ELECTROCHEMICAL STUDY OF ALOE GEL AND EMODIN ON A SCREEN PRINTED CARBON ELECTRODE

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ABSTRACT: The most useful part of natural aloe vera is aloe-gel (AG) and aloe-emodin(AE). AE has various pharmacological effects including, antiviral, antimicrobial and laxative activities, while AG has mainly been used as an anti- inflammable agent. Some medical activities are related to their redox activity. This paper presents a simple strategy to carry out of AG and AE based on screen printed carbon electrode (SPCE). The electrochemistry of AG and AE was investigated at pH 7.05 by cyclic voltammetry and differential pulse voltammetry. The redox mechanism is discussed. Results showed that the available working potential range for the study was the potential window between 0.60 V to -0.40 V and the peak currents of the cathodic peak increased linearly with the square root of scan rate. The peak potentials of the cathodic peaks shifted negatively as pH increased from 3.05 to 9.07. The appearance of other cathodic and anodic peak in fresh aloe vera sample indicates that the fresh aloe vera consists of several redox active species. It is concluded that a low cost, easy and convenient detection of aloe emodin was successfully achieved with this electrochemical system.

Keywords: Aloe gel, Emodin, Screen printed electrode, Electrochemical redox mechanism

1. INTRODUCTION

Aloe vera is a medicinal plant of Liliaceae family and a significant source of 'aloin' (4.5 to 25 %)[1]. It has been widely used in food products, beverages and pharmaceuticals as well as cosmetics because of its pharmacological properties such as anti-oxidant, anti-inflammatory and anti-cancer activities [2–8]. The two basic products of this plant are aloe gel and latex. Aloe latex (or aloe juice) is the bitter yellow exudate from the pericyclic tubules in the outer skin of the leaves. The major and active constituents of aloe latex are hydroxyanthracene derivatives (15–40%) such as the anthraquinone glycosides aloin A and B [9]. Aloe latex is known for its laxative properties. Aloe gel is the colourless gel contained in the inner part of the fresh leaves [10]. The gel consists primarily of water (>98%) and polysaccharides (pectins, cellulose, hemicellulose, glucomannan, acemannan and mannose derivatives). Acemannan is considered the main functional component of aloe vera and is composed of a long chain of acetylated mannose [11-13]

Aloe-emodin (Fig.1), one of the main bioactive constituents in aloe vera leaves, has a specific in vitro and in vivo antineuroectodermal tumor activity because of the [8] hydroxyanthraquinone presence. In the measurement of the anti-oxidant activity of aloeemodin, it was found that the interaction between aloe-emodin and DNA was concentration dependent [10].

Because of the chemical structure of aloe emodin, it is classified as an anthraquinone derivative. Investigations of emodin have included spectroscopic methods [14] and micellar electrokinetic capillary chromatography [15].



Fig. 1 The structure of aloe-emodin

It has been shown that multi-wall carbon nanotube modified glassy carbon electrode has better electrocatalytic effects for the redox of emodin than that of bare glassy carbon electrode [16]. Among various analytical techniques, electrochemical techniques have the advantage of speed, simplicity and high sensitivity. To support these requirements, screen printed carbon electrode (SPCE) was used to investigate the electrochemical behavior of extracted aloe emodin and fresh aloe gel. Therefore a new possible method for the investigation of fresh and extracted aloe emodin is described herein.

2. MATERIALS AND METHODS

2.1 Experiments and apparatus

The three electrodes in one single strip: a carbon working electrode, a carbon counter electrode and a silver pseudo-reference electrode from Dropsensavailable from Palm Instruments, was used in this experiment as a screen-printed electrochemical cell. A computer-controlled Autolab PGSTAT (302Nperformance) with general-purposes High electrochemical software operating system (NOVA version 10.1.1) from Eco Chemie B.V., The Netherlands, was used for the electrochemical measurements. The integrated three electrode strips were connected to the Autolab PGSTAT-302N with a specially adapted electrical connector. The pH values were determined with a Radiometer pH meter.

2.2 Experimental conditions

Measurements were performed by dropping a 50ul of a PBS solution prepared from a known sample from a dry weight of methanol extracted aloe emodin or a fresh aloe vera sample onto the surface of the SPCE. The electrochemical characterization of solution samples were investigated by cyclic voltammetric and differential pulse voltammetric technique.

2.3 Sample preparation

The fresh leaves of aloe vera were washed with distilled water and were cut into 2'' - 3'' pieces. The upper green skin of leaves was scratched with a sterilized knife. These scratched pieces were cut into the small pieces and extracted with a known volume of methanol. Hydroxyanthracene derivatives were extracted with methanol. Samples were sonicated in an ultrasonic bath for 10 min, then filtered through 0.2 µm membrane filters. The filtrate was dried by a freezing drying process. The dry aloe emodin sample was used to prepare the known concentration for analysis. Fresh aloe gel samples were filtered via a 0.2 µm membrane filter and mixed with a PBS buffer solution before electrochemical measurement.

