smaller amount. The honey bees collect the floral nectar from different sources of flowers and plants. The nectar is converted into honey through natural regurgitation and evaporation process in gastrointestinal tract (GIT) of bees. These bees are prone to several bacterial infections like American foulbrood and European foulbrood (Forsgren *et al*., 2018) [8] and fungal diseases. In order to protect the lives of honey bees from various infectious diseases and to increase the production of honey so as to meet the increasing demand owing to its therapeutic properties, the apiculturist treats the bees by feeding them with antibiotics. This in turn results in the occurrence of antibiotics in honey (Sapna & Nimisha, 2010) [21]. Tetracycline ($C_{22}H_{24}N_2O_8$) is one of the most prevalent antibiotics used by apiculturists to treat honey bees for various bacterial and fungal infections. Several studies have reported tetracycline residues in honey (Taylor *et al*.,2006) (Zhang *et al*., 2019) [25]**.** Tetracycline has a molecular weight of 444.44 and a melting point of 170-173°C. Each unit has a di(methyl) amino substituent and a phenol substituent at positions 4 and 10 respectively (Abraham *et al*., 2020) [1] (Masawat & Slater, 2007) [15]. Continuous exposure to even mild dosages of TC can cause several health-related ailments such as eyesight issues, tooth staining, and allergic reactions (Al-Waili *et al*., 2012) [2] and is toxic to humans (Korkmaz *et al*., 2017) [12].

Capillary electrophoresis (Nozal *et al*., 2004; J. Zhou *et al*., 1999) [17, 26], fluorescence (Tan *et al*., 2013) [22], UV-Vis spectroscopy, liquid chromatography- tandem mass spectrometry (Zhang *et al*., 2019) [25], LC-MS/MS (Ribeiro *et al*., 2018) [19] and dispersive solid-phase extraction HPLC–MS/MS (Pang *et al*., 2021) [18] have all been used to determine tetracycline. Many aptasensors (Huang *et al*., 2019) [10] (Li *et al*., 2019) [13], molecularly imprinted polymers (Devkota *et al*., 2018), paper-based analytical devices (Huy *et al*., 2020; T. Zhou *et al*., 2019) [11, 27] and disposable immunosensors (Conzuelo *et al*., 2013) [6] have been developed for the detection of tetracycline. (Lorenzetti *et al*., 2020) [14] developed a disposable rGO-based screen-printed electrodes for detecting tetracycline in milk and river samples using an adsorptive transfer stripping DPV approach. (Ni *et al*., 2011) [16] used differential pulse stripping voltammetric technique for determining tetracycline, oxytetracycline and chlortetracycline simultaneously by electro reduction at a hanging mercury drop electrode. (Hayat & Marty, 2014) [9] highlighted the advantages of using screen printed electrodes for detection of various analytes and emphasized on its sensitivity and portability.

(Bougrini *et al*., 2016) [3] developed a MIP biosensor for detecting tetracycline in honey. The sophisticated analytical methods for tetracycline detection require expensive instruments and skilled technicians, high operation cost and detailed sample preparation procedure. Screen printed electrodes (SPE) are considered to be an alternative to the existing analytical method owing to its low cost, miniaturized size and easy sample preparation in less time. Studies on disposable SPE for tetracycline detection are in progress. (Veseli *et al*., 2019) [24] developed a carbon SPE modified with sodium dodecyl sulfate using phosphate buffer (pH 8.5) as electrolyte. Recently (Cánovas *et al*., 2021) [5] studied the electro oxidation of the tetracycline in pH ranging from 2 to 12 using unmodified SPE by square wave voltammetry. Not much work has been reported on detection of tetracycline antibiotics using mild acids as buffer electrolytes, as they are readily available, easy to handle and are low cost. The main objective of this work is to study the electrochemical oxidation of tetracycline in different buffer electrolytes using voltammetric technique and to detect tetracycline in honey by using screen printed electrode sensor.

2. Materials and Methods

2.1 Materials

Tetracycline hydrochloride (TCHC), sulphuric acid (SA), anhydrous citric acid (CA), hydrochloric acid (HA) and sodium hydroxide were purchased from Sigma Aldrich and supplied by M/s. Ponmani Scientific pvt. ltd., Trichy, Tamil Nadu, India. Honey samples (free from any antibiotic residues) were purchased from an apiculture farm in Theni, Tamil Nadu. The chemicals used in this study were all analytical grade and used directly with no purification.

