Homogeneous electron-transfer of chlorophyll and its derivative chlorophyllin at gold electrode

Transferencia electrónica homogénea de clorofila y su derivado clorofilina en un electrodo de oro

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SCIENTIFIC RESEARCH

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ABSTRACT

Introduction: Chlorophyll is a light harvesting pigment, which absorbs light in the visible spectrum of sunlight and promotes electron transfer, Chlorophyllin (CHL) is One of the most important derivative molecules of chlorophyll. Nowadays, chlorophyll pigment and its derivatives are utilised in organic photosynthetic solar cells for their desirable photovoltaic properties. Cyclic voltammetry (CV) is an essential technique. It is extensively used to study electroactive species to interpret the intermediates of reactions, supply information about the thermodynamics of oxidation-reduction reactions and elucidate the kinetics of electron transfer reactions**. Materials and Methods**: Prior to the electrochemical study, the working gold (Au) electrode surface was prepared by immersing it in the various concentrations of chlorophyllin for a period time. The electrolyte was degassed by using N_2 for approximately 30 minutes inside a Faraday cage before any electrochemical experiment was performed. A three electrode system was used with, Ag/AgCl as a reference electrode, graphite as a counter and the working electrode (Au). **Results and Discussion**: As a route to develop new chemical systems for artificial photosynthesis, this work reports the effectiveness of different parameters in transferring electrons between chlorophyllin (CHL) pigment and the working electrode surface (gold). These parameters such as the adsorption time, the electrolyte nature and concentration and chlorophyllin concentration are investigated. The use of chlorophyllin as a redox mediator is examined, with a gold electrode being employed. The importance of gold electrode surface preparation in determining the mechanism of redox is described, and the environment of adsorption process of the different concentrations of chlorophyllin on the surface of the gold electrode has been elucidated in this study. **Conclusiones**: The electrochemical method showed that the cyclic voltammetry responses of studied adsorption chlorophyllin pigment on the gold electrode were more efficient. In addition, the redox reaction was successful electrochemically in aqueous solution than the organic solution. It was suggested that electrons reduce to the chlorophyllin pigment by adding active species in the bulk solution homogeneous transfer. Finally, detections of chl on spinach leaves using various methods are reported.

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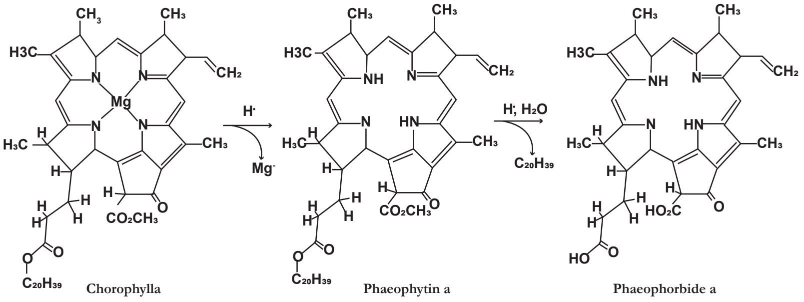
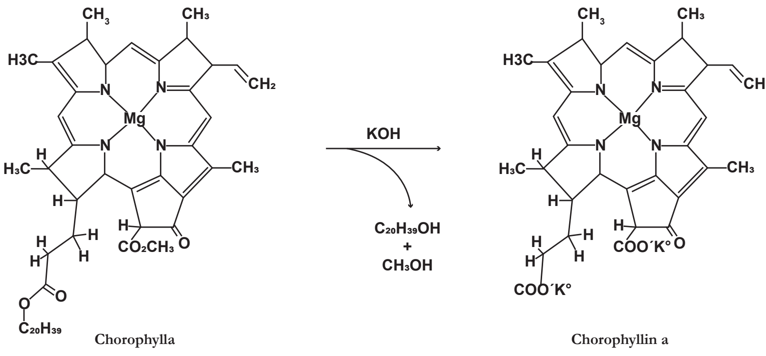
INTRODUCTION

Natural pigments play a crucial role in harvesting solar energy and converting visible light into electrical energy (1-4). The light conversion process is supported with sensitisation of numerous semiconductors by appropriate dyes (5, 6). Several organic dyes and metal complexes have been synthesised and used as sensitisers. Although the most effective sensitisers are ruthenium-based complexes, due to their properties, charge transfer between metal/ligand and absorption over wide visible range (6, 7), they are costly to manufacture and environmentally to pollute. Therefore, an alternative method is suggested such as natural dyes from plants and fruits with low cost, high light-harvesting efficiency and eco-friendliness (8-10). In this regard, several dyes have been used as sensitizers such as anthocyanins, carotenoids and chlorophyll which are easily extracted from natural sources (11, 12). Chlorophyllin (CHL) is the most critical derivative molecules of natural green pigment CHL (13), CHL as a hydrophilic molecule, is more soluble in water than chlorophyll and is more stable in moderate light, heat, oxygenated conditions, extreme absorption in the visible light and low pH (14-17). Chlorophyll and their derivatives are common light-sensitive compounds of photosensitizers and are selectively retained by tumour cells (18, 19). The therapeutic potential lies in the ability of the porphyrin structure to undergo photosensitization upon exposure to light. An illumination of the molecule converts it to a short-lived triplet excited state. Typically, sensitiser molecules in the triplet state can abstract an electron (or hydrogen atom) from, or donate an electron (or hydrogen atom) to, a substrate molecule. The anionic or cationic radicals of the sensitiser can then react with oxygen and form reactive oxygen species. These species rapidly react with some electron-rich molecules such as unsaturated lipids, amino acids, DNA-bases and so forth, thereby the interference with the normal activities of subcellular structures resulted in the injury and death of cells in proximity to the sensitiser molecule (20-23).

Green plant chlorophyll is considered to be the electronic centre of the photosynthesis process. This pigment captures solar energy and converts it into chemical energy through many steps (24-26). In addition, during this process chlorophyll acts as both a reductant and an oxidant due to its molecular structure (the central magnesium ion and a phytol chain), see mechanisms 1 and 2 (27):



Mechanism 1. *Chlorophyll a with acid*



Mechanism 2. *Chlorophyll a with base*

The donor-acceptor systems containing chlorophyll have, thus, been widely explored by various methods. These methods including self-assembled tetra pyrrole-carbon nanotubes for light-induced electron transfer applications, photo-induced ET between chl a and Au nanoparticles by fluorescence, polarisation transient grating technique on several chlorophylls as donor molecules and the redox potentials of chlorophylls using cyclic voltammetry (CV) and square wave voltammetry (SWV) (22, 28-30). Numerous investigations have been conducted on the activities of chlorophylls and their derivatives. Though, less research has been carried out on CHL. Novak et al. described oxidation mechanisms of CHL at a glassy carbon electrode using square-wave voltammetry. Therefore, more research should be done to understand the redox behaviour of CHL. Voltammetric techniques provide the comprehensive tools for investigation the electrochemical mechanisms of CHL(31).

Metallic electrodes such as gold (AuE), silver and platinum have usually been used while materials of graphite and its derivatives such as carbon are employed as supports (32-34). In spite of numerous reports of oxides on gold electrodes, they are useful in electrochemical applications especially sensors constrictions due to their properties such as chemical inertness, high electrical conductivity, flexibility for electrode manufacture and large potential (35-37). In the present work, effort has been made to investigate the electron transfer induce between modified electrode with either chlorophyll or its analogues (CHL) and some species in bulk solution.

