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# Electrochemical Detection of Aloe Emodin using Platinum Electrode Based Voltammetry Technique

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## ABSTRACT

In this work, a noble metal based platinum (Pt) electrode has been explored to detect one of the important phytochemical Aloe Emodin (AE) in Liliaceae family. A sensitive three-electrode system was equipped to assess the electrochemical behavior of AE using Pt electrode as a working electrode along with silver/silver chloride (saturated KCl) and a steel as a reference electrode and a counter electrode, respectively. The redox response of Pt electrode against AE was analyzed using cyclic voltammetry (CV) at a scan rate ranging from 0.01 $Vs^{-1}$ to 0.4 $Vs^{-1}$ that showed well-defined reversible peaks in phosphate buffer saline (PBS at pH 6.0). Under optimized experimental condition, DPV peak currents were linear over concentration range 1 µM -150 µM with $R^2$ value of 0.987 In addition, the sensitivity of the electrode was excellent with sensitivity factor of 1.3 A/M and the limit of detection (LOD) was obtained 0.2 µM. Principal component analysis (PCA) was performed on the response data to demonstrate diverse discrimination of different concentration of AE. The developed sensor showed excellent repeatability and can be successfully used to detect AE in Aloe.

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**Keywords:** Aloe Emodin, Platinum Electrode, Cyclic Voltammetry, Differential Pulse Voltammetry, Principal Component Analysis

## Introduction

Since from medieval times to till date almost 80% of the population in some Asian and African countries till habits traditional plant materials and its extracts as complementary for their primary health due to the presence of pharmacological effects as reported by World Health Organization (WHO). Varieties of phytochemicals found in those medicinal plants stimulate the discovery of drugs and traditional medicines [1-4]. Anthraquinones is a commanding aromatic compound in the class of naturally arising phenolic compounds based on 9,10-anthraqunone skeleton [5-6]. Among 79 naturally occurring anthraquinones, Aloe Emodin (1,8-dihydroxy-3-hydroxymethyl-anthraquinone), is one of the naturally occurring anthraquinones mainly found in Aloe, Rhheum, and Rhamnus genera plants [7-9]. Aloe Emodin (an isomer of Emodin shown in Figure 1), holds enormous range of bioactivities, such as laxative, anticancer, anti-inflammatory anti-microbial, anti-aging, antioxidant, antitumor, diuretic, and phytogenic activities that leads to clinical uses for many diseases [10-16]. Besides, this naturally produced phytochemical has immense attention due to abrupt consumption through herbal drugs as an alternatives to modern medicine [13]. Again, due to harmful side effects of commercial chemotherapeutic drugs, AE shows anti-proliferative activity by producing cytotoxic effects, cell cycle arrest and apoptosis, immune signalling regulation in human tongue and breast cancer cells without damaging normal cells [17-20]. Literature survey revealed numerous studies for the quantitative and qualitative estimation of AE by Thinlayer chromatography (TLC), High Performance Thin Layer Chromatography (HPTLC), Solid-phase extraction coupled with HPLC analysis, Capillary Electrophoresis (CE), Gas Chromatography/Mass Spectrometry (GC/MS), and in combination by HPLC [21-26]. But these techniques are complicated to determine the amount of each compound in an herb because of existence of many active components in it. Also, these analytical methods require costly and complex instruments along with elongated periods of time for extraction and quantification.