2.2 Preparation of the electrolytic buffers and tetracycline standards

The buffers were prepared from 0.1 N Sulphuric acid, 0.1 N Hydrochloric acid, and 0.1M Citric acid, which were freshly prepared before each electrochemical measurement. The buffers SA, HA, and CA were prepared at different pH ranging from 2 to 6 by adding an acid/alkali for pH adjustment. The tetracycline standard stock solution was prepared by adding 10 g of TCHC in 10 ml ethanol and stored in dark refrigerated conditions. The working solutions were prepared from the standard stock solution freshly before every measurement.

2.3 Three electrode system

The three electrode system was used for conducting the optimization studies of the buffer and its pH. It consists of an electrochemical cell (ECC) with a carbon working electrode (WE), Ag/AgCl reference electrode (RE) and a platinum counter electrode (CE) (fig.1). The ECC is connected to a palmsens4 electrochemical interface. Cyclic voltammetry (CV) is used to determine the reduction-oxidation process occurring in a particular sample. A sweeping potential (V) is supplied to the sample through the working electrode, and the current output is measured. For each peak, there is an equal amount of current flowing, and this is indicative of the concentration of the redox molecules present. The optimization studies were conducted using CV with the t equilibration of 10 s, E begin at 0, E vertex 1 at -2.0 V, E vertex 2 at +2.0 V, step potential of 0.01 V and a scan rate of 1.0 V/s

The buffers 0.1 N sulphuric acid, 0.1 N hydrochloric acid and 0.1M citric acid at pH ranging from 2 to 6 were electrochemically analyzed by CV to study the oxidation and reduction potential using a three electrode system. In all the buffer electrolytes, the buffer pH which gives the highest current response was optimized. The optimized pH in each buffer was then compared to optimize the buffer, which is further used to conduct the DPV studies for the detection the TCHC residues.

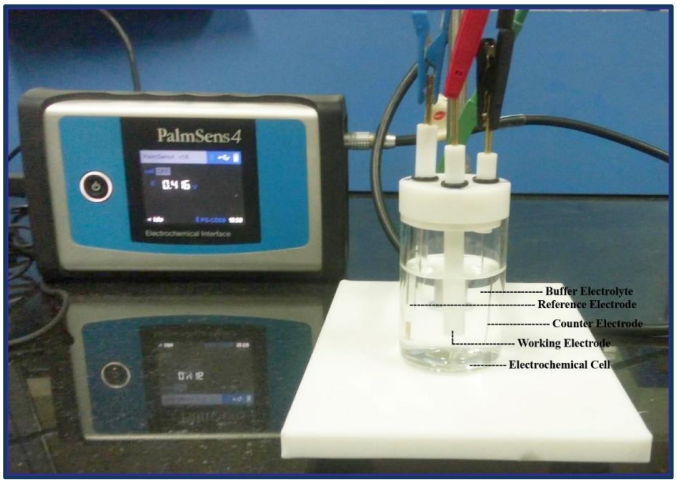

Fig 1: Three electrode system consisting of WE, RE and CE

2.3.1 TCHC detection using Screen printed electrodes

The screen printed electrodes (SPE) are a miniaturized version of a three electrode system in which the WE, RE and CE are printed on a strip and is connected to the palmsens4 electrochemical interface by means of an adapter as shown in fig.2. SPE were used to study the electro-oxidation behavior of TCHC in the optimized buffer and pH by CV and differential pulse voltammetry (DPV) technique. The DPV was conducted with the following voltammetric settings. The potential scan from -2V to +2V, with step E of 0.01V, E pulse 0.2V, t pulse of 0.02 s and a scan rate of 0.05V/s

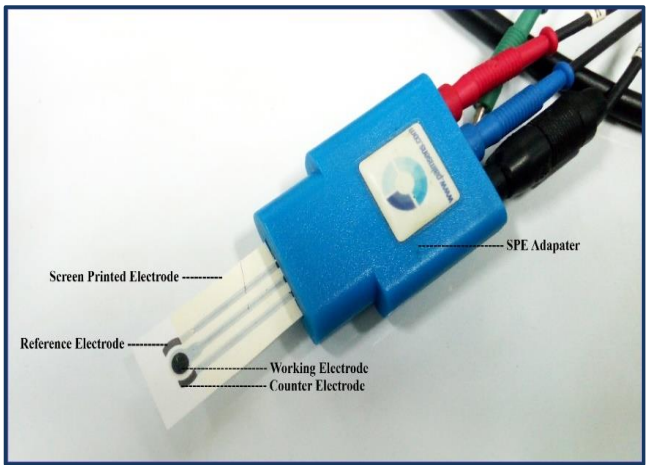

Fig 2: Screen printed electrode

2.3.2 TCHC detection in honey

Honey samples were spiked with TCHC at a concentration ranging from 10 µl/l to 100 µl/l. The DPV technique was optimized and was used to determine TCHC resides in spiked honey samples, using the optimized experimental conditions. The spiked honey samples were analyzed in triplicate and the recovery (%) was calculated from the calibration curve of DPV.