The objective of the study was to see if the oxidation catalytic activity occurred between modified electrode with chlorophyll /CHL and an aqueous solution containing some active species such as CPZ. HCl, L-Cyst.H and KI in the presence and absence of Triton X100 and Vitamin K_1.

EXPERIMENTAL SECTION

REAGENTS

All chemical reagents were used in this research without further purification. Deionised water with 18 MΩ cm resistivity was used to prepare all aqueous solutions; the temperature was 20 ± 3 °C. The electrolyte solutions were purged for 10-30 minutes with nitrogen or Aragon. Standard solutions such as chl and CHL were prepared daily and protected from light by using aluminium foil.

Chlorophyllin, coppered trisodium salt, Hydrochloric acid >99.99%, Octyl phenol ethoxylate (TritonX100), Potassium iodide >99.99%, Phylloquinone (Vitamin K1), Acetone, Ethanol, Methanol, Hydrogen peroxide >30%, Sulphuric acid>95%, Methyl cyanide >99.9% , potassium chloride >99.9%, Argon gas 99.9%, Nitrogen gas 99.9%, were purchased from Alfa Aesar, Sigma-Aldrich, VWR chemicals(BDH), Fisher Scientific, BOC Gases, UK, Energas LTD

INSTRUMENTATION AND EXPERIMENTAL SETUP

The experimental equipment used in this research were potentiostats manufactured by Metrohm® µAutolab Type III and equipped with General Purpose Electrochemical System (GPES)10.1 software for all voltammetric measurements, written by Metrohm®. The temperature was maintained at 296 ± 0.5 K in the dark for all electrochemical experiments. In all cases, a conventional three-electrode system was employed in all experiments. Graphite as a counter electrode, and silver/silver chloride (3mol L^{-1}) as a reference electrode while a working electrode is a Metrohm® gold disk electrode, (2mm diameter, 80mm length). Prior to voltammetry, all solutions were purged with free N_2 or Ar gas for 30 minutes, while the experiments themselves were conducted under the stem of these gases atmosphere on the solution surface.

In all experiments, the redox reactions were undertaken at the surface of a working electrode. Therefore, the working electrode required frequent polishing by the appropriate size of carborundum paper (400, 1200 2400 grade, Presi, France) with 3µm alumina paste (Presi, France). Thus, reproducible results were obtained, and the absorbed species was removed from the surface of this electrode. The UV-Visible spectrometry was undertaken using a Perkin-Elmer (USA) UV-Vis spectrophotometer, (model Bio Lambda 10), with a clear quartz cuvette of path length 1 cm. The spectrometer was controlled using UV-Vis Chemstation software.

MODIFIED WORKING ELECTRODE (MWE)

In the past two decades, modifications of working electrodes have seen many widely differing applications in the electrochemical field. Through modification, the surface properties of the selected electrode, such as stability and sensitivity will improve, therefore it can be applied in particular areas such as electrochemical sensors and photoelectrochemical devices (38-41). The idea underpinning modified electrodes is to localise chemical reagents on the WE surface so as to keep a locally high concentration of reactant. This can be achieved by covering the electrode surface with a mediator solution and then allowing the mediator to evaporate (42, 43). Different compounds have been used to modify WEs in this way; some reaction requirements have been achieved such as electrocatalytic, electrochemical and photochemical properties (44-47).

Prior to each experiment, the gold disk substrate electrode was immersed for 10 minutes in piranha solution (3:1 proportion of sulfuric acid: hydrogen peroxide 30%). To form a smooth surface on the working electrode, it was polished with wetting cloth using 0.3µm alumina slurry for at least 60 seconds. It was then rinsed with distilled water and dried at room temperature before use in each experiment. The working electrode was modified by immersing in the chlorophyllin copper salt solution for a period ranging from two hours to three days. After that, the modified electrode surface was rinsed with distilled water, which was coated successfully with chlorophyllin before immersing in the appropriate solution. The solutions were degassed with high-purity nitrogen before the electrochemical measurements.

PREPARATION OF MEDIATOR ELECTROLYTE

A mediator electrolyte plays a crucial role in reducing the resistivity of the solution and overcomes the charged migration of electroactive species (48-50). Therefore, the mediator electrolyte must be inert and ionic for electrochemical work. In this study, a 50/50% ratio of aqueous/surfactant (hydrochloric acid-TritonX100) was used as supporting electrolyte. The mixture was heated, with vigorous stirring under nitrogen to 70^{o}C for at least two hours, and then the mixture was allowed to cool slowly to room temperature 25^{o}C, before further experiments that examined chlorophyllin, plant pigment and vitamin K_1.

PIGMENT EXTRACTION

The crude chlorophyll was extracted from fresh spinach leaves as described previously in protocols (51-55). The spinach was purchased from a local market. Spinach leaves (*Spinacia oleracea*) were separated from the stems, and then about 20 grams were weighed and mixed with an aqueous acetone solution [4:1(v/v) acetone/water], stirred for approximately two hours at room temperature. Following filtration, the solvent was removed using a rotary evaporator, and the resulting solid examined *via* UV/visible spectroscopy in ethanol which is absorbed light between wavelengths 300 and 800 nm.

RESULTS AND DISCUSSION

THE INFLUENCE OF ELECTROCHEMICAL PARAMETERS ON CHL ADSORPTION AT THE ELECTRODE SURFACE

Adsorption of the substance on the electrode surface is a phenomenon, which affects electrochemical signals. Conversely, on the electric field at an electrode surface may enlarge adsorption, with current signals that may trigger binding and unbinding of the analyte to the electrode. The binding is either a chemical bond (chemisorption) or a physical bond (physisorption). Chemisorption is stronger than physisorption, because it consists of ionic or covalent bonding of the molecules, whereas physisorption consists of weak intermolecular forces such as van der Waals' forces and dipole-dipole interactions (56, 57).

There are various conditions for the amount of active species which are adsorbed on the working electrode, such as the material of the surface, the nature of the molecules, the applied potential, temperature and so forth (58, 59). In the study presented here, some of these parameters are examined.

THE INFLUENCE OF ELECTROLYTES NATURE ON THE REDOX REACTION OF CHL

Cyclic voltammograms were recorded for the electrochemical redox reactions of 10 mM CHL on the gold electrode as working and Ag/AgCl as a reference electrode, graphite as a counter in 0.1 M for both inorganic (HCl) and organic (acetonitrile) electrolytes. Figure 1 illustrates the responses at the gold electrode, which was immersed in a CHL solution for two hours, followed by using an inorganic electrolyte (HCl) in an electrochemical cell.

