Optical Sensor based Chemical Modification as a Porous Cellulose Acetate Film and Its Application for Ethanol Sensor

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Abstract. A new approach to design and construction of an optical ethanol sensor has been developed by immobilizing a direct dye at a porous cellulosic polymer film. This sensor was fabricated by binding Nile Red to a cellulose acetate membrane that had previously been subjected to an exhaustive base hydrolysis. The prepared optical ethanol sensor was enhanced by adding pluronic as a porogen in the membrane. The addition of pluronic surfactant into cellulose acetate membrane increased the hydrophilic and porous properties of membrane. Advantageous features of the design include simple and easy of fabrication. Variable affecting sensor performance of dye concentration have been fully evaluated and optimized. The rapid response results from the porous structure of the polymeric support, which minimizes barriers to mass transport. Signal of optical sensor based on reaction of dye nile red over the membrane with ethanol and will produce the purple colored product. Result was obtained that maximum intensity of dye nile red reacted with alcohol is at 630-640 nm. Linear regression equation (r^2), limit of detection, and limit of quantitation of membrane with 2% dye was 0.9625, 0.29%, and 0.97%. Performance of optical sensor was also evaluated through methanol, ethanol and propanol. This study was purposed to measure the polarity and selectivity of optic sensor toward the alcohol derivatives. Fluorescence intensity of optic sensor membrane for methanol 5%, ethanol 5% and propanol 5% was 15113.56, 16573.75 and 18495.97 respectively.

1. Introduction
In everyday life, brewers supply several liquor (alcoholic drink) such as beer, brandy, wine, and whisky and people are fond of them. However, in brewery, it takes many times to check alcohol concentration in product liquors, by using distillation method and gas chromatography or liquid chromatography. Therefore, development of a simple and quick detection system of alcohol concentration in liquors is strongly required. Alcohol contained in several liquors is ethanol. Ethanol also used in food, and medicinal products [2]. In recent year, several methods has been used in detecting ethanol such as time FTIR, gas chromatography, and raman spectrophotometer [3]–[5]. However, these traditional methods have some disadvantage, such as more time consuming and require large sample, complicated operations, and well trained operation [6]. Hence, a rapid and accurate method for the on-site detection of ethanol is an emerging need from the perspective for safety to monitor alcohol consumers.

Recently, ultraviolet-visible absorption spectroscopy based on optical fiber sensors have received much attention in relation to ethanol sensing because of their high sensitivity, real-time and onsite detection capability, and rapid response and recovery time. Another option is biosensor. Biosensor is
a sensor that uses biological materials such as an enzyme, antibody and DNA to identify the molecules. Biosensor for ethanol commonly used alcohol oxidase enzyme (AOx) and alcohol dehydrogenase. Biosensor technique have the ability to detecting ethanol quickly, low limit detection and accurate. The use of enzymes in biosensor technique need high cost, susceptible to temperature, pH and pressure [7]. Optical sensor can be one of the method that able to detect ethanol quickly and easy fabrication.

Optical sensor based on the reaction of analyt with a sensitive layer that caused the change of absorbance, light is reflected of objects. Optical sensor development very interesting application in biology, biotechnology and ecology. Optical sensor advantage because easy to fabrication, low cost, high sensitivity and selectivity. Optical sensor consisting the solution of dye reagents that moved to the organic or inorganic matrix [8]. Optical sensors capable to detecting ethanol in the form of a liquid or gas. Solvatochromic dye used to detect the analyt. Commonly solvatochromic dye used in optical sensor are nile red, nile blue, and Reichardt’s dye. Immobilization of ionofor into optical sensors could be by entrapping, multilayer film, sol-gel and by covalent bond [9]–[11]. Cobalt optical sensor using red pyrogallol dye immobilized into cellulose acetate membrane. Ensafi et al. 2015 reported that cellulose acetate as immobilize dye matrix good accuracy and precision.

Cellulose acetate membrane is a synthetic biodegradable polymer that have the properties high permaebility, nontoxic and could be composited with various materials. Membrane modified by mixing with supporting material to support the nature of the membrane. The material commonly used in membrane modification such as pluronic and polyethylene glycol [12], [13]. Kalathimekkad et al. [14] had making the gas sensor based on alcohol fluorescence using nile red as dye and immobilized on Polydimethylsiloxane (PDMS) polymers. The sensor have the ability to detect the presence of ethanol vapor based on color changing and optical properties changing of the dye. Nile red dye has potential to detect the ethanol on ethanol sensor. The develop of red nile on optical sensor which the analite is liquid still on progress. The aims of this study to make and evaluate the etanol optic sensors based on cellulose acetate/pluronic/red nile.

2. Experimental

2.1 Fabrication of Membrane

Cellulose acetate (CA) membrane (Sigma Aldrich) were fabricated by inversion phase process. The membrane were prepared by flooding the surface of glass plate with polymer solution. Polymer solution contained CA and pluronic (80:20) in 100 ml acetone. After drying, the membrane were hydrolyzed in 0.1 M KOH for 24 h. Nile red as a fluorescent indicator was obtained from Sigma Aldrich. The Nile red was immobilized at the porous polymeric membrane with a classical dye bath recipe. This consisted of immersing a hydrolyzed membrane in an electrolytic dye bath for 20 min. The temperature of the dye bath was held 60°C. After removal from the dye bath, excess reagent was washed from the substrate with deionized water. This terminology derives from the ability of these dyes to adsorb strongly to cellulose-based polymers simply by immersing the polymer into a hot dye solution with a high ionic strength. Nile red is almost nonfluorescent in water and other polar solvents but undergoes fluorescence enhancement and large absorption and emission blue shifts in nonpolar environments (excitation/emission maxima ~552/636 nm in methanol). The factors that govern the formation and adsorption strength of such dyes are a complex mixture of chemical, physical, and structural effects. For Nile Red, it is apparent the chemical interactions of tertiary amine with the hydroxyl groups of the cellulose support play an important role in the formation of the immobilized structure. The relative importance of the molecular planarity (flatness) and solubility, both of which have been found to contribute at differing degrees to the binding strength.

