UNIVERSITI PUTRA MALAYSIA

ELECTRICAL PROPERTIES OF CHITOSAN FILMS WITH METAL ION

PADILAH ABU BAKAR

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ELECTRICAL PROPERTIES OF CHITOSAN FILMS WITH METAL ION

By

PADILAH ABU BAKAR

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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DEDICATION

This thesis is dedicated to my family and friends through thick and thin. Alhamdulillah. Thank you ALLAH.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

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March 2020

Chairman : Nurul Huda Osman, PhD
Faculty : Science

Metal ion, unlike other types of pollutant, can easily enter the human body but very difficult to degrade. Metal ions in trace amount is essential nutrient, however consumption at high dose may cause disorder in plant and animals, as well as fatality due to toxicology. The purpose of this study is to measure and determine the electrical properties of chitosan film with metal ion. Intrinsically, chitosan plays important role in the adsorption process of metal ion in the water. The experiment was conducted by soaking chitosan film with dimension of 8 mm by 8 mm into copper, cadmium and zinc ions solutions for 20 minutes at various concentrations. The selections and concentration of metal ion were determined according to the level of toxicity in drinking water that allowed by EPA regulations for common contaminants. The soaked chitosan was then attached onto the interdigitated electrode that connected to LCR meter. The principle of chitosan film measurement is based on determination of the impedance, capacitance, and resistance. When the concentration metal ion was set at 50 mg/L, zinc possess the highest resistance whilst the highest capacitance value is given by copper ions. The standard deviation of capacitance value for chitosan film with copper, cadmium and zinc are 7.01 nF, 74 nF and 48 nF respectively. The results were then elaborated and analysed through Nyquist plot to identify the circuit arrangement between chitosan film and interdigitated electrode. The dielectric material and conductivity pattern show that polarization occur at low frequency that lead to decrement in dielectric constant and dielectric loss. The absence of semicircle in Nyquist graph indicates the arrangement between the chitosan film and interdigitated electrode is in series. The finding of this study shows the potential of chitosan as portable metal ion sensor due to its ability to provide authentic amount of ions in the water through detection of samples' electrical changes in real-time.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

SIFAT-SIFAT ELEKTRIK SELAPUT CITOSAN DENGAN ION LOGAM

Oleh

PADILAH ABU BAKAR

Mac 2020

Pengerusi : Nurul Huda Osman, PhD
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Ion logam, tidak seperti bahan pencemar yang lain di mana ianya mudah memasuki tubuh manusia tetapi sukar untuk diuraikan. Ion logam merupakan nutrisi penting pada kuantiti yang sedikit, tetapi dos yang tinggi boleh menyebabkan gangguan kepada tumbuhan dan binatang serta kematian disebabkan kesan toksik. Tujuan kajian ini adalah untuk mengukur dan mengenalpasti sifat elektrik bagi saput tipis citosan dengan ion logam. Citosan secara intrinsik memainkan peranan penting dalam proses serapan ion logam dalam air. Ujikaji dijalankan dengan merendam saput tipis citosan berdimensi 8 mm x 8 mm ke dalam larutan ion tembaga, kadmium dan zink selama 20 minit pada kepekatan yang berbeza. Penentuan pemilihan dan kepekatan ion logam adalah berdasarkan tahap ketoksikan dalam air minuman yang dibenarkan oleh peraturan EPA bagi pencemaran biasa. Saput citosan yang telah direndam kemudiannya diletakkan di atas elektrod interdigital yang bersambung dengan LCR meter. Prinsip pengukuran saput tipis citosan adalah berdasarkan penentuan nilai impedan, kapasitan dan rintangan. Apabila kepekatan ion logam ditentukan pada 50 mg/L, zink memiliki nilai kerintangan yang paling tinggi manakala nilai kapasitan tertinggi adalah dari ion tembaga. Sisihan piawai nilai kapasitan untuk saput citosan dengan ion metal bagi ion tembaga, zink dan kadmium adalah masing-masing 7.01 nF, 74 nF and 48 nF. Hasil dapatan kemudiannya diperinci dan dianalisis menggunakan plot Nyquist untuk mengenalpasti susun atur litar di antara saput citosan dan elektrod interdigital. Pola dielektrik dan kekonduksian bahan menunjukkan polarasi berlaku pada frekuensi rendah yang menyebabkan penurunan pemalar elektrik dan kehilangan dielektrik. Ketiadaan semi-bulatan pada graf Nyquist menunjukkan bahawa susunan antara saput citosan dan elekrod interdigital adalah secara sesiri. Hasil dapatan dari kajian ini menunjukkan potensi citosan sebagai sensor ion logam boleh-alih berikutan keupayaannya mengesahkan jumlah ion di dalam air melalui pengesanan perubahan elektrik sampel pada masa nyata.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Declaration by graduate student