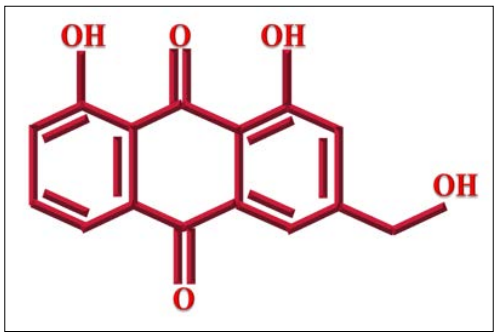


**Figure 1:** Chemical Structure of Aloe Emodin (AE)

It is important to establish a simple, rapid and accurate quantitative and qualitative method for the detection of AE found in medicinal plants as well as commercial formulated products. To resolve these issues, electrochemical techniques have been proven to be an excellent analytical tool in chemistry field for monitoring of organic molecules in pharmaceutical and biological samples due to its simple operation technique, low time consumption, robustness,versatility, and highest sensitivity with excellent selectivity, fast response, real time detection and no sample pre-treatmentssteps, Voltammetry is proven to be the best among the existing electrochemical methods like potentiometry, conductometry, spectrometry etc. due to its higher sensitivity [27]. Tiwari et al. and Bhattacharyya et al. used this technique to discriminate honey and black tea liquor, respectively [28-29]. To the best of our knowledge, no voltammetric detection technique with platinum as working electrode was used for the determination of Aloe Emodin.

In the proposed work, voltammetric system was used to detect the AE in three-electrode system comprising of a platinum working electrode (2.5 mm inner diameter), an Ag/AgCl reference electrode, and a steel counter electrode. Here, Pt wire was used as a working electrode due to its excellent corrosion resistance to oxidation and capable to pass current without forming any surface insulating layer. The principal component analysis (PCA) was used to established qualitative discrimination between several concentrations of Aloe Emodin.

## Experimentation

### Chemical and Reagents

Aloe Emodin (Molecular mass of 270.24 g/M) was purchased from Sigma-Aldrich, India. Standard stock solution (1 mM of AE) was prepared by directly dissolving 0.027024 g AE in 100 mL ethanol through ultra-sonicator in a volumetric flask and then preserved in refrigerator. All other lower concentration of AE required for experiment was prepared by simple dilution with ethanol. Platinum wire was received from ERH, India. Ethanol was purchased from Merck, India. Millipore water used for preparing solutions was received from Merck Millipore system (Resistance of about 18Ω). Phosphate Buffer Saline (PBS), Citrate Buffer saline (CBS) and Acetate Buffer Saline (ABS) having concentration 0.1 M were prepared in laboratory and were used with Aloe Emodin solution for measurement. For the preparation of supporting electrolyte, 0.1 M $Na_2H_2PO_4$ and $NaHPO_4$ were used and pH was adjusted by NaOH/HCL. All the chemicals used in this work were pure and analytical grade. Whole experiment was conducted in room temperature.

### Preparation and Activation of the Platinum Electrode

Platinum wire (length: 15 mm) was used a working electrode. One end of this electrode was connected with copper wire to make electrical contact. Platinum wire was first polished with emery paper very carefully. The open platinum wire tip was immersed in aqua regia for few minutes and then rinsed with Millipore water. In order to obtain stable and sensitive response, the surface of the as-prepared platinum wire was pretreated by CV scan for 10 times in PBS 6.0 solution.

### Apparatus and Instruments

Analysis of AE was carried out using three-electrode system composed of a platinum wire working electrode, an Ag/AgCl reference electrode, and a steel counter electrode (Figure 2). A computer controlled AutolabPGSTAT1010 with software NOVA 1.11 (MetrohomAutolab) was used for this electrochemical measurement for the graphical analysis of CV and DPV data. An ultrasonicator (Labman scientific Instrument) was used for sonicating required chemical solutions used in the experiment.

