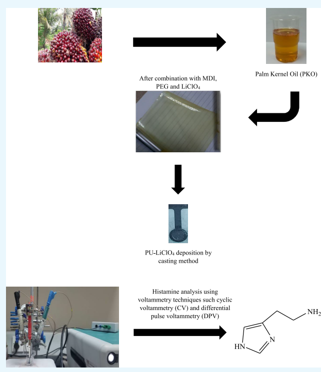
ACS OMEGA

http://pubs.acs.org/journal/acsodf Article

The Application of Polyurethane-$LiClO_4$ to Modify Screen-Printed Electrodes Analyzing Histamine in Mackerel Using a Voltammetric Approach

Muhammad Abdurrahman Munir,* Khairiah Haji Badri, Lee Yook Heng, Ahlam Inayatullah, Eva Nurinda, Daru Estiningsih, Annisa Fatmawati, Veriani Aprilia, and Nur Syafitri

Cite This: *ACS Omega* 2022, 7, 5982−5991 Read Online



ABSTRACT: Histamine is an important substance that can be applied as a parameter for allergic reactions and food freshness. This study develops a method to produce a histamine sensor based on electrodes modified using polyurethane-$LiClO_4$. A sensor method was developed where this sensor was produced from polyurethane. The application of 4,4′-diphenylmethane diisocyanate (hard compound) and palm kernel oil-based monoester polyol (soft compound) to produce polyurethane (PU) based on bio-polyol. The addition of lithium perchlorate ($LiClO_4$) was done in order to increase the conductivity of PU. The oxidation process was detected using cyclic voltammetry, whereas the electrochemical impedance spectroscopy was used to analyze the conductivity of the polymer. The polyurethane-$LiClO_4$ was attached on a screen-printed electrode (SPE) within 45 min. Moreover, the 1% $LiClO_4$-PU-SPE presented satisfactory selectivity for the detection of histamine in the pH 7.5 solution. The $LiClO_4$-PU-SPE presented a good correlation coefficient (R = 0.9991) in the range 0.015−1 mmol·L^{-1}. The detection limit was 0.17 mmol·L^{-1}. Moreover, the histamine concentration of mackerel samples was detected by the PU-SEP-$LiClO_4$. Several amine compounds were chosen to study the selectivity of histamine detection using SPE-PU-$LiClO_4$. The interference was from several major interfering compounds such as aniline, cadaverine, hexamine, putrescine, and xanthine. The technique showed a satisfactory selective analysis compared to the other amines. A satisfactory recovery performance toward varying concentrations of histamine was obtained at 94 and 103% for histamine at 0.01 and 0.1 mmol·L^{-1}, respectively. The application of PU-SEP-$LiClO_4$ as an electrochemical sensor has a great prospect to analyze histamine content in fish mackerel as a consequence of PU-SEP-$LiClO_4$ having good selectivity and simplicity.

1. INTRODUCTION

Nowadays, food security becomes the main attention of the food industry due to various foods that have been produced caused by the high demand. Several factors influence the stability of food content such as the presence of bacteria, the storage and packaging methods, and the production of chemical compounds such as biogenic amines, particularly histamine.[1,2] Histamine analysis in foods draws huge attention from several researchers because of not only the capability to poison the consumers but also the stability of histamine to withstand inside foods during the cooking or heating process.[3,4]

Various methods have been developed by researchers in order to analyze histamine in various samples such as fish, meat, cheese, fruits, milk, etc. Liquid chromatography and gas chromatography are the popular techniques chosen by researchers based on their ability to determine histamine concentration. Furthermore, the ability of these techniques is unquestionable such as being very selective, sensitive, robust, and well established.[5−9] However, these methods have several disadvantages such as being time-consuming, requiring various chemical reagents, high price, and the fact that merely people who study analytical chemistry can comprehend these machines. Furthermore, histamine is a less chromophore and unvaporized compound, thus the modification of histamine structure can be done by a derivatization process only.[10,11]

These issues can be solved by electrochemical sensor application. They are very fast, inexpensive, have fewer chemical materials, and are easily used. The approaches of these techniques are different compared to chromatography techniques. In order to detect histamine, the sensors require a specific receptor, biological (enzymes) receptors, or chemical receptors.[12,13] Nevertheless, the biological receptor of the sensor known as biosensor offers instability and expensive test

Received: November 8, 2021
Accepted: January 11, 2022
Published: February 10, 2022