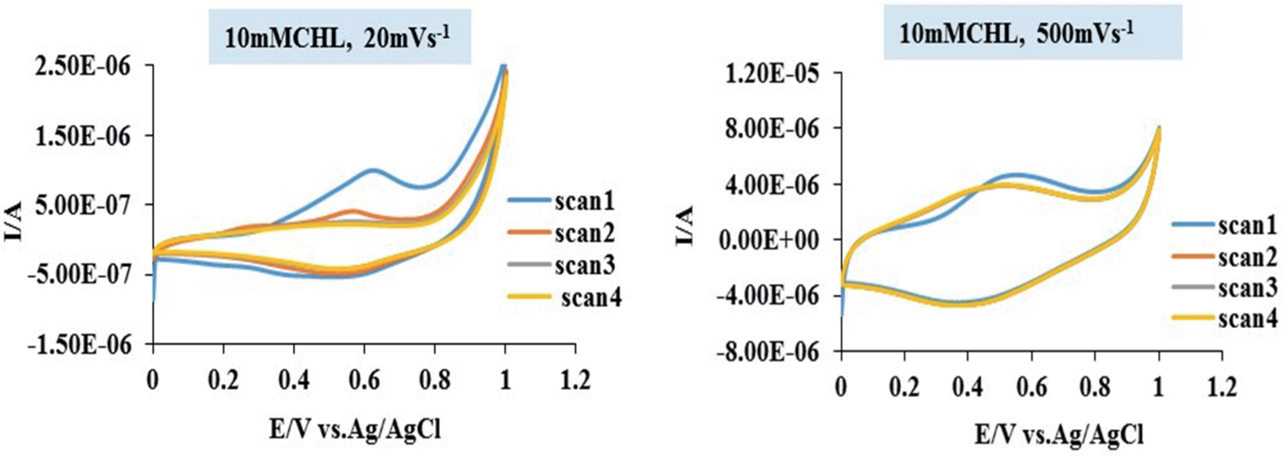
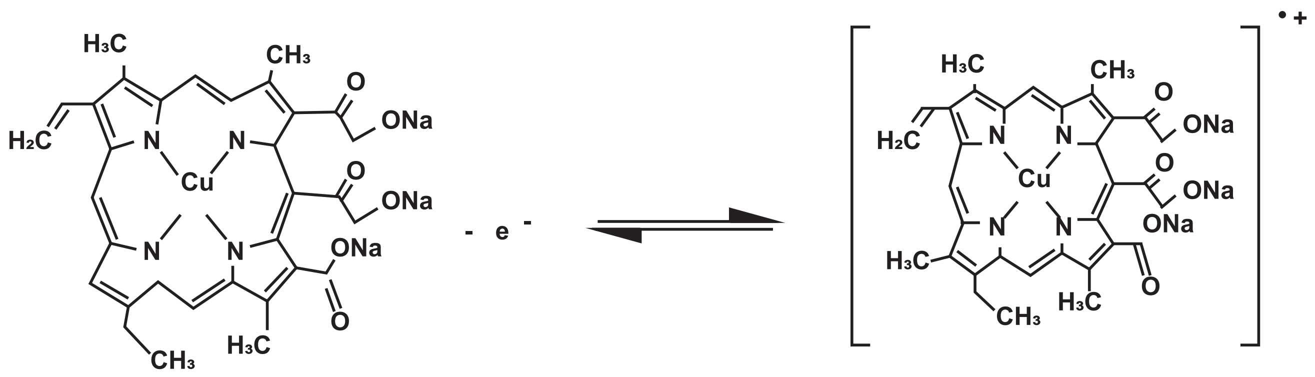


Figure 1. Cyclic voltammograms 20 and 500 mV s^{-1} are detailing the response of 10 mM CHL in 0.1 M HCl, which was adsorbed on the gold electrode for two hours

The voltammograms show a well-defined oxidation peak at +0.58 V due to the single-electron oxidation of CHL to form the chemically stable radical cation, which is shown in the Scheme 1. Here was an increase in peak current with increasing scan rates. Thus, the gold electrode was sufficient for adsorbing CHL pigment on its surface.



Scheme 1. *one electron oxidation of CHL to obtain the cation radical*

The redox catalysis of 10 mM CHL was carried out again in 0.1 M organic solution of acetonitrile (MeCN), as shown in Figure 2.

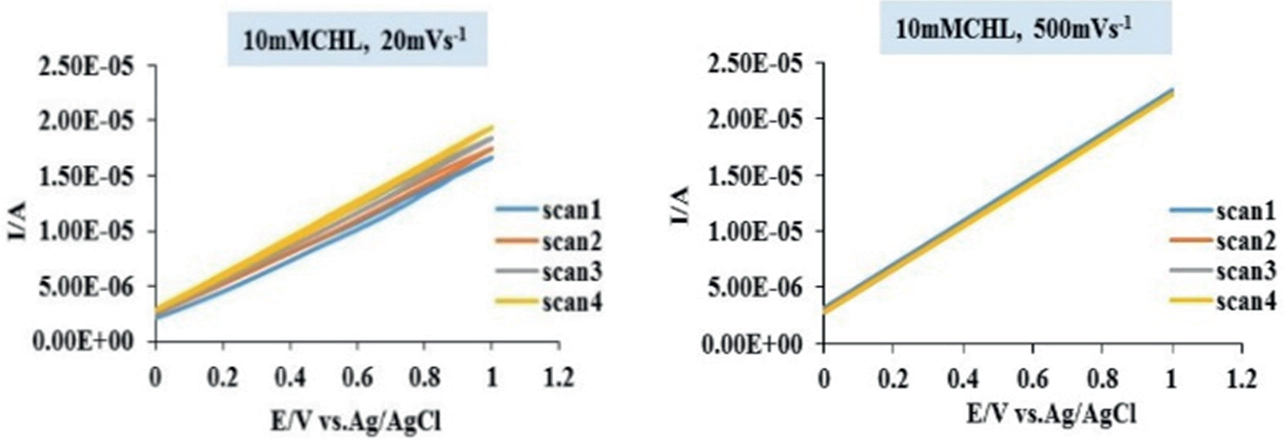


Figure 2. Cyclic voltammograms 20, and 500 mV s-1 detailing the response of the CHL (10mM) in 0.1M acetonitrile, which was adsorbed on the gold electrode for two hours

Figure 2 reveals that there were no analogous peak currents at all scan rates the response is pure resistance indicating that the solution lacks sufficient electrical conductivity.

VOLTAMMETRY OF ADSORBED CHL PIGMENT ON THE GOLD ELECTRODE IN CONSECUTIVELY TIMES

The voltammetry of adsorbed CHL was achieved by soaking the gold electrode in 10 mM CHL for two hours, and consecutively three times of ten minutes. After which it was rinsed with deionised water prior to undertaking voltammetry in 0.1M HCl using the same reference and counter electrodes as in the previous experiment, with scan rates 20 to 2000 mV s^{-1}. Figure 3 shows four consecutive voltammetry sweeps for the pigment above.