3. Results and Discussion

3.1 Optimization of buffer and pH

3.1.1 Effect of pH on the CV of SA buffer

The CV studies were conducted for the SA buffer with pH 2, pH 3, pH 4, pH 5 and pH 6 and their voltammograms are shown in figure.3. It was observed that in the anodic region two oxidation peaks appeared for all the pH buffers. The first oxidation peak occurred at a negative potential (around -0.390V to -0.560 V) with a maximum peak current of 1.271 mA at a potential of -0.460 V for pH 6 SA buffer. The second oxidation peak was observed at a potential ranging from 0.05V to 1.399 V with the highest peak value of 1.529 mA at 1.399 V for pH 4 SA buffer. It has to be noted that the intensity of secondary oxidation at the positive potential is higher than the primary oxidation that occurred at the negative potential. As the pH increases from 2 to 4, the oxidation also increases resulting in higher current values. at pH 5 there is a drop in the current both in the first and second peaks.

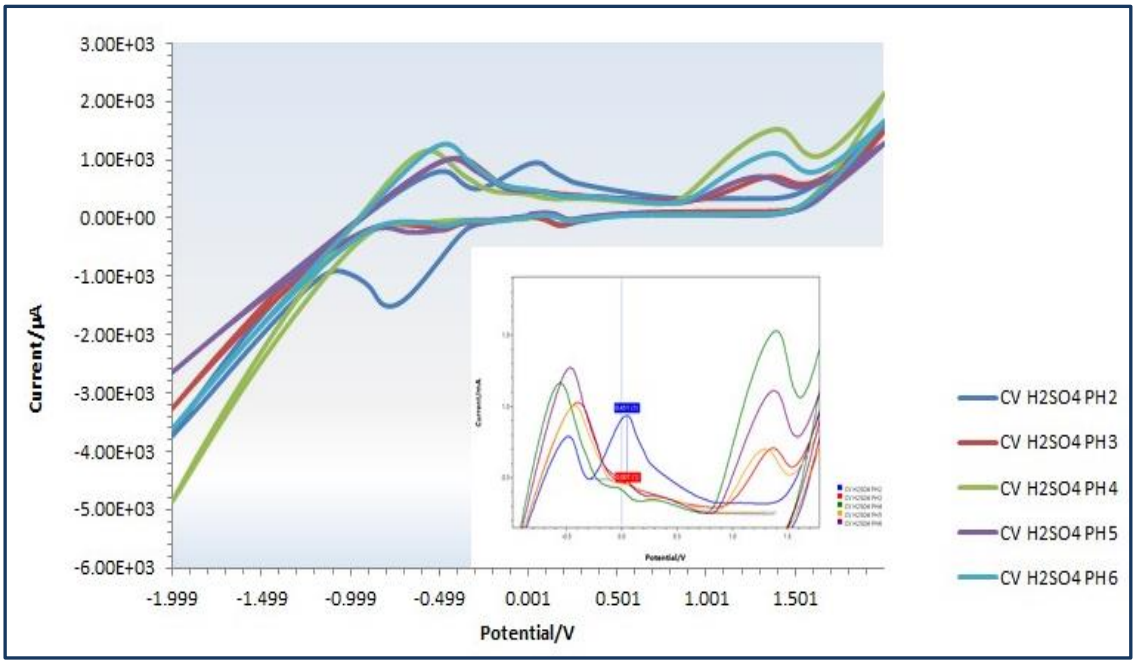

Fig 3: CV of 0.1N H_2SO_4 buffer from pH 2 to 6

3.1.2 Effect of pH on the CV of CA buffer

Fig.4 shows the CV curves of CA buffer at pH 2, pH 3, pH 4, pH 5 and pH 6. The oxidation peak occurred only once for pH 2, 3 and 5 CA buffers, whereas for pH 4 and pH 6 CA buffer it occurred twice. The current value increases with increasing pH till pH 4 and then started to decrease in pH 5 and pH 6 buffers. For pH 4 CA buffer, a maximum peak current of 1.345 mA and 1.344 mA was observed at -0.029 V and at -0.039 V respectively. The reduction occurred in the cathodic region.

