Entrapment of phenol red pH indicator into polyaniline sol-gel

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***Abstract*—Optical pH sensors offer a promising alternative method over the existence pH electrochemical sensor and other. Due to ability to achieve high performance, electrical passive operation, simplicity and price effectiveness. Recently, significant research efforts have been devoted to pH sensors for the detection of pH variation in high resolution short range changes. It becomes important to consider ways to heighten the sensitivity of the indicator by improving combination of the material and simple method of sensor fabrication. Effort has been put in studying the fabrication and the sensitivity of film towards pH range in physiological application. Most optical sensors consist of an indicator which is immobilized in a polymer matrix. In this research, polyaniline act as a sol - gel matrix to support pH sensitive indicator molecules which is phenol red. Polyaniline has been found to be versatile functional material which is the most suitable organic material to act as a matrix in aqueous medium and capability to sense on pH changes. The sensing capabilities of the device in term its optical absorption intensity with different pH values were explored. Besides that, simpler and low cost methods was prepared and developed. Through the final investigations, it was found that the phenol red immobilized in a polyaniline film on a portion of fiber optic developed by deposited for 4 layers at thickness is 88.46 nm, withdrawal speed with 15 mm/s and re-cladded length is 0.5 cm is the best optimized parameters.**

***Index Terms*— Polyaniline, phenol red, plastic optical fiber, pH sensor, sol-gel**

I. Introduction

MANYTYPES of pH sensor are easily available in commercial market like pH strips, indicator reagent and amperometric or potentiometric device are the most commonly used [1]. The earliest chemical indicator of pH measurement is pH strips or litmus paper and is still in use for laboratory activities at school. Conveniently used in simple applications, the colour of litmus paper between blue and red might be used to determine variation in pH. However, it suffers certain limitation on fulfilling to test at some point and unable to use in high accuracy cases [2]. The first commercial pH meters were invented around 1936 by Arnold Beckman consisting of glass electrode, reference cell and electrometer [3]. The pH meter will produce a small voltage and converted to pH units. However, this electrochemical device has several problems including electromagnetic interface interfering with each other and cause degrading efficiency and performance of device [4].

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In the recent years, optical method has been introduced and investigated to be successfully used as sensors and in some cases its performance surpassed the other electrochemical sensors [5-7]. The unique feature about this technique is application on fiber-based devices to act as remote sensing to produces the spectral characteristics. Besides that, optical devices are suitable for harsh conditions, ability to achieve high-performance, electrically passive operation, freedom from electromagnetic interference, multiplexed detections [8], continuously detection [9], large dynamic range, simplicity and cost effectiveness [6]. Now, optical pH sensor is the preferred choice for applications over conventional pH sensor and extensively development for many physiological applications such as brain pH monitoring, blood pH monitoring and gastric pH sensing. Peterson is the first person to introduce and develop fiber pH sensors to measure blood pH in human body in 1980 [10] encouraging many other researchers to continue on this investigation.

Recently, significant research efforts have been devoted to pH sensors for the detection of pH variation in small resolution changes as well as subtle changes. There are already a few reports on sensors with this capability such as research done by Schyrr *et al.* [11], was using ORMOSILs (organically modified silicate) entrapped with bromophenol blue. They are only used absorption detection of bromophenol blue at pH range 3 to 9. Where ORMOSILs just act as the polymer host matrix. It becomes significant to study ways to enhance the sensitivity by improving the material and method of sensor fabrication [12]. In this paper, the work focused on the use of polyaniline in which act as the polymer host matrix. Polyaniline also known in short form as PANI is an organic conducting polymer was found by Mac Diarmid in 1985 [13]. Polyaniline has been reported as sensing layers of many devices due to its wide range of conductivity from insulating to metallic boundary. Furthermore, this indicator-based optical pH sensor films inherent optical response properties and wider dynamic range for pH measurement. This versatility makes polyaniline frequently used in numerous applications either electrical or optical sensors such as gas sensor [14], chemical sensor [6, 15-17], pH sensor [18-21]. Moreover, it is also capable to act as sol-gel matrix to support indicator molecules since it has a high permeability for water and ions [17, 22, 23]. There appears to be no research on pH optical sensor using pH indicator based on polyaniline membranes as support.

An optical pH sensor was fabricated using absorbance indicators with polyaniline. With the mention advantages and potential of polyaniline to response pH variation have open the new routes to enhance the performance of sensor device while doped with pH absobance dependence dye. As a result, there have two sensitive dye operate in the same time.

