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VOLTAMMETRIC SENSORS FOR PHARMACEUTICAL USING ZINC LAYERED HYDROXIDE/MULTIWALLED CARBON NANOTUBES PASTE

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ABSTRACT

This study aims to develop a voltammetric sensors of acetaminophen, dopamine and hydroquinone using zinc layered hydroxide-*L*-phenylalanate/multiwalled carbon nanotubes, zinc layered hydroxide-sodium dodecyl sulphate-isoprocarb/multiwalled carbon nanotubes and zinc layered hydroxide-ferulate/multiwalled carbon nanotubes, respectively. The surface morphology of these layered materials and multiwalled carbon nanotubes were determined using scanning electron microscope and transmission electron microscope, while the rate of electron transfer on the surface of these electrodes were determined by electrochemical impedance spectroscopy. The square wave voltammetry method was used to study the performance of these electrodes. Several experimental conditions influencing the voltammetric responses such as percentage of modifiers, type and concentration of supporting electrolyte, pH of the solutions and square wave voltammetry parameters were optimized. Under optimum conditions, these electrodes showed linear response ranges for the determination of acetaminophen, dopamine and hydroquinone from 0.3 µM to 0.1 mM (correlation coefficient: 0.9965), 1.0 µM to 0.3 mM (correlation coefficient = 0.9971) and 10.0 µM to 1.0 mM (correlation coefficient = 0.9957) with the limit of detection was obtained at 0.83 nM, 0.43 µM and 5.7 µM, respectively. Interferences of several ions and compounds were studied and most of them did not interfere on the voltammetric responses. As a conclusion, the fabricated electrodes displayed excellent analytical performance with wider linear range, lower limit of detection and also exhibited good reproducibility, repeatability and stability. In its implication, these proposed electrodes were successfully applied for determination of acetaminophen, dopamine and hydroquinone in pharmaceutical tablet, dopamine hydrochloride injection, water samples and cosmetic cream, respectively.

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PENDERIA VOLTAMMETRI UNTUK FARMASEUTIKAL MENGGUNAKAN PES ZINK BERLAPIS HIDROKSIDA/KARBON NANOTIUB BERBILANG DINDING TERUBAHSUAI

ABSTRAK

Kajian ini bertujuan membangunkan masing-masing penderia voltammetri asetaminofen, dopamina dan hidrokuinon menggunakan zink berlapis hidroksida-*L*-fenilalanat/karbon nanotiub berbilang dinding, zink berlapis hidroksida-natrium dodekil sulfat-isoprokarb/karbon nanotiub berbilang dinding dan zink berlapis hidroksida-ferulat/karbon nanotiub berbilang dinding. Morfologi permukaan bahan berlapis dan karbon nanotiub berbilang dinding telah ditentukan menggunakan mikroskop pengimbas elektron dan mikroskop transmisi elektron, manakala kadar pemindahan elektron pada permukaan elektrod-elektrod tersebut telah ditentukan menggunakan spektroskopi impedans elektrokimia. Kaedah voltammetri gelombang segiempat sama telah digunakan untuk menguji prestasi elektrod-elektrod tersebut. Beberapa keadaan eksperimen yang mempengaruhi gerak balas voltammetri seperti peratus pengubahsuai, jenis dan kepekatan elektrolit penyokong, pH larutan dan parameter-parameter voltammetri gelombang segiempat sama telah dioptimumkan. Di bawah keadaan-keadaan optimum, elektrod-elektrod tersebut menunjukkan gerak balas linear bagi penentuan asetaminofen, dopamina dan hidrokuinon pada julat 0.3 µM hingga 0.1 mM (pekali korelasi = 0.9965), 1.0 µM hingga 0.3 mM (pekali korelasi = 0.9971) dan 10.0 µM hingga 1.0 mM (pekali korelasi = 0.9957) dengan had pengesanan telah diperolehi masing-masing pada 0.83 nM, 0.43 µM dan 5.7 µM. Gangguan daripada beberapa ion dan sebatian telah dikaji dan kebanyakannya tidak mengganggu gerak balas voltammetri. Sebagai kesimpulannya, elektrod-elektrod yang telah direka bentuk ini mempamerkan prestasi analisis yang sangat baik dengan julat linear yang lebih luas, had pengesanan yang lebih rendah dan juga menunjukkan kebolehasilan, kebolehulangan dan kestabilan yang baik. Implikasinya, elektrod-elektrod yang dicadangkan tersebut juga telah berjaya diaplikasikan bagi penentuan masing-masing asetaminofen, dopamina dan hidrokuinon dalam tablet farmaseutikal, suntikan dopamina hidroklorida, sampel air dan krim kosmetik.