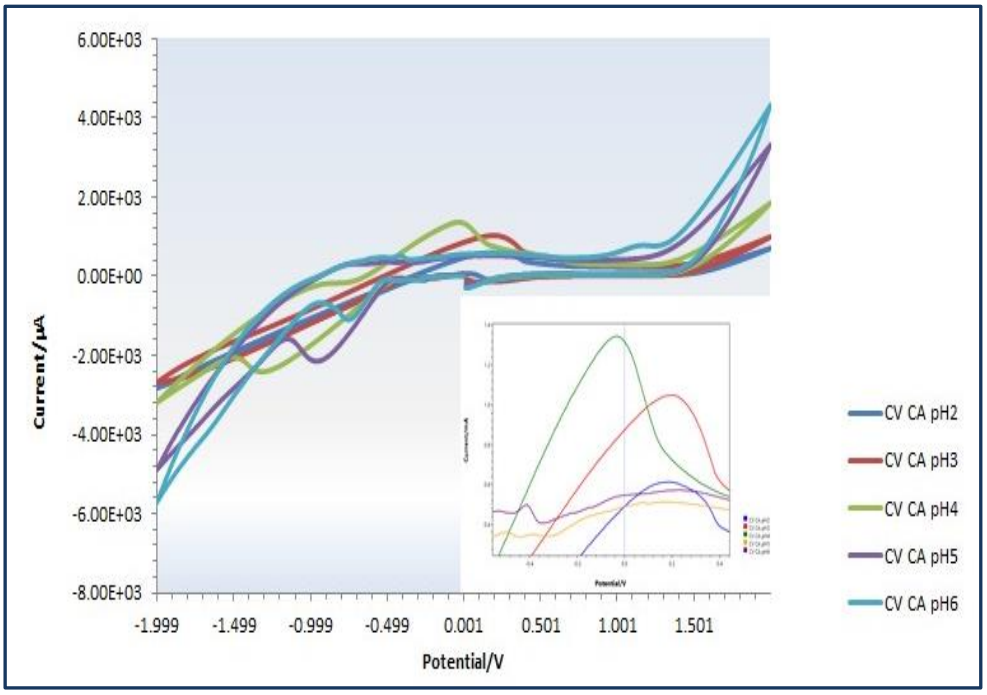

Fig 4: CV of 0.1M Citric acid buffer from pH 2 to 6

3.1.3 Effect of pH on the CV of HA buffer

The cyclic voltammograms of HA buffer were shown in fig.5. From the CV curves it was observed that the current value shows an increasing trend with increase in the pH of HA buffer in both the first and second oxidation peaks. For the first oxidation peak, the current value increases from 0.825 mA to 1.25 mA (highest current value observed) in the potential between -0.32 V to -0.45 V. The current for the second oxidation peak also shows an increasing trend similar to the first oxidation peak but lies in the positive potential ranging from 0.04 V to 1.439 V. The highest peak current in both first and second oxidation peaks was observed in pH 6 CA buffer.