In this research describes the development simple, cost effective method and high sensitivity of an optical pH sensor for monitoring high resolution at short range of pH. It is based on the incorporation in sol-gel system of polyaniline and precisely for the immobilized of pH indicators which is phenol red. The organic sol-gel layer deposited on the core of a polymer optical fiber, replacing the original cladding. In order to improve the dye entrapment efficiency and sensitivity, optical pH sensor based on polyaniline and phenol red were developed and the preparation conditions optimized. The sensing layer was characterized in term of optical to pH. The characterization of a fiber optic pH sensor based on the leaky evanescent wave is presented.

II. EXPERIMENTAL

This section discusses on the methodology of producing the sensitive membrane film of immobilized phenol red in polyaniline towards the application of optical pH sensor. An active membrane film as a pH sensing will be studied dependence of the optical properties measurement. The design and development of a pH sensor is the critical part to be investigated because it will effect on their sensitivity, repeatability, linearity and dynamic range of the sensor. The fabrication and its characterization method of deposited films was carried out and described in this section.

A. Fabrication of membrane sensing of pH sensor

The mixture of 0.62 g of polyaniline emeraldine base powder and 20ml of N,N-Dimethylformamide (DMF) solution was stirred for 24 hours to ensure that the polymer is well dispersed in the solvent. It was stirred on a hot plate stirrer using a magnetic stirrer. The ready filtered polyaniline sol-gel are used for doped with 2.0 mg/ml of phenol red powder. The sol-gel was stirred for 1 hours to ensure that the polymer is well dispersed. The dip coating method has been used in this work to deposit the sol-gel coated on core. The thickness dependency with deposited different number of layers are studied in this research which is 1, 2, 3 and 4 layers. The polyaniline sol-gel was placed in the beaker and a substrate was dipped into and withdrawn speed were optimized from 10, 15, 20 and 25 mm/s. The cycle and duration submerged was set for 5 times and 30 seconds respectively. Optimized parameter for number of deposited layers and withdrawal speed were carried on in fabrication of different deposited length which is 0.5, 1.5, 2.5 and 3.5 cm. Then, coated multilayers of membrane films were obtained subsequent dip coating method after drying at 80 ºC for 15 min. These sample are ready to characterized after further heating at 80 ºC for 5 hours.

B. Instrumentation

Fig. 1 shows the experimental setup of the fiber optic pH sensor based on absorbance intensity of light. The maximum absorbance wavelength for phenol red is 441 nm. So, we decided to use 460 nm single LED as the light source. Transmission of pulsed LED light in the fiber optic is measured and detected by spectrometer (USB2+H15335). Before test, the sample were immersed for 15 minutes in distilled water to allow the unbound dye to leach out. A portion of recladding with pH sensitive membrane was immersed in pH buffer solution. The optical absorption of the sample was captured in computer. This absorption phenomena is using leaky evanescent wave [6]. The flow charts in Fig. 2 is a brief explanation on the pH test setup.

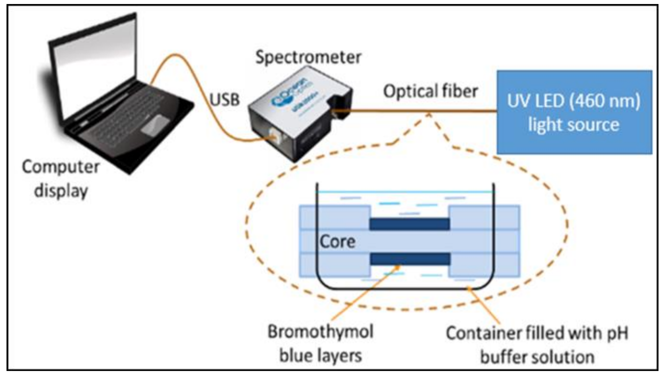

Fig. 1. Experimental setup to measure the spectral response of the fiber optic pH sensor