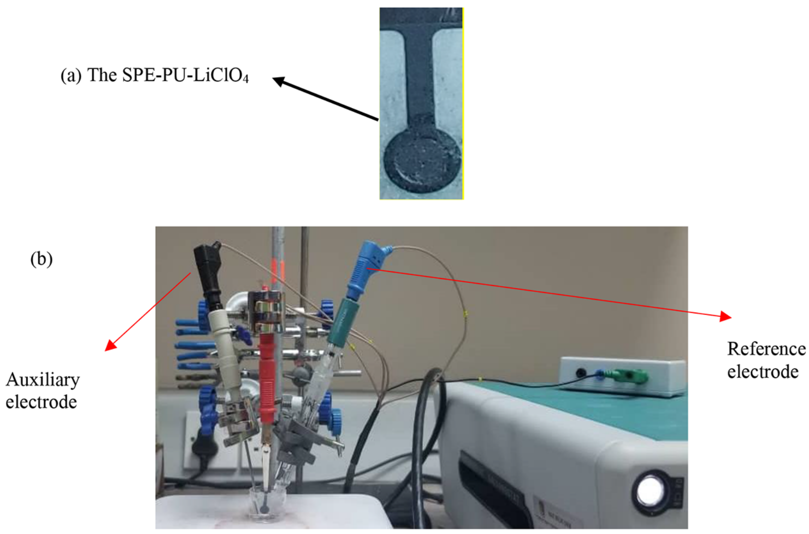


Figure 1. (a) SPE-PU-$LiClO_4$ and (b) instrument employed to analyze several techniques such as the CV, DPV, and EIS techniques. (Photograph courtesy of Muhammad Abdurrahman Munir. Copyright 2021).

kits. Several studies reported the application of enzymes is unstable owing to many factors that can affect it such as temperature and pH. Several foods also contain metals that can work as an inhibitor to inhibit enzyme activity.[14−16] A chemical sensor is a better choice in order to avoid the use of biological receptors. Nowadays, screen-printed electrodes (SPEs) modified with conducting polymer have been developed for various electrochemical sensing. The SPE becomes the best solution owing to its frugal manufacture, tiny size, ability to be produced on a large scale, and can be applied for on-site detection.[17,18] Polymers become an alternative to modify the screen-printed electrodes due to their electrical conductivity, ability to capture analyte by chemical/physical adsorption, large surface area, and making polymers that are very appealing materials from electrochemical perspectives.[19] A natural polymer such as polyurethane has recently attracted analytical chemistry researchers owing to the fact that they have a prospect to be employed in electrochemical devices. Natural polymers have several properties that can be considered for electrochemical application such as easy handling during production, having no harm to the environment, low toxicity, cost effectiveness, and biodegradability.[20−22]

Platinum, gold, and carbon are common materials used by researchers in order to modify electrodes.[23,24] Furthermore, carbon, gold, and platinum are expensive and should be modified before being applied as electrochemical sensors. Lithium perchlorate ($LiClO_4$) is an alternative in order to modify the conductivity of the polymer. Not only the price is cheaper but also the production of PU-$LiClO_4$ is easy. In this study, $LiClO_4$ was employed owing to having lattice energy. It contains cations and anions. Furthermore, the ionic conductivity is affected by the size where the current is produced by the diffusion rate of anions and cations. Thus, it can be concluded that not only $LiClO_4$ is a good conductivity but also the production is easy. Furthermore, this material is a better solution compared to other materials (gold, carbon, platinum, and graphene) due to the interfacial resistance being low. Thus, $LiClO_4$ can be diluted in most solvents due to possession of dissociation energy.[25,26]

Such advantages of SPE-PU-$LiClO_4$ encourage us to construct a new electrode for electrochemical sensing, and no study was published on histamine detection using SPE-PU-$LiClO_4$ by an electrochemical approach. Thus, this study can be considered as a new approach to electro-analysis of histamine. Histamine was then determined using a voltammetric approach. The sensor was applied to monitor the histamine concentration in fish mackerel.

2. EXPERIMENTAL SECTION

2.1. Materials and Preparation of SPE-PU-$LiClO_4$. Palm kernel oil (PKO)p was supplied by UKM Technology Sdn. Bhd. through MPOB/UKM Station Plant, Pekan Bangi Lama, Selangor and prepared using Badri et al.'s method. 4,4-Diphenylmethane diisocyanate (MDI) was acquired from Cosmopolyurethane (M) Sdn. Bhd., Klang, Malaysia.[27] Lithium perchlorate ($LiClO_4$), polyethylene glycol (PEG) 400, and acetone solution were obtained from Sigma Aldrich Sdn. Bhd, Shah Alam and have been employed to produce SPE-PU-$LiClO_4$. Film production was produced using a casting method.

In this work, 10.0 g of palm kernel oil (PKO) and 2.0 g of PEG 400 were dissolved in 10 mL of the solution of 30% acetone and then stirred at ambient temperature for 5 min to acquire a homogenized solution. Afterward, 10.0 g of MDI was dissolved in 10 mL of 30% acetone and stirred. The MDI solution was poured slowly into PKO and PEG 400 solution in order to control the exothermic reaction, and stirred until the homogenized solution was obtained. Various amounts of 1, 3, and 5% of lithium perchlorate ($LiClO_4$) were employed and put into the mixture until a homogenized solution was acquired. The solution was poured onto the screen-printed electrode using the casting method and left at room temperature to dry the film. Thereby, SPE-PU-$LiClO_4$ was obtained.

2.2. Instruments and Chemicals. Metrohm Autolab Electrochemical Workstation (UKM, Bangi, Malaysia) (Figure 1) was used to conduct cyclic voltammetry (CV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS) analysis. All electrochemical experiments were performed using three electrodes as SPE-PU-$LiClO_4$ as a working electrode, Ag/AgCl applied as a reference electrode, and platinum wire was employed as an auxiliary electrode. All

https://doi.org/10.1021/acsomega.1c06295
ACS Omega 2022, 7, 5982−5991