Detection of Cadmium Ion by *Evanescent Wave* Based Chitosan Coated Optical Fiber Sensor

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Abstract. Evanescent wave based-optical fiber sensor to detect cadmium ion is proposed. Chitosan was used by using the *dip-coating* method. The sensor was fabricated in *U-bent* shape. *U-bent* optical sensor at aconcentration of 2ppm and 5ppm had asensitivity of 0.2067 dBm/ppm and -0.7995 dBm/ppm, respectively. At a level of 2ppm - 5ppm, the optical sensor has a linear response with asensitivity of -0.283 dBm/ppm. The sensor takes 9.5 minutes to reach steady stateat aconcentration of 1 ppm. Atalevel of 2ppm - 5ppm, the sensor takes 5 minutes to 10.45 minutes to reach steady state.

1. Introduction

The presence of heavy metal in water is a grave threat to human health and environment[1]. Heavy metal ions are very dangerous because it tends to accumulate[2], is not readily biodegradable (persistent) in the human body, and is toxic[3]. Among metal ions, cadmium is a contaminant that has a high toxicity, even at very low concentration[1]. The limit of cadmium ion concentration in drinking water is 0.05 ppm[1]. Medically, cadmium can affect human health, especially blood and renal system [4].

There are various methods to detect cadmium in the environment such as theconventional method by extracting the sample solution, solid phase extraction by adsorption or ion exchange, and electro-analytical techniques[1]. The methods have many disadvantages, such as: the measurement cannot be done real-time, in situ, and cannot be multiplexed. To overcome to disadvantages of the method described above, optical fiber sensorswere developed.

Optical fiber sensorisanother application of optical fiber technology which is initially applied in anoptical communication system to transmit light carrying anoptical signal. Optical fiber sensors have attracted significant attention due to its advantages such as high sensitivity, fast response, small size, electromagnetic interference independence, simple fabrication, and iseasy to implement[5].

Fiber optic sensor to detect heavy metal ions has been developed by various methods such as reflectance[6, 7], absorption[8], Fabry-Perot interferometer[9, 10], and fluorescence [11]. The reflectance method hasan intricate design that is not suitable to be used in multiplexed sensor systems. Meanwhile, thefluorescent method has the advantage of having high sensitivity. However, this technique has drawbacks such as complicated fabrication techniques and high costs. Whereas, absorption method has advantages regarding simple fabrication. However, it has alittle sensitivity. Another technique which exploits the evanescent wave phenomenon was also used for various application. Like absorption method, the evanescent wave technology also provides simple fabrication process.

An optical sensor which utilizes loss due to macro-bending has also been developed since it is easy to fabricate, has a linear response, and has a relatively good sensitivity[12]. One of the optical sensors

which utilize macro-bending is a*U-bent* optical sensor. *U-bent* optical fiber sensor has been developed for many applications, such as optical bio sensor for detection of anti-IgG[13], optical fiber sensor for detection of explosive vapors [14]and optical bio sensor for detection of E.coli[15]. Therefore, in this work, an optical fiber sensor for cadmium ion detection was developed by using *U-bent optical fiber*using evanescent wave absorption technique.

2. Working Principle of the Sensor

To make an optical fiber serves as cadmium ion sensor, the optical fiber should be modified so that one of the light parameters, such as wavelength, intensity or phase, is modulated by the change of cadmium ion concentration. In evanescent wave absorption method, the variation of optical power due to absorption of the evanescent wave was used as anobserved parameter to detect the presence of the measurand.

In principle, theevanescent field is part of thelight that penetrate through the core-cladding interface. As the evanescent field penetrates into the cladding, the intensity decays exponentially as shown in Figure 1.
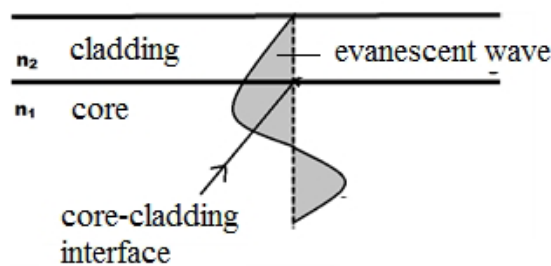