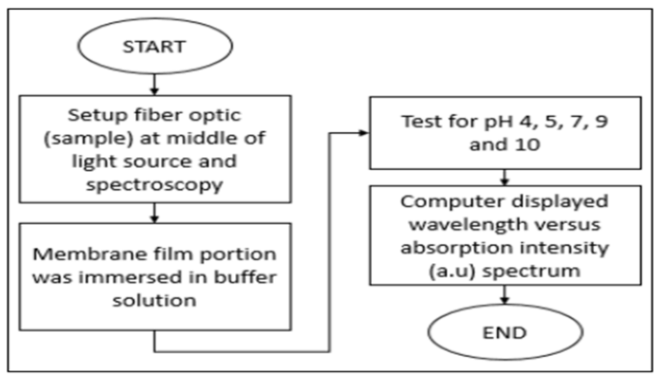

Fig. 2. Flowchart of pH test setup

III. RESULT AND DISCUSSION

The characteristics of fabricated immobilized phenol red thin film on fiber optic will be discussed. Various parameters were explored in order to get the optimize membrane film for optical pH sensor. All of the manipulated parameters play important role to produce a good and reliable membrane film. In this research, the thickness dependency parameter which is number of layers and withdrawal speed are studied. Besides that, deposited length of un-cladded fiber optic also were varied. All of the deposited film were measured by UV-Vis spectroscopy.

A. Optical properties of phenol red entrapped in polyaniline sol-gel

In this topic, the characteristics of fabricated immobilized phenol red thin film on fiber optic will be discussed. Various parameters were explored in order to get the optimize membrane film for optical pH sensor. All of the manipulated parameters play important role to produce a good and reliable membrane film. In this research, the thickness dependency parameters which is number of layers and withdrawal speed are studied. Besides that, deposited length of un-cladded fiber optic also were varied. All of the deposited film were measured by UV-Vis spectroscopy.

Fig. 3 demonstrates is to study the effect of thickness dependency upon different number deposited layers. The measurement using plastic optical fiber that possible for a given excitation power using blue LED light source (460 nm). This test to identify the intensity of an absorption spectrum changes with the thickness of sample. From the result, it can be seen that the films thicknesses increase as the deposition process (number of deposited layer) increase. The samples thickness for 1, 2, 3 and 4 layers are 80.68, 83.5, 81.41 and 86.13 nm respectively measured by cross section FESEM. Observed that higher absorbance intensity for 4 layer deposited membrane film with thickness is 86.13 nm. This is probably due to increases in presence of phenol red molecules on film proportionally increases of deposited layer and thickness of membrane film.

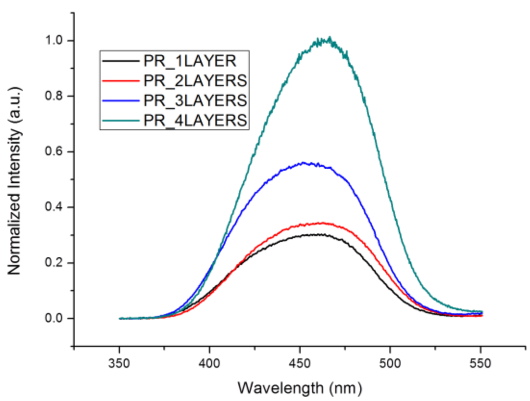

Fig. 3. Normalized absorbance spectrum of pH sensor with different number of layers of phenol red film coated on unclad portion of fiber optic

Fig. 4 shows results obtained from immobilized phenol red film deposited by dip coating with different withdrawal speed. This suggest that the film thickness gives more effect to the optical characteristic. The film thickness increases with the withdrawal speed increases. From the result obtained, withdrawal speed at 10, 15, 20 and 25 mm/s has membrane film thickness is 86.13, 86.92, 88.43 and 89.03 nm respectively. As obtained, thickness at 86.92 nm is the highest absorbance of light.

Besides the thickness dependency, deposited membrane film on difference un-cladded length of fiber optic is one of the important steps to produce a good sensing membrane. Four different deposited length which is 0.5, 1.5, 2.5 and 3.5 cm were used to investigate the absorbance intensity of light as shown in Fig. 5. This measurement to study the influence of deposited length of membrane film on the response of the optical membrane. It is found highest absorbance intensity of light travel in fiber optic at deposited length is 0.5 cm. Then, after the deposited length was increased into 1.5, 2.5 and 3.5 cm, the absorbance intensity slightly decreases.

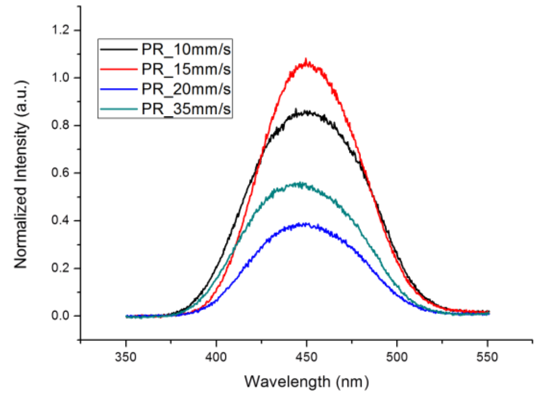

Fig. 4. Normalized absorbance spectrum of pH sensor with different withdrawal speed of phenol red film coated on unclad portion of fiber optic