I hereby confirm that:

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This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
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LIST OF ABBREVIATIONS

AAS	Atomic Adsorption/Emission Spectrometry
AdSV	Adsorptive Stripping Voltammetry
AFS	Atomic Fluorescence Spectrometry
ASV	Anodic Stripping Voltammetry
CB	Calcein Blue
CBC	Chitosan-Blended Cellulose
CNTs	Cathode Nanotube
CSV	Cathodic Stripping Voltammetry
CVARS	Cold Vapor Atomic Fluorescence Spectrometry
DNA	Deoxyribonucleic Acid
EAPap	Electroactive Paper
GNPs	Gold Nanoparticles
HCL	Hollow Cathode Lamp
ICP-MS	Inductively Couple Plasma Mass Spectrometry
ICP-MS	Inductively Couple Plasma Mass Spectrometry
IDE	Interdigitated Electrode
LCR	Inductance Capacitance And Resistance Meter
NH_2	Amino Group
OH	Hydroxyl Group
PSA	Potentiometric Stripping Analysis
RHD	Rhodamine Derivative
SAW	Surface Akustic Wave
SPR	Surface Plasmon Resonance
US-EPA	United State Environmental Protection Agency
WHO	World Health Organization

LIST OF SYMBOLS

A	Absorbance
A_{ab}	adsorption in the percentage
Ag^{+}	Argentum ions
As	Asenic
C	Capacitance
c	Concentration
C	Capacitance value of dielectric material
Cd^{2+}	Cadmium ions
C_f	residual concentration
C_o	initial concentration
C_o	Capacitance value in air or vacuum
Cr	Chromium
Cr^{3+}	Chromium ions
Cu^{2+}	Copper ions
Fe	Ferum
H_2	Hidrogen
Hc	High Current (H CUR)- signal input for series measurement
Hg	Mercury
Hp	High Potential (H POT)- signal input/output for parallel measurement
I	Intensity of light passing through the sample
I	Current
l	Path length
I_0	Intensity of light passing through reference cell
Lc	Low Current (L CUR)- signal output for series measurement
Lp	Low Potential (L POT)- signal input for parallel measurement
m_1	Initial concentration
m_2	Diluted concentration
Mn^{2+}	Manganese ions
M_r	Real electrical modulus
M_r	Imaginary electrical modulus
Ni	Nickel
Pb	Plumbum
R	Resistance

t	Time
V	Voltage
V_1	Initial of original volume
V_2	Final volume
V_m	Maximum voltage
Z	Impedance
Zn^{2+}	Zinc ions
ε	Molar adsorption coefficient (molar adsorption constant)
ε_i	Dielectric loss
ε_r	Dielectric material
φ	Phase difference
ω	Cycle frequency

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Pollution and its effect are among major concern of worldwide. Due to the rapid industrial development, pollution is on the rise. Unlike developed countries, such as Japan and Korea, Malaysia as a developing country is facing a huge problem in handling the pollution, especially in wastewater and soil (composition of minerals, gas, water,soil organic matter and living organism). One source of the pollution is metal ion where the contamination generally comes from the mining and industries sector. Untreated waste from these industrial usually enters the river and sea directly. Thus, causing problem affecting the marine system and the source of drinking water.

Table 1.1 shows the main sources of three metal ions (Cu^{2+}, Cd^{2+}, Zn^{2+}) and their effects to human if consumed more than permissible limit by the US-EPA and WHO. United States Environmental Protection Agency,(“US- EPA,” 2019) World Health Organization, (“WHO,” 2008).

Table 1.1: The permissible limit of selected metal ion in drinking water.