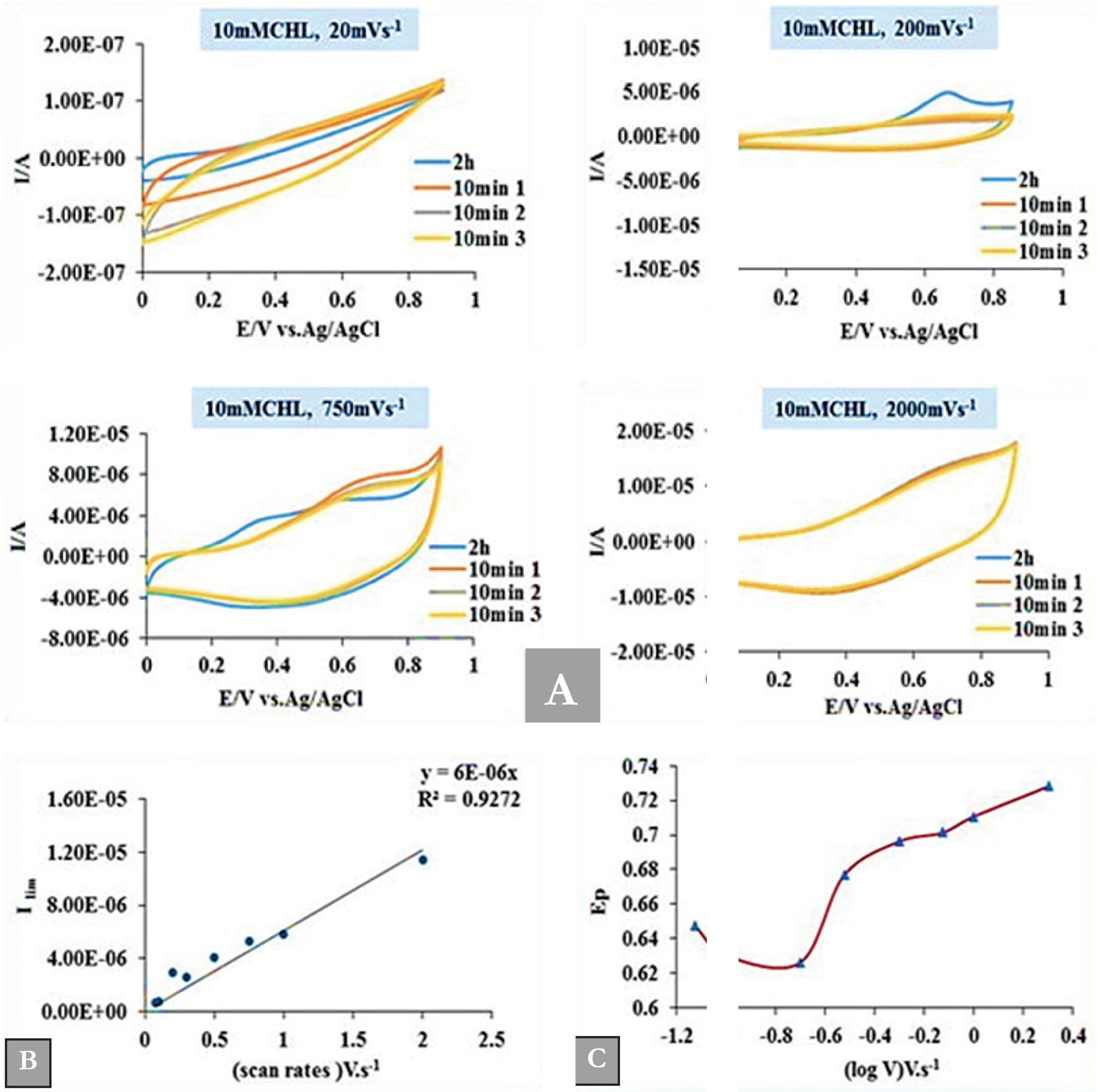


Figure 3. A. Scan rate dependence CVs of 10 mM CHL in 0.1 M HCl on AuE at 20-2000 mV s^{-1}, B. anodic current as a function of the scan rates (V) and (C). Potential as a function of the scan rates logarithms 20-2000 mV s^{-1}

Figure 3(A) demonstrates the oxidation peaks *via* scan rates of the system. There was an increase in the peak current, which was coupled with a slight positive shift in peak potentials with an increase in scan rates from 20 to 2000 mV s^{-1} and adsorption incubation time. A plot of oxidation peak current (I_{lim}) against scan rates, (B), shows a linear trend with coefficient value R^2 (0.9272), which is suggestive of control diffusion. While plot (C) performs a fluctuation in the oxidative peaks of potential *via* logarithm of scan rates, this means that the electron transfer process is complex.

Furthermore, the slight shift in potential with an increase in time adsorption for all scan rates highlights the one-electron oxidation of CHL is becoming more difficult, which indicates that there was no pigment adsorption on the electrode surface.

THE OXIDATIVE VOLTAMMETRY OF CHL USING SOME ELECTRO ACTIVE SPECIES

This part of the study will focus on the thermodynamics of the CHL pigment in bulk solution using cyclic voltammetry. Measurements were carried out in 0.1M HCl with the presence of some electro active species such as L-Cyst.H, KCl, and CPZ.H. These solutions were purged with a constant flow of N_2 at varying scan rates of 20-2000 mV s^{-1}, and the following explains this in detail.

CHL ADSORPTION ON GOLD IN THE PRESENCE OF L-CYST.H

The adsorption of CHL on AuE was tested with varying concentrations of L-Cyst.H 0.5, 1.0, 2.0, 5.0, and 10.0 mM . The curves at Figure 4 (a) shows the dependence of net peak currents of the adsorption of CHL at the AuE surface on the concentration of L-Cst.H. In low (0.5 mM) and high (5, and 10 mM) concentrations of L-Cys.H there are two anodic and cathodic peaks observed for all scan rates. The net peak potentials of the adsorption CV response shifted toward lower values by increasing the concentration of L-Cyst.H, indicating more facile electron transfer. Figur4 (b) shows the relationship between peak currents and scan rates for oxidative waves. The maxim current holds on approximate proportionally with scan rates as expected for surface-attached species. The plot of peak potentials *via* logarithms of scan rates for the oxidation peaks for all concentrations of L-Cyst.H as in Figure 5(c) generally, move to higher potential with increasing scan rate, suggesting a complex interplay between heterogeneous and homogeneous kinetics.