Figure 1. Illustration of evanescent wave

The optical power of the transmitted light through optical fiber $P(z)$ depends on the evanescent wave absorption coefficient as defined by

$$P(z) = P(0)e^{(-\gamma l)} \qquad (1)$$

Where $P(0)$ is the input optical power, l is the optical fiber length, and γ is the evanescent wave absorption coefficient. Meanwhile, the evanescent wave absorption coefficient value depends on core refractive index (n_1) and cladding refractive index (n_2) and other parameters as given by

$$\gamma = \left(\frac{\lambda n_2 c \, \theta c \, \theta}{2\pi \, n_1^2 c \, {}^2\theta_c \sqrt{si \, {}^2\theta - si \, {}^2\theta_c}}\right)\alpha \qquad (2)$$

Where r is the optical fiber core radius, θ is the angle between the ray and the normal to the interface, $\theta_c$is the critical angle, and α is the absorption coefficient of thebulk material. Thus, the optical power of the transmitted light is profoundly affected by the refractive index of the core and cladding material. Therefore, by replacing optical fiber coating with other documents which its refractive index change with the presence of measurand, the optical fiber can serve as measurand transducer. To be used as aheavy metal sensor, various types of materials can be coated on the fiber, such as citizen for detection of lead and mercury [16]and Pyrrole and chitosan for the detection of cadmium, lead and mercury[17]. In this work, the material used to replace the cladding layer is chitosan.

3. Experiment

Silica multimode optical fiber with acladding diameter of 125 μm and acore diameter of 50 μm was used in the sensor fabrication. The first step of themanufacturing process was removing the jacket and the buffer of the fiber using Fiber opticstripper threeholes (H-119CC)at the region where the cladding layer would be replaced by chitosan. After the buffer layer had removed, the next step was etched the coating layer by immersing the fiber into 50% HF solution for 56 minutes. Before the etching process, the fiber was cleaned using alcohol. The chitosan was then coated on the cladding-removed area by

using thedip-coating technique. Before coated on the fiber, the chitosan was first prepared by solving it using distilled water and 1% acetate acid. The process was done using magnetic stirrer at atemperature of 100°C for 3 hours. The chitosan coated-fiber was dried at room temperature for 24 hours. To improve the sensitivity, the fiber was bent at the chitosan coated region. The last step was attaching theoptical connector to both ends of the fibers.

4. Characterization of the Sensor

Characterization of the sensor was done by dipping an optical fiber that has been coated with chitosan into asolution of cadmium in various concentration values which are 0.9, 2, 3, 4, 5 and 6 ppm. Cadmium solution used in the characterization has a pH value of 7.One end of the optical fiber was connected to the optical light source, while the other end was attached to an optical power meter to measure the intensity of the light transmitted through the solution, as shown in Figure 2.
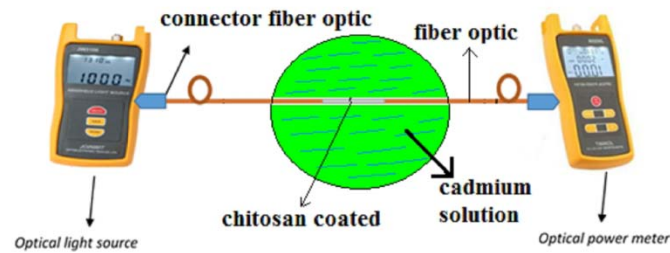

Figure 2. Characterization set-up

The response time of the sensor was measuredby recording the change of the output intensity for each value of the concentration. The response time is the time required for the sensor to reach 90% of the final value which is the valuein an equilibriumstate.