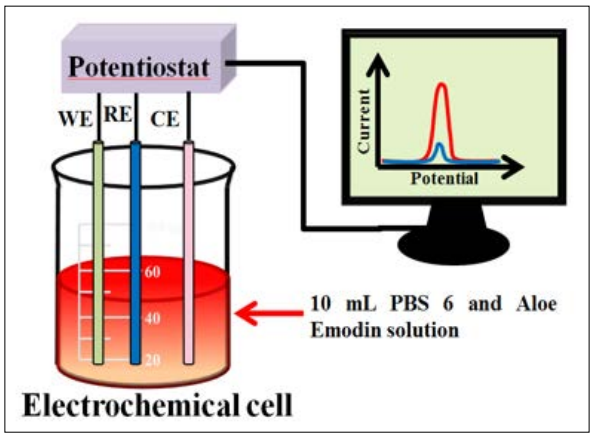


**Figure 2:** Voltammetric Cell Setup with Three Electrode Configuration

### Data Analysis

The voltammograms data obtained from NOVA 1.11 was analysed using MATLAB and Origin software. Electrochemical behaviour of Pt electrode was analysed by using PCA tool. Four measurements were taken for each of five concentrations 1µM, 10 µM, 50 µM, and 100 µM in 10 mL AE solution containing PBS 6.

### Measurement Procedure

Electrochemical measurement was performed by using 10 mL PBS of selected pH containing required concentration of AE in three electrode voltammetric cell. The potential is applied between Pt and Ag/AgCl electrode and anodic and cathodic currents were measured between Pt and steel electrode. This measured current versus potential plot showed two reversible redox peaks due to the diffusion of AE molecules to the surface of the working electrode.

## Results and Discussion

### Electrochemical Behaviour of Pt Working Electrode

Cyclic voltammetry technique was used to detect AE at Pt working electrode. 100 µM of AE was used in cyclic voltammetric measurement in the presence of PBS at pH value of 6.0 supporting electrolyte over the potential range -1.4 V to 0.7 V at scan rate of 0.05 $Vs^{-1}$. The recorded cyclic voltammogram shown in Figure 3 depicts a pair of two redox peaks in the presence of target molecules AE, whereas in the absence of AE molecules in the solution, peak vanishes. An anodic peak was seen at potential -0.051 V with peak current 0.54 mA. A cathodic peak was observed at -0.53 with peak current 0.47 mA that confirms the electrochemical reaction with target molecules AE.

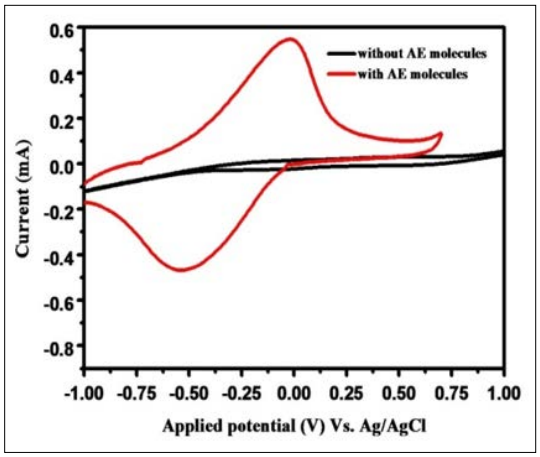


**Figure 3:** Cyclic Voltammogram of Pt Working Electrode with and without AE in PBS

**Effect of Buffer Variation**

Cyclic voltammetry investigation of Pt electrode with different buffer solution was conducted over the potential range -1.4 V to 0.7 V at scan rate of 0.05 $Vs^{-1}$ to analyse the effect of buffer solution to detect AE (100 µM) at Pt electrode. Maximum response was achieved in PBS buffer with peak current 0.58 mA at PBS 6.0 at a scan rate of 0.05 $Vs^{-1}$ as compared to CBS and ABS as shown in Figure 4.