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LIST OF ABBREVIATIONS

AA	Ascorbic acid
ACM	Acetaminophen
AGR	Activated graphene
BPA	Bisphenol A
CILE	Carbon ionic liquid electrode
CNT	Carbon nanotubes
CNTPE	Carbon nanotubes paste electrode
CPE	Carbon paste electrode
CV	Cyclic voltammetry
DOP	Dopamine
DPV	Differential pulse voltammetry
DWCNT	Double-walled carbon nanotubes
EIS	Electrochemical impedance spectroscopy
EU	European Union
FA	Folic acid
FeA	Ferulic acid
GC	Gas chromatography
GCE	Glassy carbon electrode
GO	Graphene oxide
HPLC	High performance liquid chromatography
HQ	Hydroquinone
LDH	Layered double hydroxide
LHS	Layered hydroxide salt
MA	Mefenamic acid
MWCNT	Multiwalled carbon nanotubes

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NPV	Normal pulse voltammetry
PBS	Phosphate buffer solution
RMM	Relative molecular mass
RSD	Relative standard deviation
SEM	Scanning electron microscope
Std.	Standard
SWCNT	Single-walled carbon nanotubes
SWV	Square wave voltammetry
TEM	Transmission electron microscope
UA	Uric acid
UK	United Kingdom
USA	United State of America
ZLH	Zinc layered hydroxide
ZLH-F	Zinc layered hydroxide-ferulate
ZLH-LP	Zinc layered hydroxide-*L*-phenylalanate
ZLH-SDS-ISO	Zinc layered hydroxide-sodium dodecyl sulphate-isoprocarb

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B1	Certificate of Conference Attendance
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C1	The independent sample *t*-test result of SWV and HPLC validation for ACM determination
C2	The independent sample *t*-test result of SWV and HPLC validation for DOP determination
C3	The independent sample *t*-test result of SWV and HPLC validation for HQ determination
D1	HPLC chromatogram of ACM
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CHAPTER 1

INTRODUCTION

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1.1 Voltammetry

Voltammetry is an electrochemical method that measure the current in dependence of an applied potential, and the resulting current versus the potential will be plotted as a voltammogram (Svancara, Vytras, Kalcher, & Walcarius, 2012; Wang, 2006). In many measurements, the applied potential or the current is measured over a period of time (*t*). Hence, all voltammetry methods can be described as a function of time (*t*), current (*I*) or potential (*E*) and have been proven to be a valuable tools for determining complexation in organic or inorganic systems, analyzing trace metals in solutions and studying diffusion and kinetics. The earliest voltammetric sensor is called polarography was developed in 1922 by Heyrovsky, uses the dropping mercury electrode (Heyrovsky, 1922).

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Voltammetry is also an electroactive method because the application of the potential will provoke an electrochemical process (reduction or oxidation) of redox species (analyte). It is causing a change in the concentration of an analyte at the surface of electrode (Settle, 1997). The redox reactions involve the Faradaic or non Faradaic processes. The Faradaic process includes the electrons transfer through the electrode-solution-interface and obeys Faraday's Law. Meanwhile, the non Faradaic process does not involve the electrons transfer and does not obey Faraday's Law. These include processes where the structure of the electrode solution interface changes with changing of potential or solution concentrations (Bond, 1980).