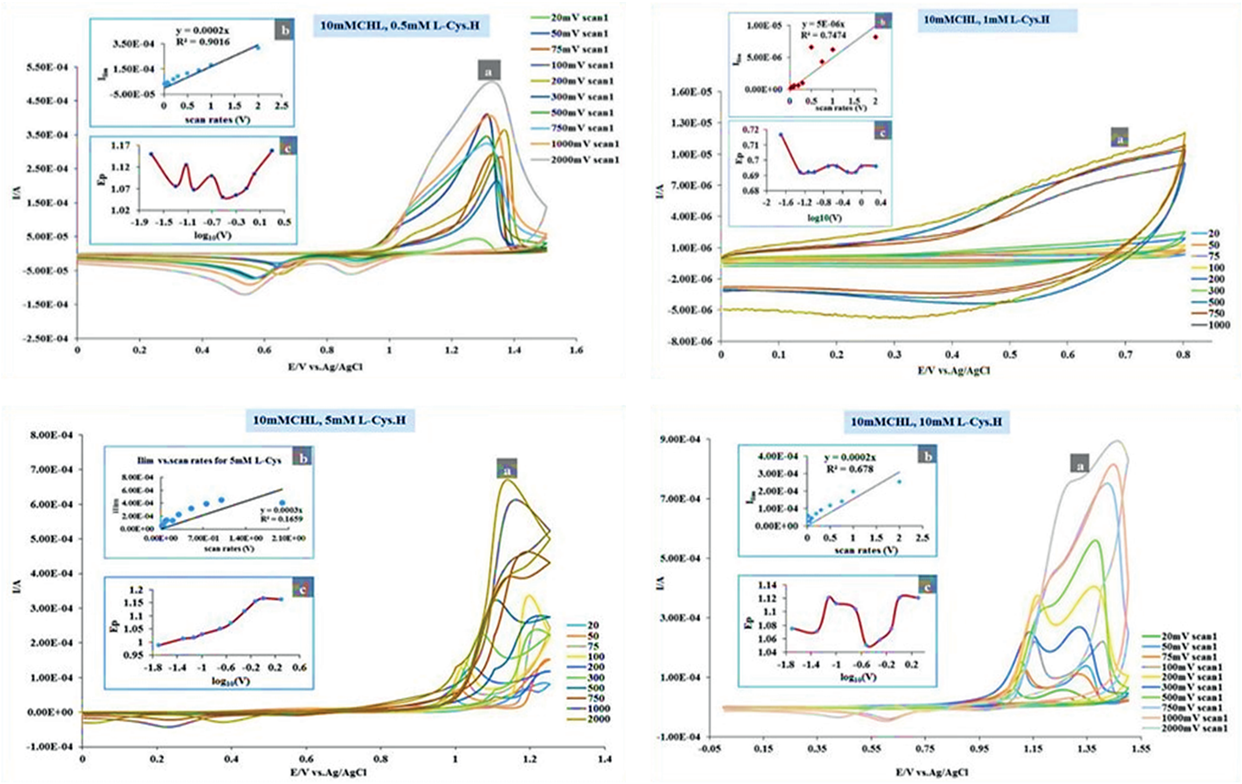


Figure 4. (a). Cyclic voltammograms for the oxidation of 10 mM CHL, two hours adsorption on the gold electrode with 0.5, 1.0, 5.0, and 10.0 mM L-Cyst.H in 0.1 M HCl. Scan rate 20-2000 mV s^{-1}. Ag/AgCl electrode served as the reference electrode, and graphite served as a counter electrode. (b). The corresponding plot of peak currents against scan rates for all concentrations of L-Cyst.H. (c). Corresponding plot of **peak** potentials against logarithms of scan rates for all concentrations of L-Cyst.H

Thus, further information on the oxidation process of CHL using L-Cyst.H at concentrations higher than 10 mM and lower than 0.5 mM was obtained. Here, the same procedure was undertaken as in the previous experiment, using 0.5 mM CHL and 20 mM L-Cyst.H, see Figure 5(a).

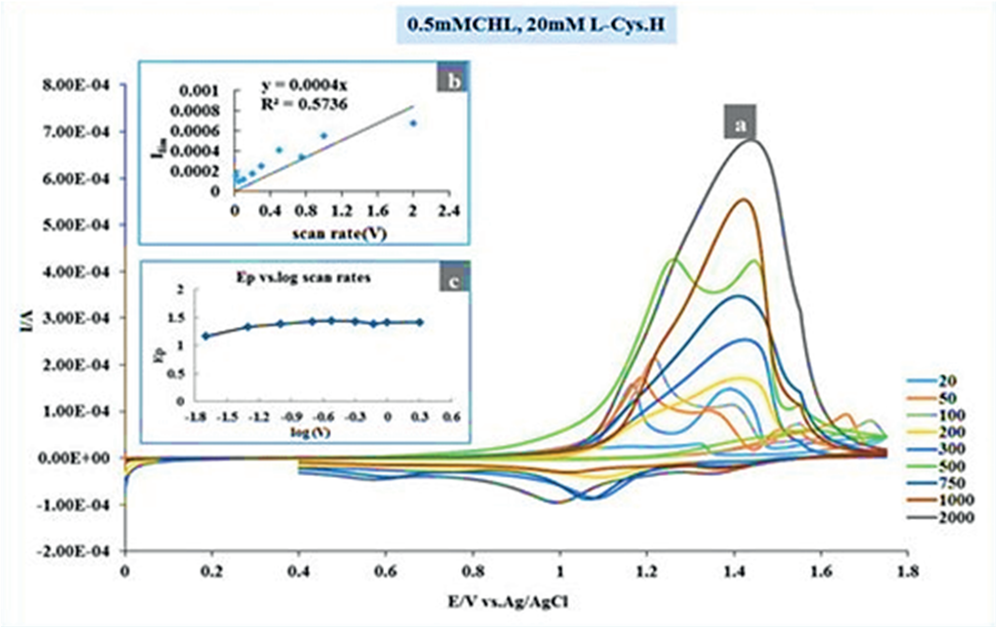


Figure 5. (a) CVs of the oxidation 0.5 mM CHL with 20 mM L-Cyst.H on AuE in 0.1 M HCl at variable scan rates (20-2000 mV s^{-1}). (b): The plot of peak currents vs. scan rates. (c): The plot of peak potentials vs log scan rates for the oxidation process

In Figure 5(a), there is the same trend as that of the oxidation of 0.5 mM L-Cyst.H. However, the peak potential (b) gives a different trend from that of 0.5mM L-Cyst.H, which confirms that the oxidation process of CHL on AuE is reversible with an increase in the concentration of L-Cyst.H.

Lower concentrations of L-Cyst.H (0.2 and 0.4 mM) were considered, again following the same conditions, using 100 mV s^{-1} scan rate, see Figure 6. It can be seen that the anodic peak, which is observed at 0.5 V, shifted to lower potential while the cathodic peak disappeared in this scan rate. In addition, it can be concluded that the reaction is chemically irreversible at low concentration of L-Cyst.H.

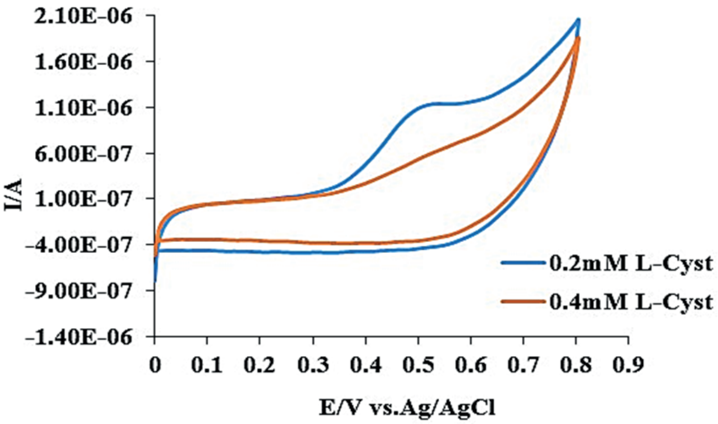


Figure 6. CVs of the oxidation 10 mM CHL with 0.2 and 0.4 mM L-Cyst.H on AuE in 0.1M HCl at 100 mV s^{-1} scan rate

CHL ADSORPTION ON AUE IN THE PRESENCE OF POTASSIUM IODIDE KI

Again, cyclic voltammetry for another active species was examined. Figure 7(a) illustrates four curves of different concentrations of KI (0.01, 0.05, 0.1, and1.0 mM) with 10 mM CHL in an aqueous solution of 0.1 M HCl. The peaks in the oxidative- reductive currents were observed for all concentrations of KI, which suggests that the redox process is reversible. Moreover, the linear voltammograms for concentrations 0.01 and 0.05 mM of KI in the plot (b) mean that the reactions are under diffusion control. The fluctuations in the peak potentials *vs* log scan rates plot in (c) confirm the reversibility of the redox process, albeit with a much experimental error in potential measurement. This likely stems from the difficulty in reproducing the surface coverage.