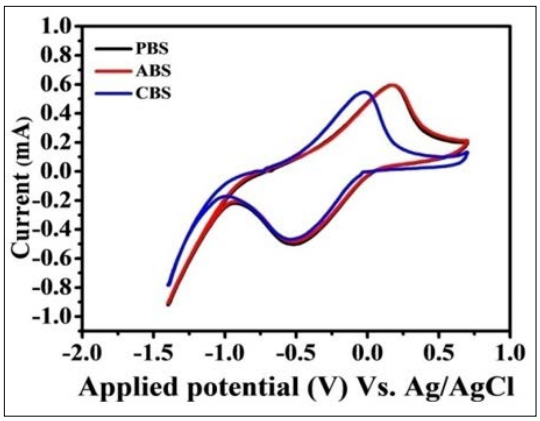


**Figure 4:** CV of Different Buffer Solution containing 100 µM

**The Effect of pH Variation**

The effect of pH on cyclic voltammogram peak of AE was investigated in 100 µM AE with different pH value. The cyclic voltammetric response of AE is strongly dependent on the pH of the solution. There is a sharp increase of peak current over pH range 3 to 6 and then decrease with the increase of pH value as shown in Figure 5. The peak potential was shifted towards more negative values as pH value of the solution was increased, indicating that electrochemical process involving protons. Inset shows a linear plot of $V_p$ vs pH with corresponding linear regression equation of $V_p(V)$=0.065pH+0.423 ($R^2$=0.963). The slope value of 0.065 $VpH^{-1}$ was close to the Nernstain hypothetical value (0.0556 $VpH^{-1}$) indicating the involvement of equal number of protons and electrons.

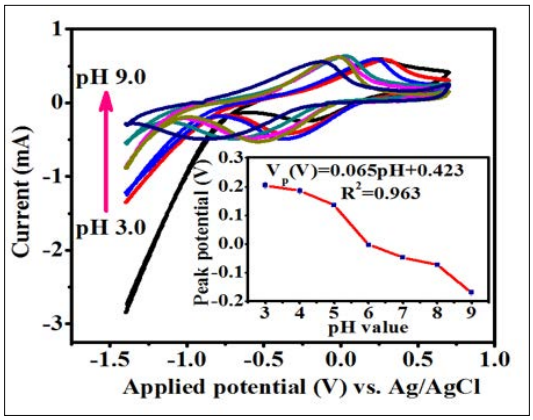


**Figure 5:** CV of PBS Buffer with Different pH Value (Inset: Anodic Peak Potential vs pH)

**The Effect of Scan Rate Variation**

The scan rate effect on peak current and peak potential of emodin was studied by using cyclic voltammetric procedure at the Pt electrode over the ranges of 0.01 $Vs^{-1}$ to 0.4 $Vs^{-1}$. Fig. 6(a) shows small adsorption of emodin molecules at the electrode surface at slow scan rates giving lower peak currents. There was a positive shift of anodic peak potential as scan rate was increased while cathodic peak potential was shifted negatively indicating that the electrochemical reaction gradually became less reversible. It is also found that the anodic peak increases linearly with the scan rate in the range 0.01 $Vs^{-1}$ to 0.4 $Vs^{-1}$ as shown in Figure 6(a). The regression equation was obtained as follows: $I_{oxd.} = 6.419S_{oxd.} + 0.199$; $R^2$ =0.995 and $I_{red.} = -4.65_{Sred.} - 0.175$; $R^2$ =0.991. This confirms that redox reaction was controlled by adsorption. Again, peak potential vs. log of scan rate was also linear (Figure 6(b)) with linear regression equations were as follows: $E_{ap}$=0.353logS+0.494; $R^2$=0.978 and $E_{cp}$=-0.39logS-1.07; $R^2$=0.973. Number of electrons (n) involved in the reaction was calculated as 1 (1.14) using the equation as follow: $E_p - E_p/2 = 0.0477\alpha n$. Where $E_p$ is the peak potential, $E_p/2$ is the half of peak potential, α is the charge transfer coefficient. The value of α was calculated to be 0.85 from the slope 2.3RT/(1-α)nF and the slope of $E_{ap}$ vs logS.