2.2 Measurement of Optical Sensor

An operational diagram of the flow cell for the sensor in a fiber-optic transmission configuration is shown in figure 1. The incoming light entered the solution cavity, which was defined by the front window, the sensor, and the thickness of a silicone rubber gasket, through an array of quartz optical
fiber (Laboratory Scale at Physic Department Bogor Agriculture University). The beam then passed through the thin-film sensor and was collected and transmitted to a monochromator by a second array of fibers. The arrays, which consisted of five fibers arranged in a vertical orientation, were sealed into slotted Plexiglas cylinders and mounted to the cell with set screws. Performance of optical sensor can be measured with size of the membrane was 1x2.5 cm then mixed with ethanol 1-40% v/v with range 5%, and the membrane rinses for 5 minutes then put in cuvette holder to measured the fluorescent intensity. Measurement the intensity of fluorescents by spectrophotometer Optic Ocean.

![Figure 1](image1.png)

**Figure 1.** Experimental setup of the flow cell of sensor

2.3 **Membrane characterization**

Performance of morphology membrane surface before and after immobilize the nile red dye were characterized by Scanning Electron Microscopy (SEM) (Carl Zeis EVO MA 10). Characterization the functional group of the membrane and compared with cellulose acetate, pluronic and nile red dye was conducted by FTIR (Perkin Elmer).

3. Result and Discussion

3.1 **Optical Sensor Ethanol**

Fluorescence intensity of optical sensor ethanol is shown in figure 2, the result showed optimum intensity of optic sensor is at $\lambda$ range 600-640nm. This result was similar to Kalithimekad et al. [14] that maximum emission of the ethanol gas sensor membrane is at $\lambda$ range 590-610 nm. Fluorescence intensity depend on ethanol concentration, the value of fluorescence intensity proportional with ethanol concentration.

![Figure 2](image2.png)

**Figure 2.** Fluorescence intensity of ethanol membrane sensor.

![Figure 3](image3.png)

**Figure 3.** Linearity of ethanol sensor membrane with various nile red dye concentration.
Figure 4 showed the difference of fluorescence intensity of three alcohol derivatives, and this is due to the difference of polarity and chain structure of the alcohol derivatives [15]. However, this can be concluded optical sensor membrane poses ability to detect the different of alcohol derivates by fluorescence intensity.

![Figure 4](image)

**Figure 4.** Fluorescence Intensity of optical sensor membrane selectivity of ethanol derivatives

### 3.2 Ethanol Sensor Membrane Performance

Evaluation and confirmation the interaction among cellulose acetate, Nile red, and Pluronic was conducted by FTIR. Figure 5b showed the cellulose acetate spectrum that representing the cellulose acetate fingerprint. The wavenumber 3430 cm⁻¹ for OH, 1754 cm⁻¹ for C=O, 1235 cm⁻¹ for C-O ester and 1052 cm⁻¹ for C-O ester. Figure 5c showed the fingerprint of Pluronic, the wavenumber 3564 cm⁻¹ for OH, 2905 cm⁻¹ for C-H alkane, and 1107 cm⁻¹ for C-O ether. Our result have the similarity with Shao D et al [16], indicated that the of peak of wavenumber has the spectrum pluronic. Stretching overlay spectrum was for OH, C-H, C=O and C-O, this caused high range intensity. The results showed that functional group of ethanol sensor membrane did not change among the analysis.

![Figure 5](image)

**Figure 5.** FT-IR characterization of ethanol sensor membrane: (a) CA/Pluronic/Nile Red, (b) Cellulose acetate, (c) Pluronic, (d) Nile red dye

### 3.3 Morphology of Optic Sensor Membrane

Morphology of optic sensor membrane is shown in figure 6. Optic sensor membrane based cellulose acetate is occupied by Nile red (figure 6a), this indicated that immobilization process of membrane was successful and Nile Red dye which mixed with cellulose acetate and pluronic was immobilized into the membrane pores. In contrast, pluronic as a porogen in membrane was not successful to form pores, and this is appropriate with the figure 6b.
Figure 6a. Morphology of cross section optic sensor membrane CA/Pluronic/Nile Red

Figure 6b. Morphology of cross section optic sensor membrane cellulose acetate/pluronic membrane/pluronic

4. Conclusion
We concluded, that cellulose acetate/Pluronic®/nile red possed potential as optical sensor ethanol membrane. Maximum intensity of optical sensor membrane at λ range 630-640 nm and fluorescence intensity increased with increase ethanol concentration. Optic sensor membrane able specific detect the ethanol with concentration range 1-30% and distinguish the different of alcohol derivates. Based on membrane characteristic with FTIR and SEM, Nile red was better immobilized to membrane pores.

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