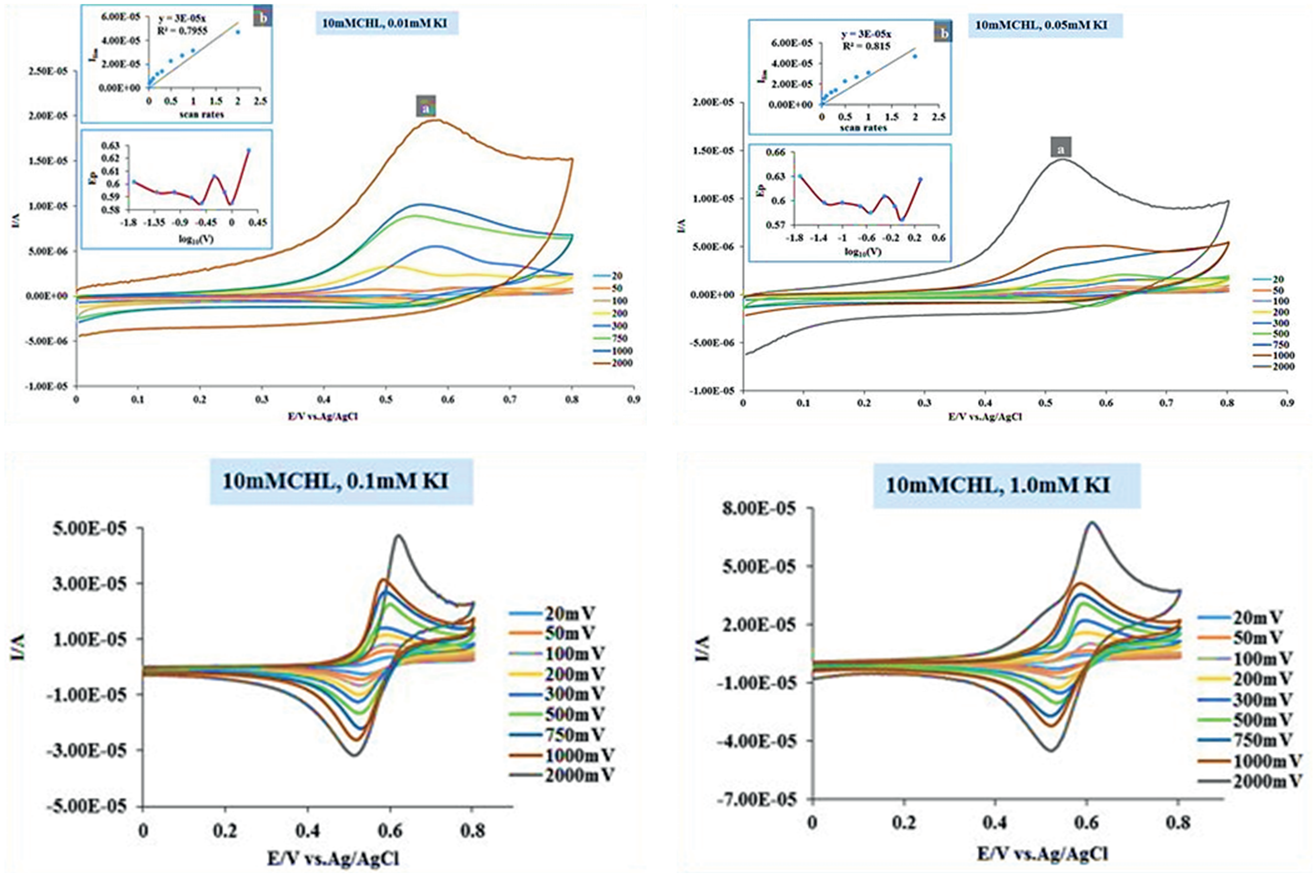


Figure 7: (a): Typical CVs observed for 10 mM CHL with varying concentrations (0.01, 0.05, 0.1 and 1.0 mM) of KI at different scan rates 20-2000 mV s^{-1}. (b): The plot of peaks current against scan rates and (c): The plot of peaks potential against logarithms of scan rates for the oxidation process

CHL adsorption on AuE in the presence of CPZ.HCl

The electrochemical work with CPZ.HCl was undertaken in 0.1 M HCl at AuE after soaking for two hours in 10 mM CHL pigment. This work shows a similar trend to that of the previous electroactive species, L-Cyst.H in the cases of peak currents and potential responses, see Figure 8 (a, b and c).

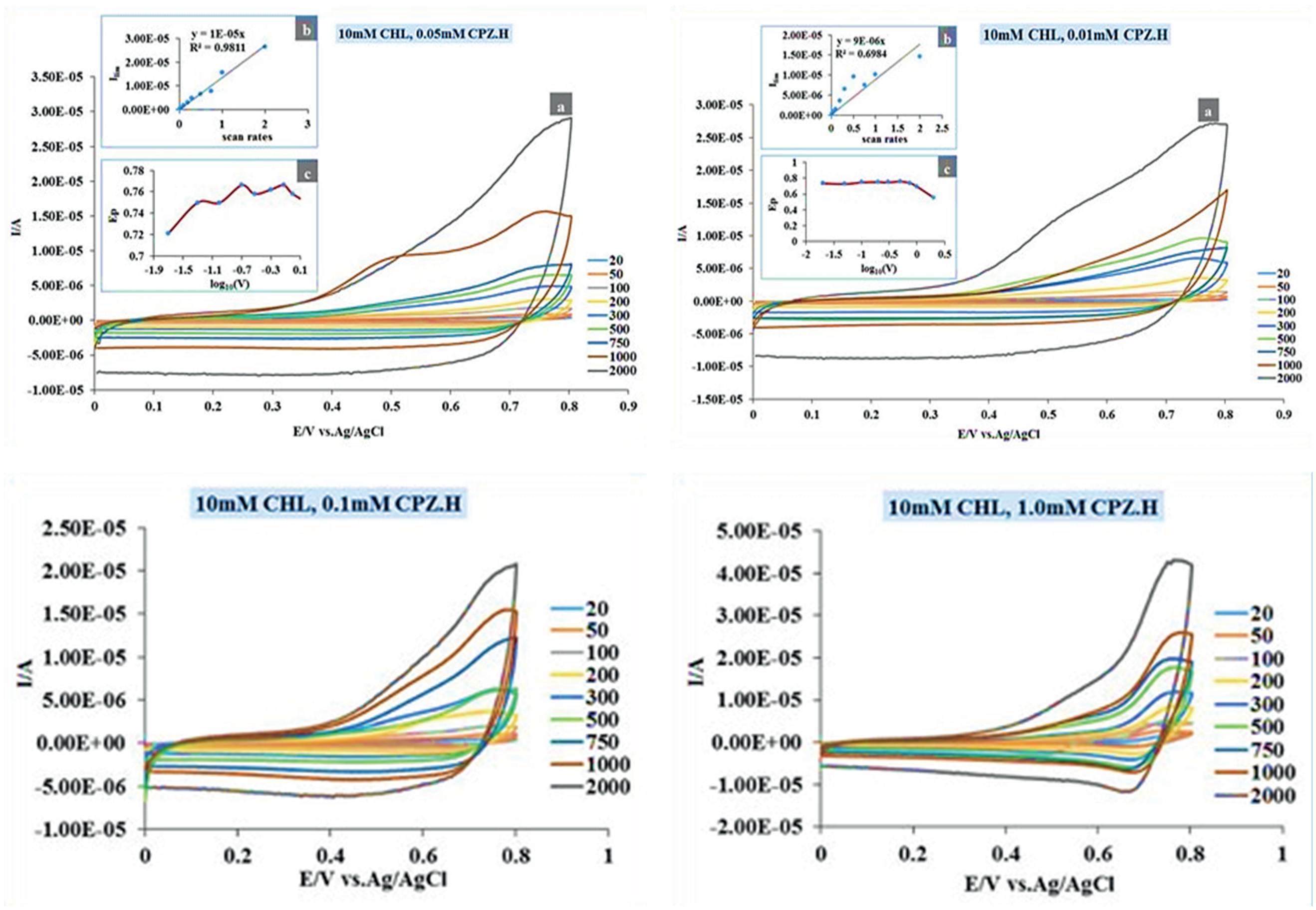


Figure 8. (a). CVs of 10 mM CHL with varying concentrations of CPZ.H at different scan rates 20-2000 mV s^{-1}, (b). The plot of peak current against scan rates and (c). The plot of peak potential against logarithms of scan rates for the oxidation process.