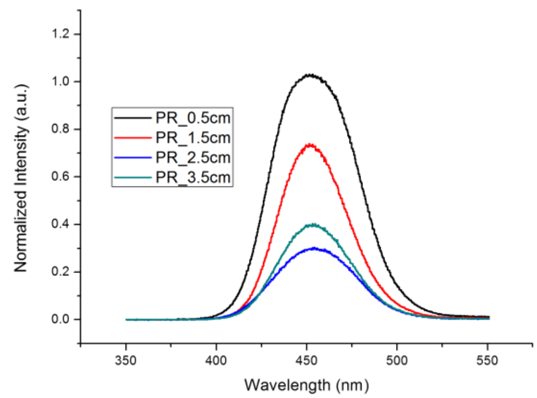

Fig. 5. Normalized absorbance spectrum of pH sensor with different deposition length of phenol red film coated on unclad portion of fiber optic

B. Sensing Analysis

Fig. 6 shows the data obtained from the different deposited layers membrane film treated in variety of buffer solution by optical measurement. From normalized absorbance intensity at 460 nm were transformed in pH versus normalized absorbance graph. From that, the slope and standard deviation of linear line were obtained. The slope and standard deviation of linear line is representing as sensitivity and linearity of the membrane film respectively. All sensitivity and linearity values are shown in graph. At pH 4 has highest absorbance intensity and decline line after continue to pH 5, 7, 9 and 10. It is representing that when light passed through membrane film, highest absorbance was absorbed in membrane film when treated in pH 4.

At first, the membrane film was deposited and dried for first layers with thickness is 80.68 nm gave the sensitivity and linearity value is 0.0069 au/pH and 0.9781 respectively. After that, the deposition and dried process repeated for second times to produce 2-layer sample with thickness is 83.5 nm. Sensitivity for this sample shown increase to 0.0164 au/pH while linearity starts to decline with 0.8661. The thickness was then increased again to 83.94 nm by 3-layer deposited process. The sensitivity and linearity obtained is 0.0125 au/pH and 0.8245 respectively. Thickness was increased to 86.13 nm by 4-layer deposited process become most suitable thickness due to highest sensitivity and linearity which is 0.0348 au/pH and 0.9626.

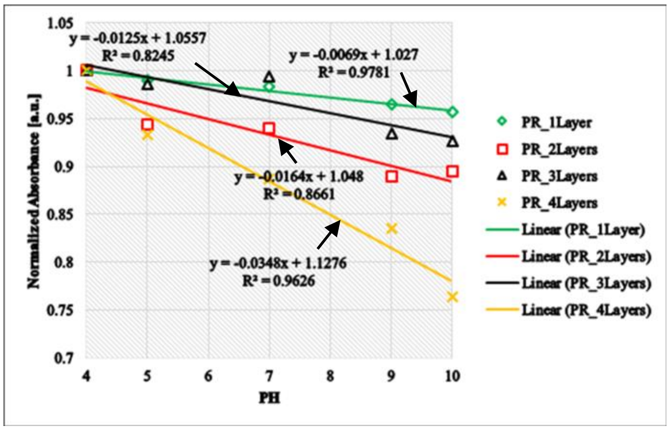

Fig. 6. Normalized absorption spectra of immobilized phenol red on unclad portion of fiber optic for different number of layers: 1, 2, 3, and 4 layers in variation pH values

Besides number of deposited layers during deposition process withdrawal speed is one of the important steps to produce different thickness. Withdrawal speed during the duration process was varied to find a relevant speed to be used. The speed was varied from 10 mm/s until 25 mm/s. The Fig. 7 provides sensitivity and linearity value for each membrane film deposited at different withdrawal speed. Obtained that membrane film deposited at lowest speed, which is 10 mm/s with thickness 86.13 nm had sensitivity and lowest linearity value with 0.0263 au/pH and 0.7999 respectively. After that, the withdrawal speed was increased to 15 mm/s, and the sensitivity and linearity value increase to 0.0305 au/pH and 0.9931. At this withdrawal speed, membrane film gave highest sensing performance. At withdrawal speed is 20 mm/s, the sensitivity and linearity start to decline to 0.0279 au/pH and 0.9131 respectively. The sensing ability was continuing decreases again when the withdrawal speed inclined to 25 mm/s with thickness 89.03 nm. The sensitivity and linearity value was dropped to 0.0201 au/pH and 0.8628.