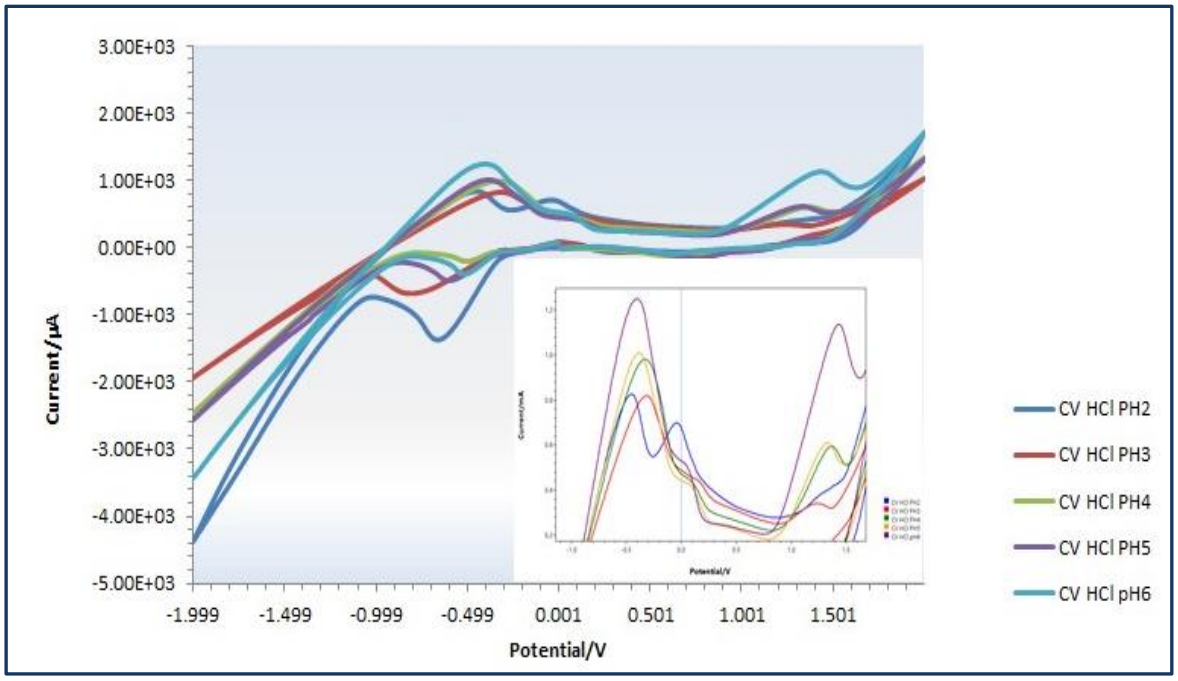

Fig 5: CV of 0.1N HCl buffer from pH 2 to 6

3.1.4 Optimization of buffer electrolyte and pH

The cyclic voltammogram of the buffers (pH 4 of SA, pH 6 of HA, pH 4 of SA) that shown maximum peak current was selected and compared to optimize the best buffer for the detection of TCHC

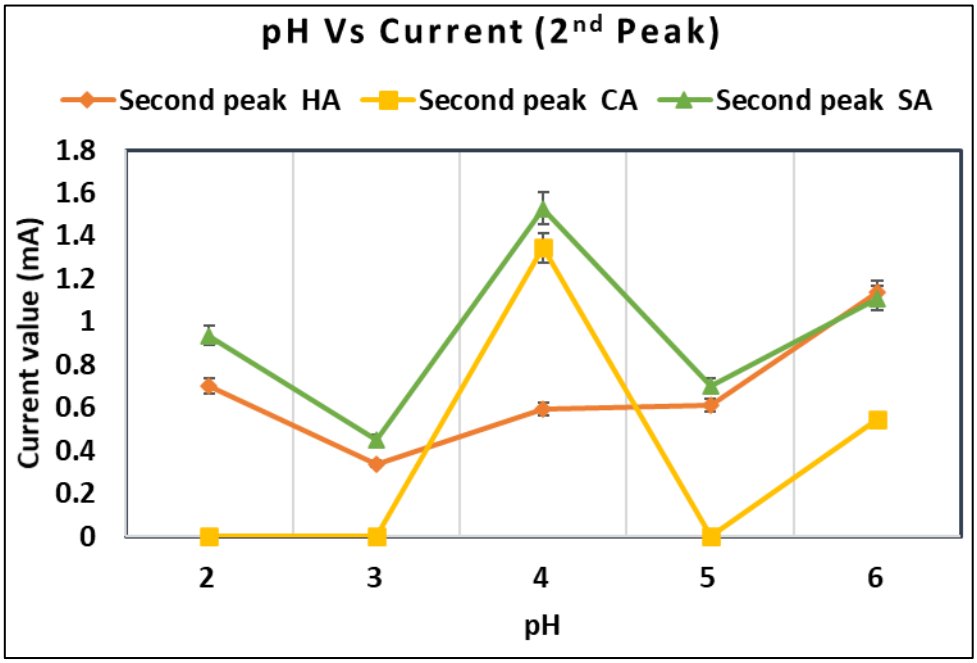

Fig 6: pH vs Peak current of buffers – HA, CA and SA

From fig.6, it was observed that the buffer SA with pH 4 exhibited maximum peak current of 1.529 mA at a potential of 1.399 V. hence the SA buffer with pH 4 has been optimized for further studies on the detection of TCHC in honey.