As a result of using different electroactive species, it is clear that the best one is KI due to the correspondence in both current and potential peaks. The reactions on the electrode surface were taking place between adsorbed CHL and active molecules. Thus, the reaction in the bulk solution will be the next study.

ELECTROCHEMICAL STUDIES OF CHL IN THE BULK SOLUTION

The above study investigated the electrochemistry of CHL on the electrode surface. In this part, we will first elucidate the electron transfer in the bulk solution between CHL and a more easily oxidised substance such as KI in the presence and absence of anionic surfactant such as Triton X 100. Secondly, we will extract chlorophyll pigment from fresh spinach and then study its characteristics in the presence of vitamin K$_1$ and Triton X 100. The latter material will enhance the electrochemical reaction by reducing the surface tension at the electrode surface or the electrode/electrolyte interface, thus making molecules spread more easily.

VOLTAMMETRY OF CHL WITH THE INTRODUCTION OF SURFACTANT

The electron transfer between electroactive species in bulk solution was elucidated. The initial examination was the effect of Triton X 100 on the electron transfer of CHL at various concentrations (0.05, 0.1, 0.2, and 0.5 mM) in 0.1 M HCl by using cyclic voltammetry, see Figure 9 (A).

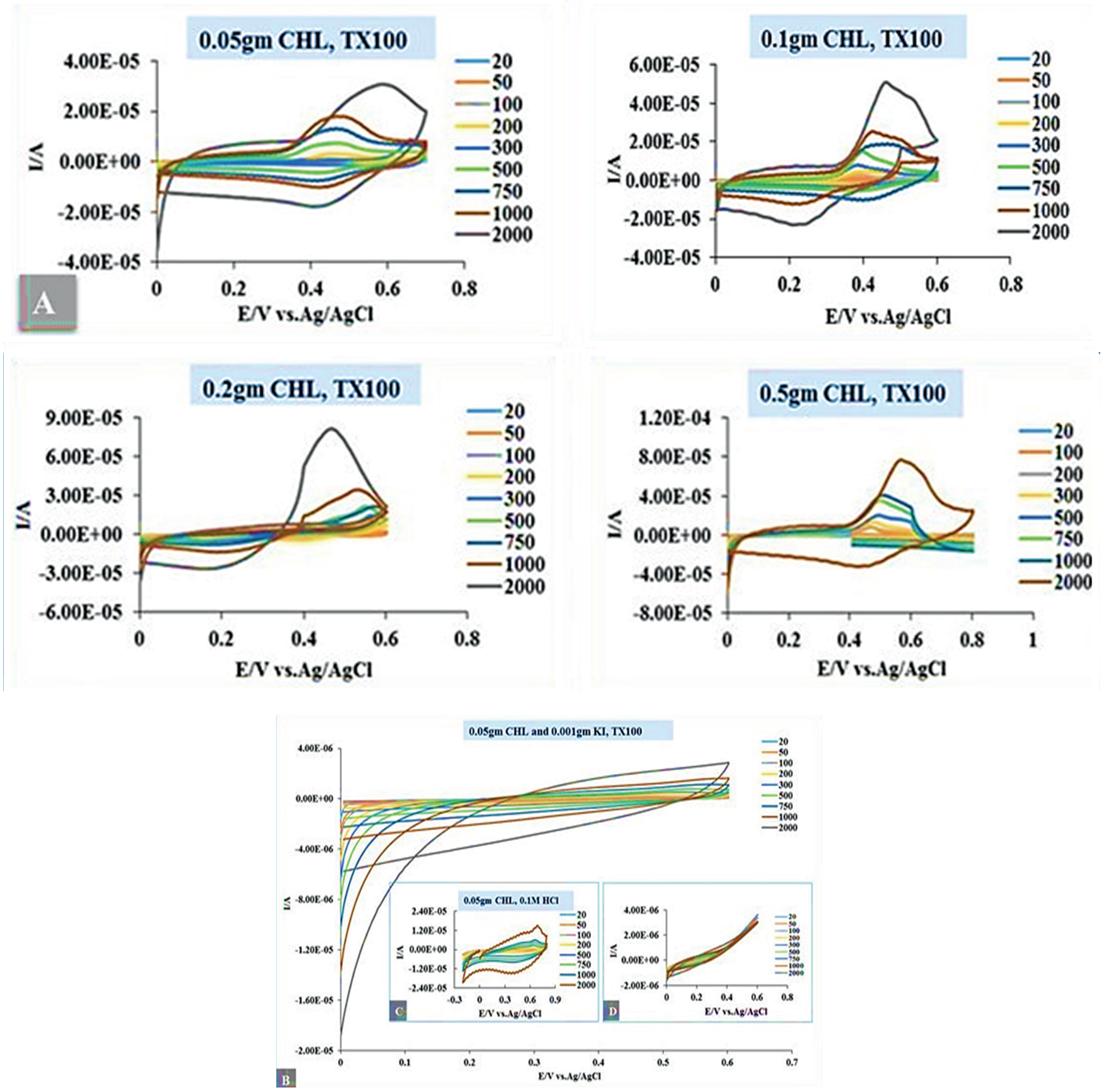


Figure 9. (A): CVs of varying concentrations of CHL in aqueous solution with T X 100 presence at different scan rates (20-2000 mV s^{-1})), (B). CVs are detailing 0.05 gm CHL in an aqueous solution containing 0.001 gm KI and 50% T X 100. Inset, (C). CVs of 0.05gm CHL in 0.1M HCl and (D). CVs of T X 100 in solution involving 0.05 gm KI

The forward and reverse peak currents of the response of CHL were increased in the presence of T X 100 in all concentrations (Fig.A). These peaks are positioned with a slight negative shift in potentials with increasing scan rate as compared with (Fig.C), suggesting that some materials were absorbed on the electrode surface. To understand the process in more detail, the scan rate dependent experiment of CHL oxidation was undertaken in the presence of TX 100 and an active species such as KI, see (Fig.B). It can be seen that the oxidative and reductive peaks current are not clear, which means that the electron transfer process in bulk solution is not readily apparent. Single-electron-oxidation between active species in the bulk solution can be assumed following this mechanism:

$$CHL - e^{-} \leftrightharpoons CHL^{+}$$

$$I^{-} - e^{-} \leftrightharpoons \frac{1}{2} I_2$$

$$CHL^{+} + I^{-} \leftrightharpoons CHL + \frac{1}{2} I_2$$

Mechanism 3. *Single-electron transferring in bulk solution*

Fig.C shows the response of CHL pigment in an aqueous solution only; there is a well-defined oxidation peak at +0.65 due to the single oxidation on the gold electrode itself to form the stable chemical cation, shown in the below mechanism:

$$6Cl^- + Au - 3e^- \leftrightharpoons Au_2\,O_2(s) \rightarrow Au^{+3}\,(aq)$$

Mechanism 4. *One-electron oxidation on the gold electrode surface*

To determine whether the same effects are observed using TX 100 to enhance the electrochemical process, the voltammetry of hydrophobic molecules such as chlorophyll and vitamin K_1 in the acidic electrolyte will be examined next.