The basic instrumentation of voltammetric measurement is a potentiostat, recorder and electrochemical cell. The function of potentiostat is to apply the potential and monitor the current. It can utilize different modes of voltammetry such as square wave voltammetry (SWV), cyclic voltammetry (CV), stripping voltammetry, pulse voltammetry and chronocoulometry. Each mode will secrete their typical potential – current and distinguished by a different form of voltammogram. The most common type of electrochemical cell used in voltammetry is the three – electrode cell. These three electrodes are working electrode, reference electrode and counter electrode which are immersed in a solution containing the analyte and supporting electrolyte. The potential is applied between the working and reference electrodes, while the current flow is measured between the working and counter electrodes. The schematic representation of a basic votammetric system is shown in Figure 1.1 (Otles, 2016; Settle, 1997).

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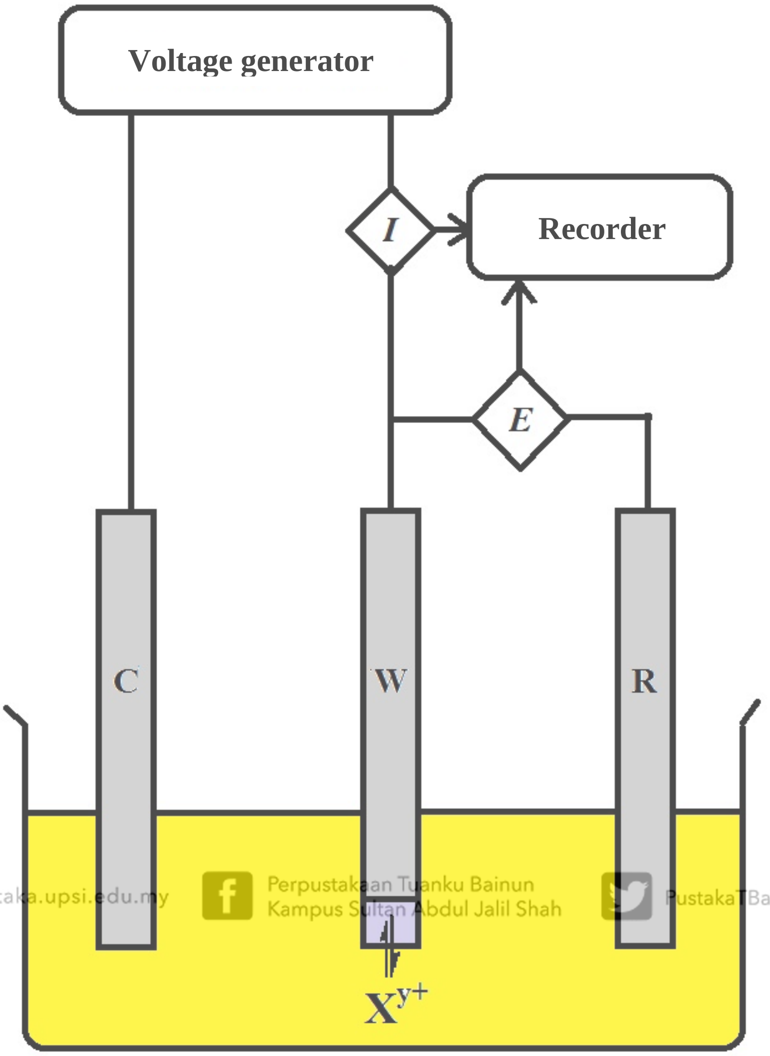

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Figure 1.1 Schematic representation of a basic voltammetric system consisting of counter (*C*), working (*W*) and reference (*R*) electrodes (Braungardt, 2015)

The working electrode is an electrode that provides the surface for electron transfer to occur for the system under investigation. The materials that used as a working electrode is important since it will reflect the selectivity and sensitivity of the voltammetric sensor. The working electrodes should be considered based on certain characteristics such as able to produce a significant reproducible response, inert, good electrical conductivity, wide potential window and surface reproducibility (Wang,

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