3.2 CV for TCHC detection

Fig.7-a shows the response of SA buffer (pH 4) to the

addition of TCHC. The anodic peak current obtained for SA buffer decreased significantly with the addition of TCHC at 1.259 V having a current value of 0.559 mA. Also, an additional peak occurred at a potential of 0.13 V with 1.252 mA which may be due to the oxidation of TCHC as no peak occurred at the given potential in the CV of pH 4 SA buffer. The electro-oxidation of TCHC at different concentration in SA (pH 4) buffer was studied with CV as shown in fig. With the addition of TCHC, initially the current value shows an increasing trend with increasing concentration at the first peak. Whereas, in the second peak, the current value shows a declining trend with the increasing concentration of TCHC. This trend of increasing in the current value followed by a declining trend may be attributed to the oxidation of TCHC in the presence of mild acids and forming an anhydrotetracycline which on further cleavage yields apoterramycin. (Ricardo *et al*., 2016) reported that the protonation of the dimethyl-amino group results in the oxidation of TCHC at an acidic pH. This protonation was mainly due to the addition of –OH group with the phenolic unit in the TCHC thereby resulting in the oxidation reaction. As the concentration of TCHC increases, more protonation occurs, thereby resulting in the drop in peak current value, which is evidenced from the cyclic voltammogram.

The background response of SA buffer (pH 4) as electrolyte exhibits an anodic wave on the positive scan in the region of +1.339 V. With the addition of TCHC, two peak anodic signal for oxidation of tetracycline was observed beginning at +0.3 V. The first peak occurred in the region of 0.03 V to +0.13 V (peak a) and +1.259 to +1.379 V (peak b) respectively. These results were comparable to results reported by (Masawat & Slater, 2007) [15] in the determination of tetracycline using 0.1 M potassium dihydrogen phosphate at pH 2 using a screen printed Au electrode. Anodic current peak varied linearly with the scan rate when tetracycline was treated with potassium dihydrogen phosphate buffer at an acidic Ph. Also the oxidation of tetracycline followed a diffusion controlled mechanism. Fig.7-b shows the calibration curve with the linear regression equation y = 0.0717x+0.5874 with a correlation coefficient $R^2$of 0.9606.

