Formaldehyde Detection using Thin Film Sensor based on Chitosan Crosslinked with Glutaraldehyde

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Abstract: In this study, chitosan was crosslinked with glutaraldehyde to fabricate a formaldehyde sensor. Chitosan based sensor was used for formaldehyde detection in various concentration (1 ppm; 1,5 ppm; and 2 ppm). The sensor fabrication was performed using electrodeposition method to form a film sensor. The cross-linking agent is glutaraldehyde, the aim of adding glutaraldehyde is to enhance the sensing properties of chitosan sensor especially the life time of the sensor. The existence of glutaraldehyde which was crosslinked with chitosan has been proved by FTIR spectra. Formaldehyde was dropped onto chitosan film surface and the response of the chitosan sensor towards formaldehyde was recorded as output voltage. The average of output voltage values for three times measurements were within the range of 0,0143 V to 0,0286 V. Increasing concentration of formaldehyde showed the increasing of output voltage value. The sensors showed good sensitivity and fast response.

1 INTRODUCTION

In Indonesian traditional markets, the control of government on utilization of prohibited and dangerous substance in food, especially formalin, is still weak. It emerges a fret as well as a worry to the customer, which may cause harm to human health (Noordiana, 2011). Although adding formalin to foods is forbidden as stated in The Regulation of Indonesian Minister of Health No. 1168 / Menkes /PER/X/1999, some industries, especially small/home scale industries still add it in foods and sell them to traditional markets. The Indonesian Agency for Drug and Food Control found that many testing samples of food products of Small-Medium Industries are proven to be positive containing formalin (Media Industry, 2006). According to WHO standard in 2002, the maximum formalin content contained in food is 1 mg/l equivalent to 1 ppm (WHO, 2002). Nowadays, the common method to detect formalin in food is gas chromatography-mass spectroscopy (GC-MS) but the analysis tool is expensive and time consuming. It is highly desirable to develop a sensitive, cheap and easy-to-use method for formaldehyde detection.

Chitosan as a natural polymer is attractive sensitive material with several plus properties. Recently it has been found that chitosan can be dramatically modified and blended to be used as an effective sensitive material. It is of interest because of the possibility to enhance sensitivity and selectivity due to modification of chitosan structure, excellent film-forming ability, high mechanical strength, adhesive, high heat stability (Yang, 2013). The high chitosan solubility in acidic media also makes chitosan easily deposited to form film onto a substrate (Sun,2011). The advantages of non-porous film layers offer high permeability, mechanical strength, and selectivity (Kanti, 2004).

Decreasing the mechanical properties of chitosan in wet conditions can be reduced by the addition of crosslinking. Cross-linking is the most effective method for improving membrane properties. Commonly used crosslinking agents are glutaraldehyde, trisodium citrate, sulfuric acid, and pentasodium tripolyphosphate (Safitri, 2016).

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Utilization of chitosan as a sensitive sensor material is rarely performed whereas chitosan has amine (-NH_2) and hydroxyl (-OH) groups in its molecular structure which enable chitosan as a sensitive material. The high chitosan solubility in acidic media also makes chitosan easily deposited in the form of film onto a substrate (Sun, 2011). So, chitosan is a potential sensitive material to be a sensing material to detect formaldehyde.

2 MATERIALS AND METHOD

2.1 Materials and Instruments

Materials which were used in this experimental work are chitosan with deacetylation degree 80% (medium molecular weight), glutaraldehyde, CH3COOH 2%, H2SO4, HNO3, CoCl2 0,01 M, KSCN 1 M, HCl 2 N (Merck). Printed circuit board (PCB) was used as a substrate of sensor. Vacuum oven, hot plate, magnetic stirrer, centrifuge, ultrasonic were used to fabricate the sensors. A set of FTIR Shimadzu IR prestige-21 was used to characterize the chitosan film and an electronic set-up was used to test the sensor.

2.2 Preparation of Chitosan Solution

Chitosan powder was supplied by Sigma–Aldrich (medium molecular weight), it was dissolved in acetic acid 2% then stirred using a magnetic bar stirrer for 24 hours at room temperature to prepare the chitosan solution gel.