5. Results and Discussion

The developed optical fiber sensor is shown in Figure 3(a) and the image of chitosan-coated optical fiber taken by CCD microscope at amagnification of 400 times is shown in Figure 3(b).It is shown that the diameter of the coated fiber is 427 μm.
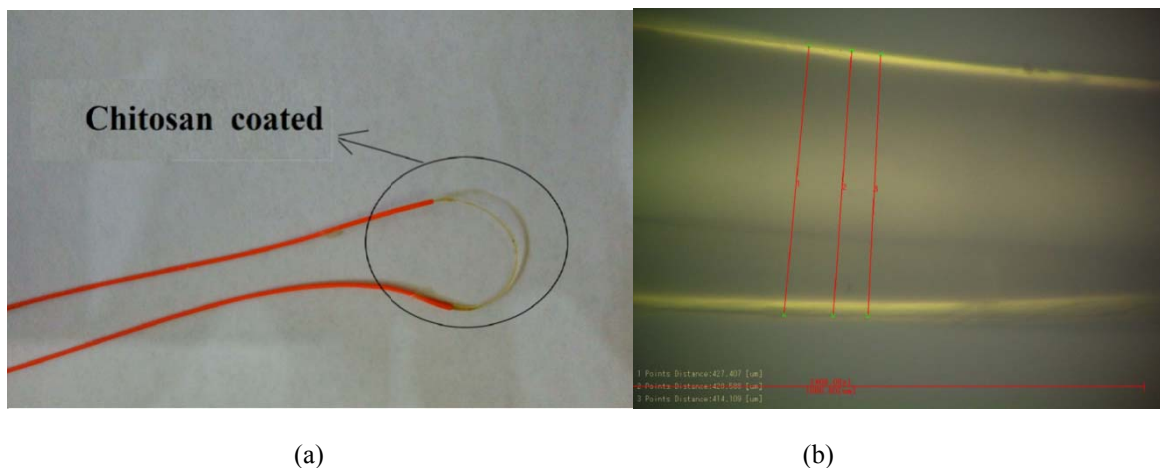

(a)   (b)

Figure 3. The fabricated *U-bent* optical fiber (a) and the microscope image of the chitosan coating (b)

The output intensity was plotted against the solution concentration as shown in Figure 4(a). Polynomial regression of the curve showed that at aconcentration of 2 ppm and 5 ppm, the sensor has asensitivity of 0.2067 dBm / ppm and - 0.7995 dBm / ppm, respectively, with a correlation factor of 0.8072. It is also shown that the sensor provides liner response in the range of 2ppm to 5ppm with

asensitivity of -0.283 dBm/ppm as shown in Figure 4(b). By using optical power meter with aresolution of 0.02dBm as adetector, the sensor can detect as low as 0.07ppm.

Contrary gradient value indicates that the light intensity decreased as theconcentration of cadmium ion increased. The decline of light intensity was caused by the increase of refractive index of the chitosan layer due to adsorption of cadmium ion. When the optical sensor was immersed in cadmium ion solution, an interaction between chitosan and cadmium ion occurred.The pores of chitosan were substituted by the cadmium ions and forming chelates structure and releasing H^+ ion [18].This process makes the chitosan surface smoother then that before it adsorbs cadmium ions and increases the chitosan density. The higher the cadmium ions concentration, the more chitosan pores substituted by cadmium ions, and thus the chitosan is denser. The increase of density results in the increase of refractive index. Therefore, as shown in equation (2), the optical power transmitted in the fiber decrease as the cladding refractive index increase and more power loss occurs during the light propagating through the fiber. However, when the dry sensor was first exposed to cadmium solution, the output intensity increased as shown in the graph. At dry state (0 ppm), the output power was -32.4dBm, while in 1ppm cadmium solution, the output intensity increased to -31.3dBm. The increase occurred since the chitosan at dry state was much denser than the chitosan in solution. Therefore, the refractive index of dry chitosan was much higher than that of wet chitosan. As a result, the output intensity of the sensor increased. It also can be observed from the results that great loss occurred as the light traveled along the sensor. The greatdamage occurred due to connection loss between fiber and laser source and optical power meter, connection loss at the fiber connector and loss due to macro-bending. However, the macro-bending loss gives advantage i.e. improving the sensor sensitivity by enhancing the absorption of the evanescent wave.
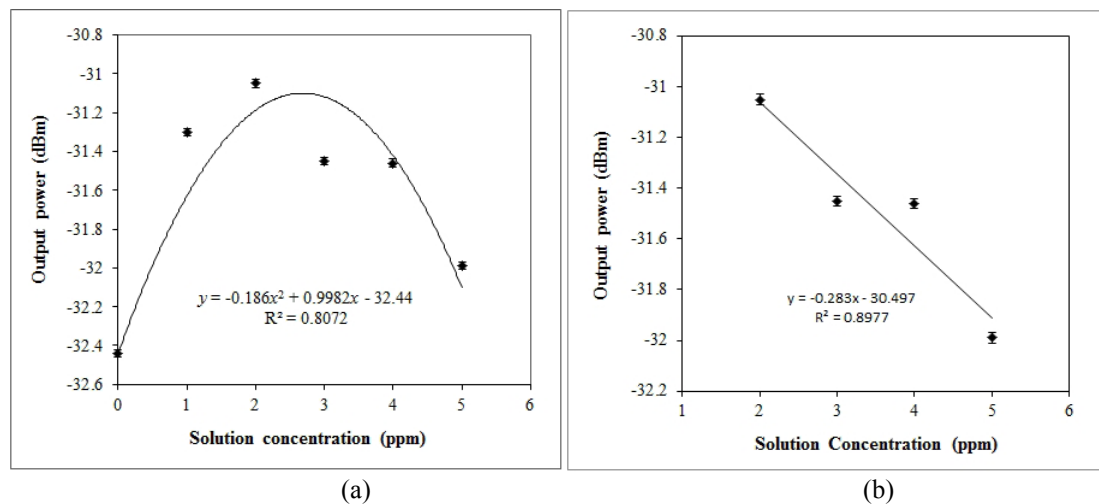