3. RESULTS AND DISCUSSION

3.1 Response characteristics

In cyclic voltammetric measurement, two potential ranges (0.60 V to -1.00V and 0.60 V to -0.40 V) were assigned to probe electrochemical processes at the SPCE. A representative CV recorded in phosphate buffer solution(PBS) at pH 7.05 is shown in Fig. 2. Because of electochemical activity of a bare carbon electrode itself in the negative potential region from -0.40 V to -1.00 V, the available working potential range for the study was the potential window between 0.60 V to -0.40 V.



Fig.2 The CV comparisons of a bare SPCE in a PBS buffer solution at pH 7.05 running from 0.60 V to -1.00 V and 0.60 V to 0.40 V at scan rate 25 mVs⁻¹ and 5 cycles.



Fig.3. CV of a bare SPCE in fresh aloe gel solution in PBS buffer solution at pH 7.05 at a scan rate 25 mVs $^{-1}$ and 5 cycles.

After the potential range was chosen between 0.60 V and -0.40 V for the voltammetric measurement, CV behaviors of fresh aloe vera gel in a PBS buffer solution of pH 7.05 at the bare SPCE was studied, and the result is shown in Fig. 3. An anodic peak can be seen at 0.185V with the peak current of 1.10×10^{-6} A. A cathodic peak can be seen at 0.068 V with the peak current of 1.80×10^{-6} A at the bare SPCE. It was also found that the peak currents of the cathodic peak increase linearly with the square root of scan rate in the range of 9 to 36 mVs⁻¹, and the linear regression could be represented as $y = (-0.74 \pm 0.121) + (0.295 \pm 0.026)x$, which indicated that it was a diffusion controlled process (Fig.4b).



Fig. 4 The effect of the scan rate on CV of the extracted aloe emodin solution in PBS buffer solution at pH 7.05 at different scan rates of 9, 16, 25 and 36 mVs^{-1} .

3.2 Electrochemical behavior of extracted aloe emodin in buffer solution at different pH values

The main bioactive compound of aloe vera is aloe emodin which consists of anthraguinone derivatives and the redox processes of anthraquinone derivatives was frequently related to participation proton Therefore [16]. the electrochemical behavior of extracted aloe emodin in buffer solutions at different pH values was studied. The relationship between the cathodic and anodic peak currents of the extracted aloe emodin at SPCE and varying pH values are shown in Fig. 4. It can be seen that the peak potentials of the cathodic peaks shifted negatively as pH increased from 3.05 to 9.07 (Fig. 5), indicating that this electrochemical process involving protons [16].



Fig. 5. The effect of different PBS pH 3.05 ,6.04 7.05 8.01 and 9.07 on CV at the same concentration of extracted aloe emodin (1056 $\,$ ppm) and a scan rate 16 mV/s^{-1}

3.3 Electrochemical behavior of extracted aloe emodin and fresh aloe gel

A differential pulse voltammetric study of the methanol extracted aloe vera sample and fresh aloe gel in a PBS buffer solution at pH 7.05 was investigated for both cathodic and anodic directions from 0.60V to -0.40V. The results show only one cathodic peak in the methanol extracted sample at -0.290V (Fig. 6) while three cathodic peaks are observed in fresh aloe gel shown at -0.312V, -0.14V and 0.087V (Fig.7a). The cathodic peak of aloe emodin should be observed at -0.312V which is different from the reduction potential using bare glassy carbon electrode or multi-wall carbon nanotube modified glassy carbon electrode [16]. The anodic peaks of aloe emodin and other oxidative species were also observed in Fig.7b. The appearance of other cathodic and anodic peak in fresh aloe vera sample indicates that fresh aloe vera consists of several redox active species.



Fig.6. DPV of a 1056 ppm extracted aloe gel in a PBS buffer solution at pH 7.05.



Fig.7 Cathodic differential pulse voltammograme (a) and anodic differential voltammograme (b) of fresh aloe vera gel in a PBS buffer solution at pH 7.05.

4. CONCLUSION

In this paper, the electrochemical behavior of aloe emodin extracts was investigated using SPCE as an active electrode. It could be assumed that the aloe emodin was presented in the extract as well as in the fresh aloe gel according to the electrochemical behavior performance at the SPCE. It was observed that the available working potential range for the study was the potential window between 0.60 V to -0.40 V and the peak currents of the cathodic peak increased linearly with the square root of scan rate in the range of 9 to 36 mVs⁻¹. The peak potentials of the cathodic peaks shifted negatively as pH increased from 3.05 to 9.07. The appearance of other cathodic and anodic peak in fresh aloe vera sample indicates that fresh aloe vera consists of several redox active species. Therefore a low cost, easy and convenient detection of aloe emodin was successfully achieved with this electrochemical system.

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