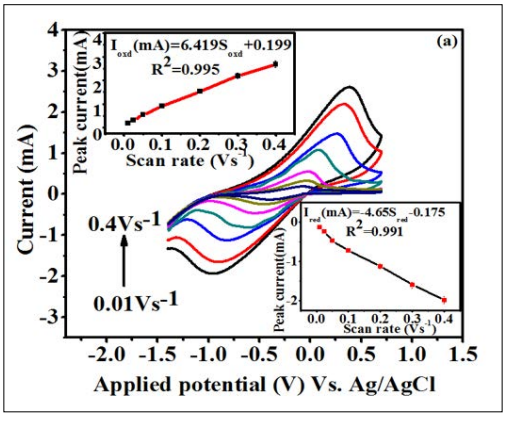


**Figure 6(a):** Effect of Scan Rate on CV (inset: Linear Plot of Scan Rate Versus Anodic Peak Current (Upper) and Scan Rate Versus Cathodic Peak Current (Below))

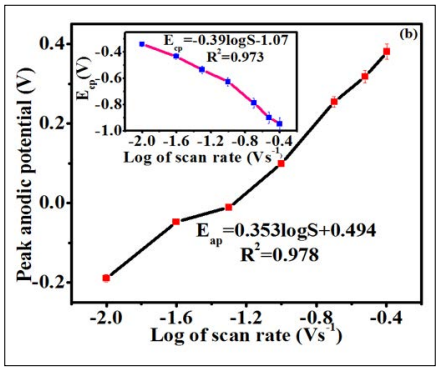


**Figure 6(b):** Log of Scan Rate Versus Anodic Peak Potential (Inset: Log of Scan Rate vs. Cathodic Peak Potential).

**Effect of Concentration Variations**

The effect of Emodin concentration on peak current was studied through differential pulse voltammetry technique (DPV) in PBS buffer solution at pH 6 over potential range -1.2 -0.5 V with varying concentration from 1 to 150 µM. There is a sharp increase of peak current with the increase of concentration as shown in Figure 7(a). Anodic peak was found at potential 0.2 V. Figure 7(b) represents the linear relationship of peak current with increasing concentration. The regression equation obtained is $I_{AE}$(mA) = $0.0013C_{AE}$ + 0.152; $R^2$ =0.987. 0.2 µM is the lowest limit of detection (LOD) was obtained using the equation LOD =$3S_y/x/m$; where $S_y/x$ is the standard deviation and m is the calibration curve slope, respectively and was comparable and even better than other reported work as given in Table 1.

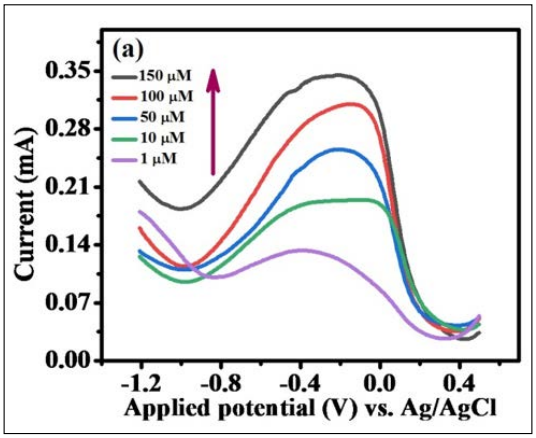


**Figure 7(a):** DPV Measurements at Pt Electrode with Different Concentration

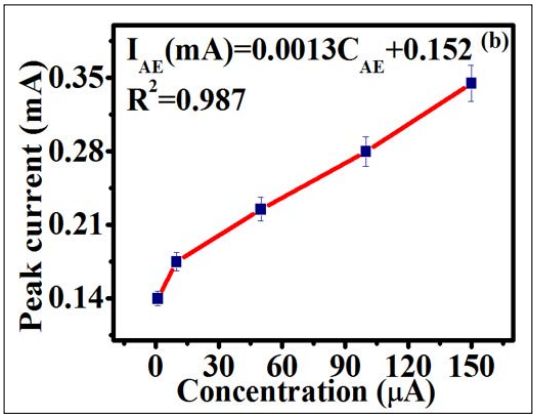


**Figure 7(b):** Concentration Versus Peak Current.

**Table1: Compression of Proposed Method with the Existing Technique**

| Methodology | Electrode material | Linear range | Limit of detection | Res. |
|---|---|---|---|---|
| DPV | B-$CuFeO_2$/ PANI | 1-30mM | 0.0313mM | [30] |
| CV | MWNTs/ GCE | 1– 100 µM | 0.3 µM | [31] |
| DPV | Platinum wire | 1 -150 µM | 0.2 µM | This work |