Metals	Main source	Health effects	Maximum Permissible Limit (mg/L of water)
Copper (Cu)	Corrosion of household plumbing materials and industrial manufacture	Gastrointestinal distress and in the long run, experience liver or kidney damage	1.30
Cadmium (Cd)	Paints, pigments, electroplated part, synthetic rubber, batteries, plastics and phosphate fertilizers	Renal toxicity, hypertension, fatigue and kidney damage	0.005
Zinc (Zn)	Tap water, rocks and meat	Stomach cramps, skin irritations, vomiting, nausea, anaemia, trouble in pancreas, generate arteriosclerosis	5.00 (Secondary Drinking water standard)

Chowdhury et al., (2016) in the study of occurrences, implications and future needs in developing countries highlighted the significant risks to human health due to contamitations in drinking water. According to the study, the drinking water mainly was contaminated with Cd, Cu, Ni, Pb, Fe, Zn and Cr from the industrial activities, tannery, domestic waste, pesticides, corrosion of pipes, pipe coatings, coolers and water tanks. Arsenic (As) is a major source of pollution in drinking water through floodplain deposits and natural anoxic conditions in the aquifers; certain types of industries and agricultural activities. Mercury (Hg) in drinking water is originated from industrial activities, packaging for bottled water, corrosion of pipe materials and coatings, amalgam in teeth, and powder laundry detergents. A few other sources of Hg include agriculture, wastewater, mining, and incineration.

In Malaysia, there are plenty of studies on the impact of metal ion to water and fish from the ergonomics (or human factors) perspective. Ching et al.,(2016) investigated the metal ion pollution at Langat River and Klang River in Malaysia, found a trace of As in Langat River and highest contamination in metal is at Klang River. Meanwhile, Authman et al.,(2015) stated that fish biomarkers are necessary for monitoring environmentally induced alterations to assess the impact of xenobiotic compounds. This is because these heavy metals will accumulate in the tissues of marine organisms and being conveyed through human by consuming the fish seafood.

A study conducted by Ismail & Saleh, (2012) showed the tilapia fish that live at close proximity to sewage tratment plant and paint factory contained zinc amounted to 64.78 mg/kg and 63.51 mg/kg respectively, as compared to the fish that lives far from any significant sources, estimatedly at 53.42 mg/kg. Contamination of copper is still below the permissible level (30 mg/kg) of the Malaysian Food Act when tested at the same location with 3.49, 0.89 and 0.53 mg/kg respectively. Meanwhile, cadmium contamination in tilapia is below detection limit.

The results were supported by Belin et al.,(2013) who found concentration of heavy metals in sediment and water are significantly higher in the coastal area of Port Klang, Malaysia compared to river bank or drainage owing to strong water currents from port activities and industrial wastage.

1.2 Chitosan applications

The structure of chitin and chitosan allows it to be chemically modified in a variety of applications by using simple chemical mixtures and process. According to Jayakumar et al., (2010), chitosan can be modified and used as a biosensor, filtered agent, tissue engineering, and recovery of metal ion, catalyst and enzyme carriers, and many more in medical and biocosmetics industries due its biocompatible, biodegradable, and non-toxic, anti-microbial and hydrating agents properties.

This is supported by Kim, et al., (2002) which stated that the chitosan can easily be blended together with cellulose because of its chemical similarity. The chitosan cellulose can enhance the transport of polar drugs across epithelial surfaces in the investigation of the electrical properties of chitosan-blended cellulose (CBC) with electroactive paper (EAPap) in order to understand its ion transport mechanism.

Chitosan can be processed into various forms such as powder, flake fibre, film and solution. Therefore, it can used into broad application for different field as shown in Table 1.2. Chitosan is insoluble in natural medium, but can be solubed by acetic acid. As in film form, chitosan appears as clear, homogeneous and flexible cause by oxygen barrier and mechanical properties. Unfortunately, chitosan is very poor in mechanical properties and its stucture in pure film form is dense and no pores. According to Angel et al.,(2018); Ahmad, et al.,(2015), and Elhefian (2014) modification of chitosan by blending or crosslinking with other material is necessary to increased the potential of chitosan as absorbent different medium. This is because the adsorption efficiency of chitosan film is poor in pristine condition. Hence, by the virtue of above factors, the electrical properties of pure chitosan performance is in focus for this study.

Chitosan is beneficial to improve the sustainability of the plant or agro products by inducing plant defence system to stimulate the growth and activity of useful microbes. This is because the chitin and chitosan are toxic to pests and pathogens, therefore it can improve crop yields by plant-microbe interactions. This is supported by positive responses to chitin and its derivatives as investigated by Sharp, (2013) that underwent the test with different section by direct antibiosis against pests and pathogen of crop. It enhanced plant defence system and growth by influencing the beneficial microbes, stimulated the plant defence responses against biotic stress and up-regulation of plant growth of development, nutrition, and tolerance against abiotic stresses.