(a)   (b)

Figure 4. Intensity vs. cadmium solution concentration: polynomial regression (a) and linear regression (b)

The response time of the sensor that indicates the time required for the sensors to reach steady state is shown in Figure 5. It is shown that at aconcentration of 1 ppm, the sensor requires 9.5 minutes to reach steady state. Meanwhile, at aconcentration of 2 ppm to 5 ppm, the sensor takes 5 minutes to 10.45 minutes to reach steady state.The pores of the membrane on the surface of the chitosan determine the time response of the sensor. The wider the pores, the faster the chitosan adsorb heavy metal ions[19]. The pore size of the chitosan depends on some of amine groups on the chitosan. It was also observed that the response time increased as the cadmium ions concentration increased. This increase of time response occurred since ahigher concentration of cadmium ions resulted in lower number of amine groups in the chitosan. Therefore, much longer time was required to reach steady state at ahigh concentration than that at low level. However, high response time was also observed also at 1 ppm which was caused by fluctuation of the optical light source that has not reach stable condition when the measurement was conducted.
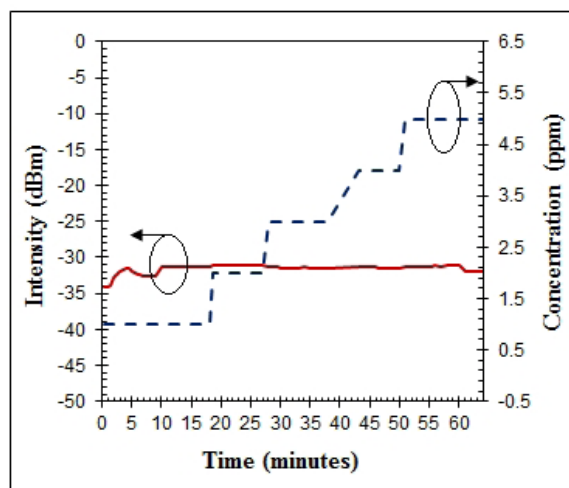
Figure 5. Response time of the optical sensor

6. Conclusions

U-bent optical fiber sensor to detect cadmium ions has been fabricated by modifying an optical fiber. Some part of optical fiber cladding was replaced with chitosan using thedip-coating technique. The sensor has alinear response in theconcentration range of 2ppm-5ppm. The sensor can measure cadmium concentration up to 0.07 ppm. This result still low compared to other published sensor [17]. However, the proposed sensor has anadvantage regarding thesimple fabrication process. The sensitivity can be improved by optimizing the coating thickness and the bending radius. About response time, the sensor needs to be improved which is the goal for our future work.

Acknowledgement

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