According to S. M. Attia *et al.* [24], the influence of withdrawal speed really dependence on the thickness, porosity and refractive index of films. They found when withdrawal speed increases, may increase its thickness and refractive index of the film due to the increased number of crystalline particle per unit area and therefore decrease the porosity. This result was an agreement to the case studies by Cristina Figus *et al.* [25], which the film thickness was monitored as a

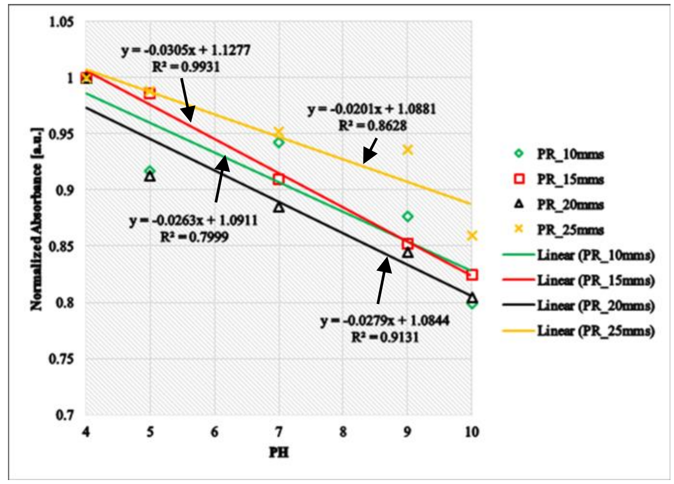

Fig. 7. Normalized absorption spectra of immobilized phenol red on unclad portion of fiber optic for different withdrawal speed: 10, 15, 20 and 25 mm/s in variation pH values

function of withdrawal speed. According that, it is important to optimized at suitable withdrawal speed because to produce good membrane film with homogenous and crack free.

In Fig. 8 clearly, at 0.5 cm deposited length has the highest sensitivity and thickness value of 0.0585 au/pH and 88.46 nm respectively. While their linearity is 0.9572. Then, after the deposited length was increased to 1.5 cm, the sensitivity, linearity and thickness started to reduce gradually with 0.534 au/pH, 0.7368 and 85.13 nm respectively. At 2.5 cm, the sensitivity is 0.0263 au/pH with thickness 84.72 nm. While, at 3.5 cm, the sensitivity is 0.0204 au/pH with thickness is 84.86 nm. The linearity for 2.5 cm and 3.5 cm is 0.9817 and 0.7887 respectively.

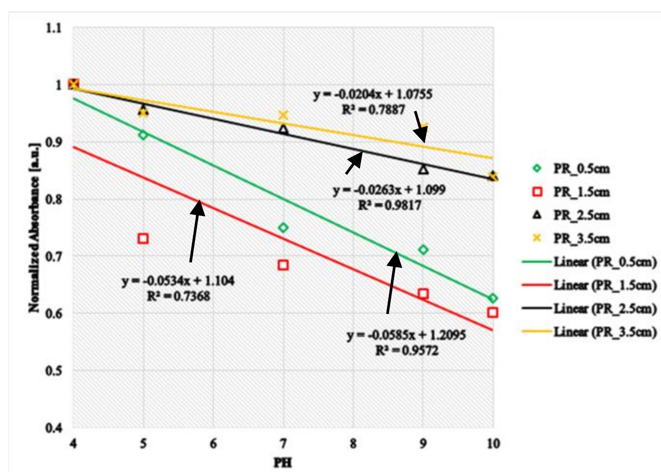

Fig. 8. Normalized absorption spectra of immobilized phenol red film coated on unclad portion of fiber optic for different deposition length: 0.5, 1.5, 2.5 and 3.5 cm in variation pH values

IV. Conclusion

This paper conclude indicator gave significant effect to optical pH sensor. It is found that the concentration of indicator gave different performance to the sensitivity and linearity of device. Furthermore, the performance of membrane films is also influenced by the thickness dependency of the films was studied while varying the number of deposited layers and withdrawal speed during deposition process. There is also significant effect to the sensitivity and linearity. Moreover, the dried duration after deposition also played an important role in enhanced performance of the device to detect pH. Lastly, the deposited length of membrane film used played important role in the determining the absorbance of light of optical pH sensor. The optimized combination of parameters producing highest sensitivity is with 4 deposited layers, withdrawal speed of 15 mm/s and coated length of 0.5 cm. These results will be the basis for the development of fiber optic pH sensor.

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