Research over the past two decades have provided a large number of published studies in variety chitosan applications. Although extensive studies on chitosan have been successfully tested, but there are only a few studies that focus on the electrical properties of pure chitosan in their research. Most of the studies using crosslinking or blending with other materials to enhanced the capability of the chitosan in research. In Table 1.2 shows a brief usage of chitosan at various fields as discussed above.

Table 1.2: Applications of chitosan in different field.

Field	Goal	References
Cosmetics	use chitin and chitosan in cosmetics	Aranaz et al., 2018
Food industry	use chitosan and its derivatives for their use in food applications	Gutiérrez, 2017
Water and waste treatment	use for Mercury detection	Adlim & Fitri, 2015
Agricultures	use chitin and its derivatives to improve crop yield	Sharp, 2013
Biopharmaceutical	use the properties of chitin and chitosan based nanofibres for biomedical applications.	Jayakumar et al., 2010

1.3 Problem statement

Although extensive studies on chitosan have been successfully carried out to test its applications in various fields, there are only a few studies that partly used pure chitosan and discussed its electrical properties. Therefore, in this study, the detection film used is made from pure chitosan to observe the electrical characteristics of chitosan film with metal ion. Hence, in this study will focused on several issues

i. How effective the incorporation of interdigitated electrode and chitosan film to determine the electrical characteristics of chitosan film?

ii. What is the outcome of the electrical characteristics with different analytes?

iii. What is the corresponding equivalent circuit between the chitosan film and interdigitated electrode?

1.4 Research Potential

In this study the electrical characteristics of chitosan film with different concentration of Cu^{2+}, Zn^{2+} and Cd^{2+} will be studied. The data obtained will be further analysed to study the behaviour of each film. The result obtained can be utilized for the construct real time 'in situ' metal ion detection system incorporating interdigitated electrode and chitosan film.

1.5 Research Objective

In order to overcome listed issues, there are three objectives listed as guideline of the research focused. The objectives of this research are

i. To fabricate chitosan film on plastic substrate suitable for testing with Interdigitated electrode and study its adsorption ability

ii. To determine the electrical characteristics of chitosan film with Cu^{2+}, Zn^{2+} and Cd^{2+} through frequency between 20 Hz to 200 MHz

iii. To identify the type of equivalent circuit between the chitosan film and interdigitated electrode.

1.6 Scope and limitations of Study

Due to some constrain, this thesis has a few limits with the methodology employed in this study. Here are the list of the scope and limitations of this study.

i. The research focused on three metal ions which are copper, cadmium and zinc only.

ii. Chitosan used in this research is medium molecular weight chitosan powder which is diluted with 1% (v/v) acetic acid and layered onto plastic film.

iii. Interdigitated Electrode used in the research is a gold electrode and the physical conditions are fixed according to the manufacture design.

1.7 Thesis Outline

This thesis features the electrical study of chitosan film with metal ion (Cu^{2+}, Zn^{2+} and Cd^{2+}) at different concentrations. It focused on the determination of electrical characteristics of chitosan film with metal ion on interdigitated electrode. This thesis is composed of five themed chapters. This thesis begins with Chapter 1 as an introduction and ended with Chapter 5 as a conclusion and summarize of the research work.

In Chapter 1, the introduction of the thesis highlights the source of the water pollutant with metal ion and the application of chitosan. Then, followed by the objectives of this research, problem statements and the research hypothesis. It also provides brief introductions to the subsequent chapters.

The structure of chitosan as adsorbent of metal ion is explained further in Chapter 2. According to the previous studies, the literature review is classified into the process of adsorption between chitosan film and metal ion, usage of the interdigitated electrode, measurement technique and suitable analysis results.

The research flow and method of this experiment is presented in Chapter 3. The preparation of chitosan film and metal ion solutions is explained. The measurement process with a measuring instrument is described further. Then, the theory of analysis of the data is explained according to the requirement of the research.

Chapter 4 presents and discusses the findings of the research, focusing on the three key themes that is the electrical characteristic of chitosan film through 10 to 200 kHz frequency, comparison in electrical characteristics between different metal ion and dielectric studies to identify the related circuit of the system.

The conclusion of this research are presented in Chapter 5. The purpose of the final chapter is to reflect the comprehensive of this study. In addition, the suggestions for potential future inventions based on the results from this study are discussed.

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