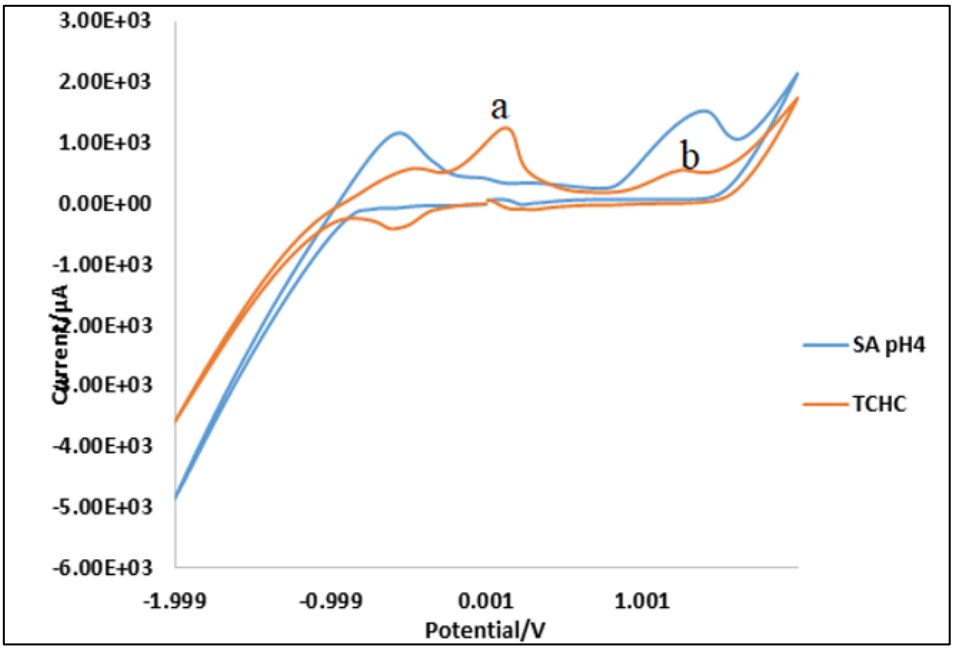

Fig 7 a. CV response of SA buffer with pH 4

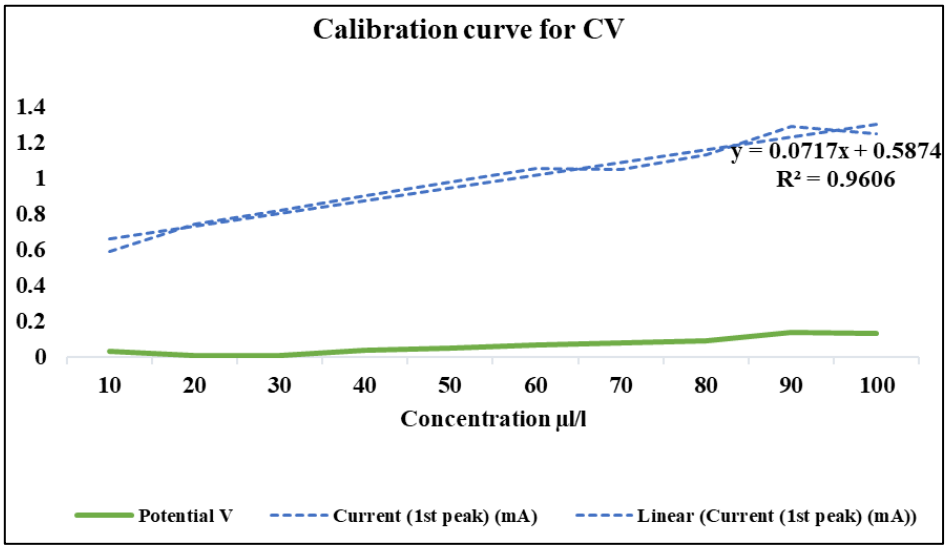

Fig 7b: CV Calibration curve at different concentration of TCHC

3.3 Differential Pulsed Voltammetry for TCHC detection

Fig.8-a shows the differential pulsed voltammogram of TCHC at different concentrations ranging from 10 µl/l to 100 µl/l. The potential scan from -2V to +2V, with step E of 0.01V, E pulse 0.2V, t pulse of 0.02 s and a scan rate of 0.05V/s. Fig.8-b shows the calibration curve for DPV at different concentration of TCHC with an R^2 value of 0.8225. The differential pulse voltammogram for TCHC in 0.1 N SA buffer at pH 4 showed a decrease in current peak from 0.466 mA (at a potential of 0.968 V) to 0.146 mA (at a potential of 0.829 V) as the concentration increases from 10 to 100 µl/l. At negative potential the increase in concentration of TCHC increases the current response whereas at positive potential the maximum peak current decreases with increasing concentration. However, as the oxidation of TCHC occurs at the potential around 0.9 V, the latter trend has been considered in this study.

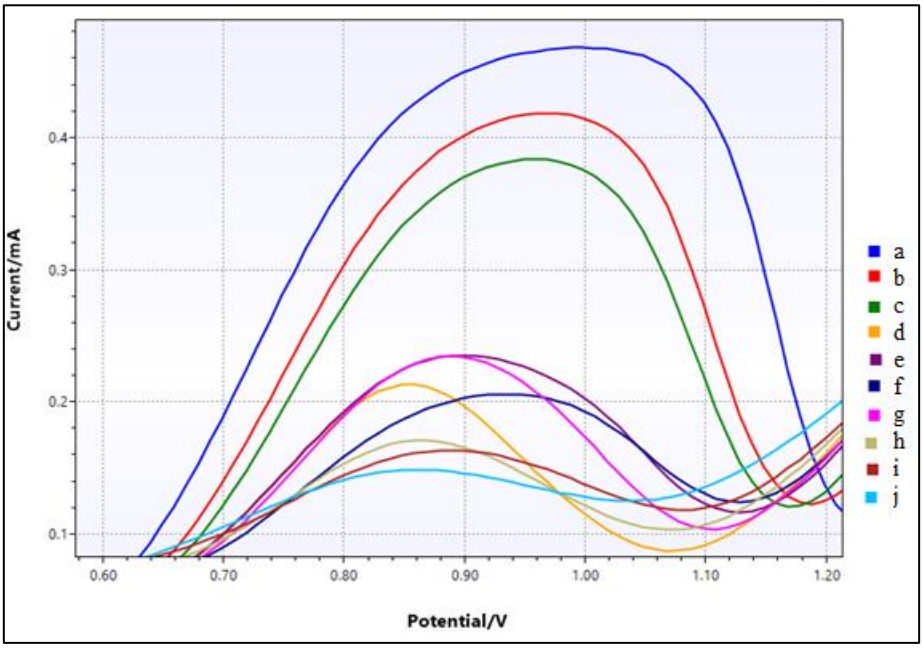

Fig 8a: DPV of different concentration of TCHC (a) 10 µl/l (b) 20 µl/l (c) 30 µl/l (d) 40 µl/l (e) 50 µl/l (f) 60 µl/l (g) 70 µl/l (h) 80 µl/l (i) 90 µl/l (j) 100 µl/l