CHLOROPHYLL: ABSORPTION SPECTRA AND ELECTROCHEMICAL REACTION

Chlorophyll was extracted from fresh spinach leaves using the procedure described in experimental section. Figure 10 (A and B) the left side show the wavelengths of a standard sample of chlorophyll and its structure, while (C) shows the recording of the absorption spectrum of chlorophyll in spinach leaves made with a UV-Visible spectrophotometer.

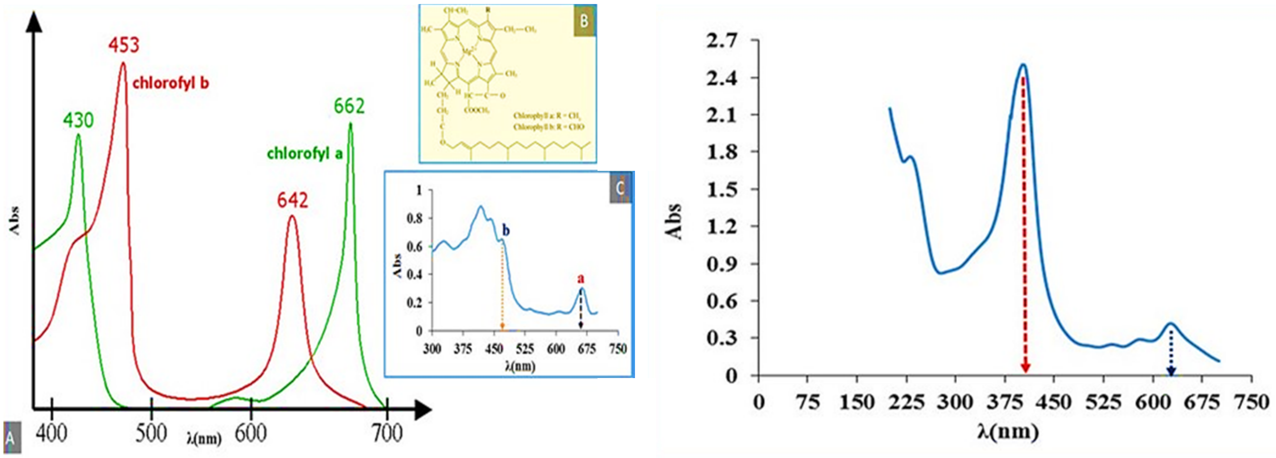


Figure 10 the left side: A. Typical wavelength of chlorophyll, B. Chlorophyll structure and C. wavelength of chlorophyll in the fresh spinach leaves. The right side: Absorption spectrum of chlorophyll derivative (chlorophyllin)

It is clear that the principal bands of chlorophyll a and b in the typical sample are in a similar position in the extracted pigment, while Figure 6.10 presents the shifting to low wavelength in both of these bands for chlorophyllin due to the changing in it structure.

ELUCIDATION CV$_S$ IN THE SYSTEM OF (EXTRACTION PIGMENT, TX 100 AND VITAMIN K$_1$)

The cyclic voltammetry of the extracted pigment (chl) in the presence of TX 100 and vitamin K_1 was examined. Figure 6.11 (**A**) illustrates voltammograms in varying scan rates (20-1000 mV s^{-1}) corresponding to the redox reaction on the surface of the AuE with 50% by weight of TX 100 in 0.1 M HCl. As shown in the same figure (insets B and C), both oxidative and reductive peak currents increased with the increase in scan rates. Both forward and backward peak potentials remained in the same position, indicating that the product in the surfactant phase is stable, although vitamin K_1 is expected to reside within T X 100 due to its hydrophobic property. In addition, single-electron transfer between chl and vitamin K_1 becomes easier. The mechanism of this reaction is shown below:

$$chl - e^- \rightarrow chl^+$$
$$chl^+ + VK_1 \rightarrow chl + VK_1{}^+$$

Mechanism 5. *Chlorophyll with vitamin K1*

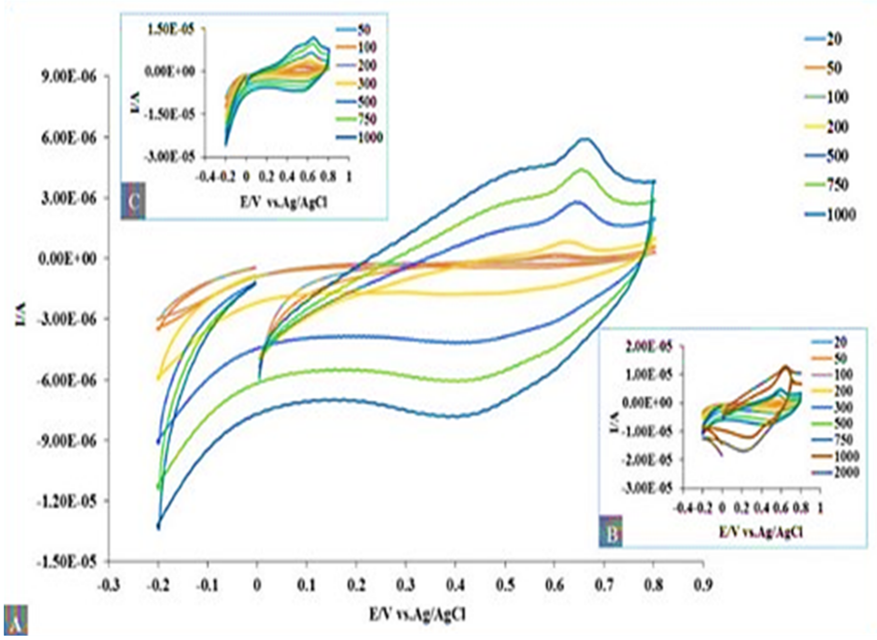


Figure 11. (A). CVs of TX100 in aqueous 0.1 M HCl at different scan rates 20-1000 mV s^{-1}.
Inset (B). CVs of (A) detailing of 0.0075 gm chl and (C): CVs of (B) in the presence of vitamin K_1

CONCLUSION

The electrochemical method showed that the cyclic voltammetry responses of adsorbing chlorophyllin pigment on the gold electrode occurred more easily in the aqueous solution than the organic solution, for all scan rates and adsorption times. Adsorbed chlorophyllin was able to participate in an electron transfer relay with iodide. The mechanism of the reaction was suggested to be a one-electron transfer. Overall, the first CV response of the environment of the gold electrode/ chlorophyllin dye interface was considered to be a quasi-reversible process and corresponds to the one-electron formation of radical cations in HCl solution.

In the second part of this study, the objective was to see if electro-induced, electron transfer process occurred between either extracted chlorophyll or chlorophyllin and some active species. It has been shown that, although the oxidation behaviour of the electroactive species potassium iodide is easy to see regarding the responses of current and potential peaks, it was electrochemically sufficient. Moreover, for the case of the redox reaction of the chlorophyll pigment in an aqueous solution of HCl in the presence of Triton X 100 and vitamin K_1, it was observed that both peaks current and potential increased with increase in the scan rates of potential due to the role of the surfactant in the bulk solution. The last part of this study has described the behaviour of extracted chl and CHL in KI solution with and without Triton X 100 and vitamin K_1. The results established that TritonX100 enhanced electron transfer in bulk solution due to the correspondence of the peak current and peak potential, while potassium iodide inhibits it in the previous solution. Finally, the mechanism of the reaction was suggested to be one-electron transfer; it is EC' reaction.

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