2.3 Preparation of Chitosan Film Sensor

Chitosan film was made by chitosan solution using electrodeposition method. On this process, printed circuit board (PCB) was used as a substrate of sensor. The electrodeposition process of chitosan films illustrates as in Figure 1. The supplied voltage was fixed at 2,5 volts and left to dry for 5 minutes at 105°C in oven. Chitosan film was cross-linked using glutaraldehyde 25%. CoCl2 0,01 M was used as a template, KSCN 1 M and HCl 2 N were used as template remover during crosslinking process. Formaldehyde solutions with various concentration (1 ppm; 1,5 ppm; 2 ppm; 5 ppm; and 10 ppm) were used to test the sensitivity of the chitosan film sensor. Formaldehyde solution was dropped onto chitosan film sensors. Sensor testing was performed using amperometric method, amperometric method is a method for detecting analyte using amperometry and the output was showed based on the characteristic of sensor. The response of the chitosan sensor towards formaldehyde was recorded as output voltage.

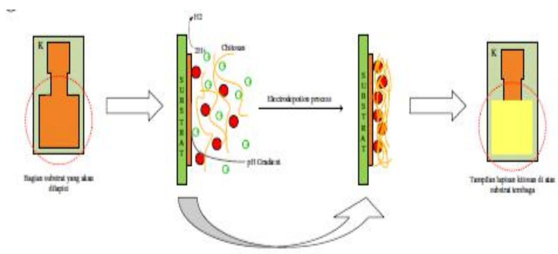

Figure 1: Deposition Process of Chitosan Film Sensor

3 RESULTS AND DISCUSSION

Chitosan is positively charged in acidic condition thus it would assemble onto the PCB surface to form a chitosan film sensor. Glutaraldehyde as a cross-linking agent made the sensing properties of chitosan high especially the shelf life of the sensor. The cross-linked chitosan sensor gave response (output voltage) to the formaldehyde in various concentration. The cross-linked chitosan sensor showed good stability in measurement, there is no any fluctuation in output voltage. The measurements were repeated three times. The output voltage values of chitosan sensor when detecting formaldehyde for 1; 1,5 and 2 ppm are reported in Table 1.

Table 1: The output voltage of chitosan sensor when detecting formaldehyde.

Formaldehyde Concentration (ppm)	Output Voltage Average (V)
1	0,0143
1,5	0,0213
2	0,0286

Table 1 shows the output voltage of chitosan sensor when its surface was dropped by formaldehyde standard solution. The output voltage values show the sensitivity of chitosan sensor during detecting various concentration of formaldehyde. The average of output voltage values for three times measurements were within the range of 0,0143 V to 0,0286 V. The highest output value (0,0286 V) was observed when chitosan sensor detecting 2 ppm of formaldehyde, while the lowest value (0,0143 V) was observed during the sensor was dropped by 1 ppm of formaldehyde. As shown by the table, increasing concentration of formaldehyde shows the increasing in output value.

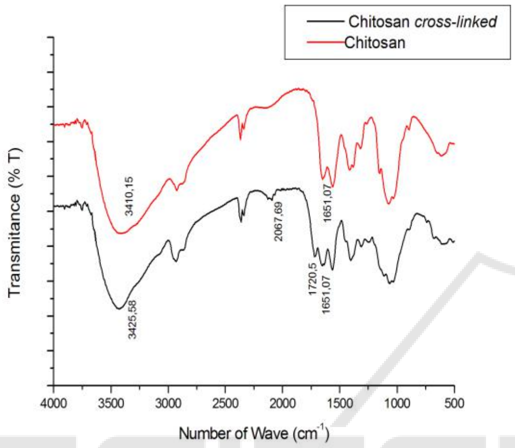

Figure 2: FTIR Spectra of Cross-linked Chitosan and Chitosan Films

The cross-linked process of chitosan has been done successfully. FT-IR was used to check the existence of cross-linking based on functional groups of chitosan. The spectrum of cross-linked chitosan shows in Figure 2. The hydroxyl groups (O-H vibration) are showed by band at 3425 cm^{-1} for cross-linked chitosan film and band at 3410 cm^{-1} for chitosan film. The presence of amine group is strengthened in 1651 cm^{-1} (chitosan cross-linked and chitosan). From the FTIR spectrum, the cross-linking has been showed at band 1720 cm^{-1} for aldehyde group.

4 CONCLUSIONS

The experimental results of chitosan sensor showed that chitosan sensor was capable to detect formaldehyde in various concentration. The chitosan sensor can differentiate the various concentration of formaldehyde. The sensitivity of chitosan sensors has been proven by the different output voltage values which were showed by the sensors during tested with different concentration of formaldehyde. Increasing concentration of formaldehyde showed the increasing on sensor output voltage values. The highest sensor output value (0,0286 V) was showed during the sensor detecting 2 ppm of formaldehyde, while the lowest value (0,0143 V) was showed during the sensor detecting 1 ppm of formaldehyde.

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