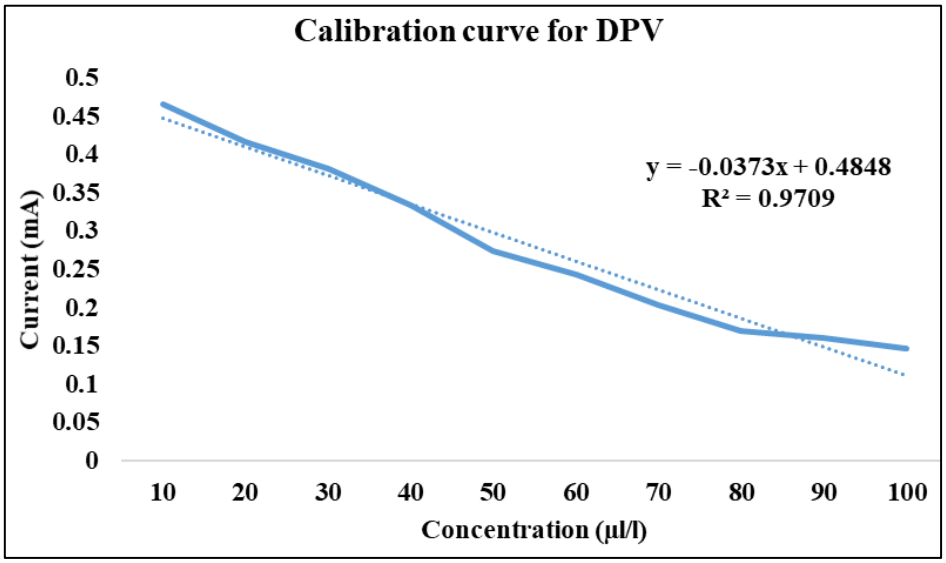

Fig 8b: Calibration curve for DPV at different concentration of TCHC

(Devkota *et al*., 2018) [7] reported a peak at 0.77 V was that of tetracycline oxidation in his work as no peak was recorded for the blank sample under the same experimental conditions. Preliminary studies by cyclic voltammetry showed an irreversible oxidation peak at the same potential. The oxidation peak increased linearly with the square root of scan rate. (Calixto *et al*., 2012) [4] observed a linear response at a concentration of 4.00-40.0 µmol l^{-1} with a LOD of 2.80 µmol l^{-1}using DPV for tetracycline detection in environmental water samples. The amount of H+ ions in the SA buffer also contributes to the peak potential and the current response in the oxidation of TCHC.

On comparing the fig.8-b and fig.9-b it was observed that the CV for TCHC oxidation shows an increasing linear trend whereas the DPV exhibited a decreasing linear trend.

3.4 Determination of tetracycline in honey

The above method of detecting tetracycline using SA buffer at pH 4 was applied for the determination of TCHC residues in honey. Honey samples were spiked with different

concentration of TCHC ranging from 10 µl/l to 100 µl/l. Using the calibration curve (fig.8-b) and the linear regression equation y= -0.0373x + 0.4848 with a correlation coefficient of 0.9709, the limit of detection was found to be 0.77 µl/l and their recovery was found to be ranging from 74 – 116.7% as shown in table 1. It was also observed that the recovery was found to decrease for concentration above 60 µl/l.

Table 1: Honey samples were spiked with different concentration of TCHC ranging from 10 µl/l to 100 µl/l.

Spiked (µl/l)	10	20	30	40	50	60	70	80	90	100
Found (µl/l)	7.45	15.62	25.42	37.13	57.41	70.03	72.85	86.42	86.77	88.03
Recovery (%)	74.57	78.11	84.74	92.83	114.83	116.72	104.07	108.02	96.41	88.03

4. Conclusion

The present study used 0.1 N SA as a buffer electrolyte for the detection of TCHC using a carbon screen printed electrode by differential pulse voltammetric technique. Some of the advantages of this method are easy sample preparation compared to the conventional analytical technique. The limit of detection of this SPE sensor using SA electrolyte was on found to be 0.77 µl/l with a percentage recovery ranging from 74-116%. The low cost, minimum reagent requirement and rapid detection with better accuracy make this method an alternative technique for tetracycline detection honey samples.

5. Acknowledgement

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