**Repeatability and stability**

Repeatability and stability of the platinum wire sensor was evaluated using DPV of 50 uM concentration of AE. Six measurements were carried out repeatedly (n=6) on a new electrode surface using the same electrode. The sensor yielded repeatable responses indicated by relative standard deviation (RSD) of 1.898% which confirmed the repeatability and hence precision of the developed sensor (Figure 8). Again, as-prepared electrode did not alter its response when measurement was done with the same sensor after one month and thus giving long-term stability.

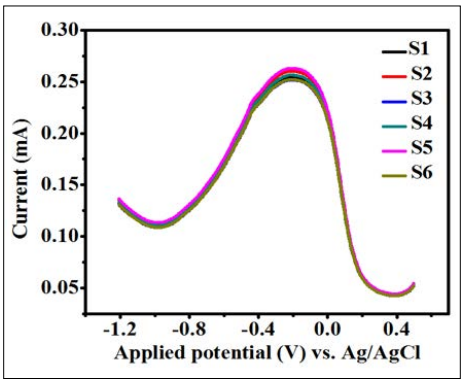


**Figure 8:** Six DPV Measurements Using Same Sensor for Repeatability Test

**PCA**

PCA is a technique to reduce the high dimensional data into two or three dimensional data to yield the maximum variance and minimum correlation in the data set. Voltammogram data for five different concentrations (naming S1 to S5)1 µM, 10 µM, 50 µM, 100 µM, and 150 µM were obtained through DPV measurements and were analysed using PCA. Four repetitions of each of five samples were taken. Hence, the data matrix of size 340 x 5 x 4 was used for the data analysis using PCA. PCA plot shows successful data discrimination in the plot depicted in Figure 9 [30-31].

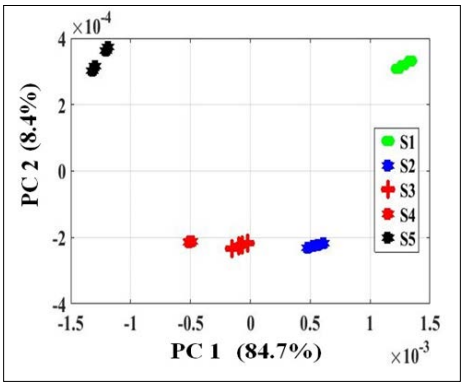


**Figure 9:** Graphical Representation of DPV Data Analysis using PCA

## Conclusion

In this paper, cyclic voltammetry technique is used to inspect electrochemical behavior of Aloe Emodin in three-electrode electrochemical cell with $P_t$ working electrode, Ag/AgCl reference electrode, and steel counter electrode. It was observed that the working potential range for the study was -1.4 V to 0.7 V and the peak currents of the anodic peak increased linearly with the scan rate in the range of 0.01 to 0.4 $Vs^{-1}$. The peak potentials of the cathodic peaks shifted negatively as pH was increased from 3 to 9. Novelty of this proposed work is that the technique is very simple, low time consuming, outstanding selectivity, excellent repeatability and sensitivity to the AE molecules. Moreover, the data obtained from the voltammogram of differential pulse voltammetry reveals a linear increase of peak currents with the increase of concentration of AE in pH 6 buffer saline with regression value of 0.987. Principal component analysis (PCA) of the voltammogram data showed a distinct discrimination of five concentration of AE. Hence, it proves that cyclic voltammetry can be used for quantitative measurement of one of the naturally occurring anthraquinone AE in wide varieties of medicinal plant.

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**Conflict of Interest:** The authors have no any conflict of interest to declare.

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