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ELECTROCHEMICAL SENSOR OF COPPER, NICKEL AND MERCURY USING FENCHONE DIAZINE LIGAND COMPLEXES-MODIFIED MULTIWALLED CARBON NANOTUBES PASTE ELECTRODES

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ABSTRACT

This study aims to develop a modified multiwalled carbon nanotubes paste electrodes based fenchone azine ligand complexes for detecting copper, nickel and mercury. The fenchone diazine ligand complexes were characterized by using nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction spectroscopy, scanning electron microscopy and transmission electron microscopy. The electrochemical properties of the modified electrodes were determined using square wave stripping voltammetry, cyclic voltammetry and electrochemical impedance spectroscopy. The results show that under optimal conditions, the electrodes showed a linear range between 0.1 nM and 1.0 µM, 10 nM and 1.0 µM, 5.0 µM and 0.1 mM with the limit of detection of 80 pM, 7.4 nM and 3.7 µM for detection of copper, nickel and mercury respectively. The interferences from Ba^{2+}, Ca^{2+}, Cd^{2+}, Ce^{3+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, Sr^{2+} and Zn^{2+} were negligible. Cyclic voltammetry and electrochemical impedance spectroscopy indicated that the charge transfer at the electrode-solution interface was excellent. The proposed electrodes were successfully applied for detection of copper, nickel, and mercury in wastewater samples, vegetables, and skin lightening creams, respectively. In conclusion, the developed modified electrodes are able to detect copper, nickel and mercury. By implication, the developed electrodes can be used as a suitable alternative for the determination of copper, nickel and mercury because it has characteristics such as sensitivity, selectivity and high reproducibility.

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PENGESAN ELEKTROKIMIA KUPRUM, NIKEL DAN MERKURI MENGGUNAKAN ELEKTROD-ELEKTROD PES KARBON NANOTIUB BERBILANG DINDING TERUBAH SUAI-KOMPLEKS- LIGAN FENCON DIAZINA

ABSTRAK

Kajian ini bertujuan membangunkan elektrod-elektrod pes karbon nanotiub berbilang dinding terubah suai berasaskan kompleks-kompleks ligan fencon diazina bagi mengesan kuprum, nikel dan merkuri. Kompleks-kompleks ligan fencon diazina dicirikan dengan menggunakan spektroskopi resonans magnet nukleus, spektroskopi inframerah transformasi Fourier, spektroskopi fotoelektron sinar-X, spektroskopi penyebaran tenaga sinar-X, spektroskopi pembelauan sinar-X, mikroskopi elektron pengimbas dan mikroskopi elektron penghantaran. Sifat-sifat elektrokimia elektrod-elektrod terubah suai telah ditentukan menggunakan kaedah voltammetri perlucutan gelombang segiempat sama, voltammetri berkitar dan spektroskopi impedans elektrokimia. Dapatan kajian menunjukkan bahawa di bawah keadaan optimum, elektrod-elektrod menunjukkan julat linear antara 0.1 nM dan 1.0 µM, 10 nM dan 1.0 µM, 5.0 µM dan 0.1 mM dengan had pengesanan 80 pM, 7.4 nM dan 3.7 µM untuk masing-masing pengesanan kuprum, nikel dan merkuri. Gangguan-gangguan oleh Ba^{2+}, Ca^{2+}, Cd^{2+}, Ce^{3+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, Sr^{2+} dan Zn^{2+} adalah terabaikan. Voltammetri berkitar dan spektroskopi impedans elektrokimia menunjukkan bahawa pemindahan cas pada antara muka elektrod-larutan adalah sangat baik. Elektrod-elektrod yang dicadangkan telah berjaya digunakan untuk pengesanan kuprum, nikel, dan merkuri masing-masing di dalam sampel-sampel air buangan, sayuran dan krim-krim pencerah kulit. Kesimpulannya, elektrod-elektrod terubah suai yang dibangunkan ini mampu mengesan kuprum, nikel, dan merkuri. Implikasinya, elektrod-elektrod yang telah dibangunkan boleh digunakan sebagai alternatif yang sesuai bagi penentuan kuprum, nikel dan merkuri kerana mempunyai ciri-ciri seperti kepekaan, kepilihan dan kebolehasilan semula yang tinggi.

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LIST OF ABBREVIATIONS

AdSV	Adsorptive stripping voltammetry
ASV	Anodic stripping voltammetry
CNTs	Carbon nanotubes
CNTsPE	Carbon nanotubes paste electrode
CPE	Carbon paste electrode
CSV	Cathodic stripping voltammetry
CV	Cyclic voltammetry
DMG	Dimethylglyoxime
DPV	Differential pulse voltammetry
EDX	Energy disperse X-ray
EIS	Electrochemical impedance spectroscopy
FTIR	Fourier transform infrared spectroscopy
GCE	Glassy carbon electrode
ICP-OES	Inductively coupled plasma-optical emission spectrometry
IIP	Ion-imprinted polymer
IL	Ionic liquid
ISE	Ion selective electrode
MWCNTs	Multiwalled carbon nanotubes
NMR	Nuclear magnetic resonance spectroscopy
NPs	Nanoparticles
RGO	Reduced graphene oxide

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RSD	Relative standard deviation
SEM	Scanning electron microscope
SWAdSV	Square wave adsorptive stripping voltammetry
SWCNTs	Single walled carbon nanotubes
SWSV	Square wave stripping voltammetry
SWV	Square wave voltammetry
TEM	Transmission electron microscope
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction spectroscopy

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CHAPTER 1

INTRODUCTION

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1.1 Electrochemical Sensor

Electrochemical sensor is one of the chemical sensor subgroups that is practically using an electrode as the transduction element that converts the various form of energy to into the useful signal (Zhang, Ju, & Wang, 2008). The largest application of electrochemical sensor is widely in medicine, environmental monitoring and industrial analysis (Hanrahan, Patil, & Wang, 2004). The broad range application of electrochemical sensors for fast, simple and low-cost procedures remains over the centuries (Stradiotto, Yamanaka, & Zanoni, 2003). The area of electrochemical sensors also broaden through the development and the modification of sensors technology and sensor materials including nanomaterials (Ganjali et al., 2011; Kim, Yun, & Han, 2009; Pumera, 2014; Pumera, Ambrosi, Bonanni, Chng, & Poh, 2010; Wang, 2005; Wu, He, Tan, Wang, & Zhang, 2013).

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Electrochemical sensor is concerned with the interrelation of electrical and chemical effects where the process take place at the electrode-solution interface. The current signal that results from the interaction of the chemical species and the recognition layer provide the desired chemical information such as the concentration or the activity of the chemical species (Privett, Shin, & Schoenfisch, 2010). Electrochemical sensor applied for a variety of reliable real-time information such as obtaining thermodynamic data about a reaction, study the spectroscopic properties or rate of decay of radical ion and investigate trace amounts of metal ions or organic species (Cornelis, 2003). The advantages of using electrochemical sensor are user friendly, simple, robust, selective, sensitive, cost-effectiveness, and allowing fast analysis without disturbing the samples (Brett, 2001; Faridbod, Gupta, & Zamani, 2011; Hanrahan et al., 2004; Kimmel, LeBlanc, Meschievitz, & Cliffel, 2012; Mead et al., 2013).

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Most of the electrochemical sensor are categorize into their mode of signal transduction, which are potentiometric, conductometric, and amperometric or voltammetric sensors. The potentiometric sensor measures the potential different between the working electrode and the reference electrode at sensor interface under the conditions of no current flow. Meanwhile, conductometric sensor measured the different electrolyte conductivity at different environments. Amperometric or voltammetric sensor measure the resulting current caused by the redox process of an electroactive species under the applied potential (Skoog, Holler, & Crouch, 2007).

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1.1.1 Potentiometric Sensor

Since early 1930's, potentiometric sensors have found the widest practical applicability due to their simplicity, easy to use, and low-cost. Walter Nernst (1889) was a first person who discovered the potentiometric methods based on Nernst equation (Nernst, 1889). The electrochemical cell for potentiometric sensor consists of two electrodes which are working electrode and reference electrode that connected to the potentiometer. The potentiometer is a sensitive potential measuring device that measures the differential potential in millivolt.

The most representative potentiometric sensor is the ion selective electrodes (ISE). ISE are mainly membrane-based devices, consisting of permselective ion-conducting materials, which separate the sample from the internal solution of the electrode. Under zero current condition, the differential potential that yields at the interface between the permselective ion-conducting materials are measured (Bobacka, Ivaska, & Lewenstam, 2008; Shea, 1998).

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The most commonly used reference electrode are silver/silver chloride electrode, mercury/mercury oxide electrode, and saturated calomel electrode, standard hydrogen electrode, and static mercury drop electrode due to their stable, reversible, and reproducible properties (Janata, 2009). In potentiometric sensors, the potential signal is proportional (in a logarithmic fashion) to the concentration (activity) of the ion of interest. The Nernst Equation is typically used to express the potential difference of cell potential (Bakker & Pretsch, 2002).

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1.1.2 Conductometric Sensor

Conductometric sensor is an electrochemical sensor that operating based on the response from the electrolyte conductivity measurement. Conductometric at a series of frequencies usually operated under alternating current supply. The main advantages of conductometric sensors are simple preparation and procedure, not involve the reference electrode, low production cost, compact and durable. The materials frequently used in conductometric sensors is thin films such as cubic cadmium sulphide thin film (Smyntyna, Golovanov, Kacˇiulis, Mattogno, & Righini, 1995), porous films of $MnWO_4$ (Qu & Meyer, 1997) oxides doped film with copper or copper oxide (Devi, Manorama, & Rao, 1995; Maekawa, Tamaki, & Miura, 1994), and semiconducting gallium oxide thin films (Fleischer & Meixner, 1995).

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The operating principle of conductometric sensors is the modulated of electrical conductivity when the electroactive species interact with the operating device. The effect of adsorption, chemical reactions, diffusion, or catalysis reaction on the surface of the sensing layer change the resistance and then, modulate its electrical conductivity. The change in the current is correlated to the concentration of the electroactive species (Wohltjen, Barger, Snow, & Jarvis, 1985).

In the conductometric method, the conductivity of the electrolyte is directly proportional to the specific conductivity of electrolyte (Wang, Xu, Zhang, & Li, 2008). Measurement of the conductivity of the liquid usually performed at low voltage due to the charge-transfer process at the electrode surface and polarization of the electrodes at the operating voltage (Fraden, 2016).

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1.1.3 Voltammetric Sensor

Voltammetric sensor is an electrochemical sensor that measures the current produced at certain potential when the potential was scanned from one present value to another. The concentration of the electroactive species is directly proportional to the current produced. The applied potential provide the driving force for the electron-transfer reaction of the electroactive species, and the rate of the electron-transfer reaction that occur on the electrode surface is the resulting current (Skoog et al., 2007). The development of voltammetric sensor was started in 1922 by Heyrovsky where the dropping mercury electrode was developed (Heyrovský, 1922).

In voltammetry, the concentration of the redox species and the rate of the reaction were controlled by applied potential. The redox reactions involve the Faradaic and non-Faradaic process. The Faradaic process includes the transfer of electrons across the electrode-solution-interface and obeys the Faraday's Law. The faradaic current is generated during this process, and its magnitude is governed by the mass transfer process such as diffusion, migration, and convection. Meanwhile, the non-Faradaic processes do not involve a transfer of electrons and hence do not obey Faraday's Law. These include processes where no charge transfer occurs because they are thermodynamically or kinetically unfavourable, or where the structure of the electrode solution interface changes with changing potential or solution concentrations (Bond, 1980).

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The basic instrumentation of voltammetric sensor as shown in Figure 1.1 consist of a three-electrode cell immersed in a supporting electrolyte containing the target

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