Study of chitosan layer-based Fabry Perot Interferometer optical fiber sensor properties for detection of Pb^{2+}, Hg^{2+} and Ni^{2+}

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Study of chitosan layer-based Fabry Perot Interferometer optical fiber sensor properties for detection of Pb^{2+}, Hg^{2+} and Ni^{2+}

I Yulianti*, N M D Putra, Fianti, N Akmalia, D A Pratiwi and I V Albadiah

Physics Department, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang, Central Java, Indonesia

*Corresponding author: ianyulianti@gmail.com

Abstract. This work presents investigation of properties of optical fiber sensor based on Fabry-Perot interferometer using chitosan to detect Pb^{2+}, Hg^{2+} and Ni^{2+}. The sensor was fabricated by employing chitosan layer on the tip of single mode optical fiber (SMF) which serves as Fabry-Perot interferometer. Some of the light transmitted in the SMF were reflected back due to multiple reflection in the interferometer. The chitosan was coated on the fiber end by using dip coating technique. Three sensors were fabricated which are sensor A, B and C with coating thickness of 141.85 µm, 105.52 µm and 129.25 µm, respectively. Characterization was done for sensitivity and response time of the sensors. The results showed that sensor B which was characterized for Hg^{2+} provided the highest sensitivity and the most stable response time.

1. Introduction

Optical fiber sensors for heavy metal ions detection have been investigated and proposed in recent decades. Various optical sensors were developed for specific heavy metal ions such as for mercury (Hg^{2+}) detection [1], chromium (Cr^{2+}) [2] and nickel (Ni^{2+})[3]. The interest in developing optical sensor for heavy metal ions detection is triggered by the presence of heavy metal ions in environment due to the huge growth of industries which is harmful to human life. Optical fiber sensors offer advantages which are not provided by conventional sensors such as immune to electromagnetic field, suitable for harsh environment, and low cost.

In early years of optical fiber invention, optical fiber was intended to be used in data transmission for telecommunication. Therefore, to be used as heavy metal ion sensor, modification to optical fiber in terms of structure and coating material should be made. Tou et.al [4] used photonic crystal fiber (PCF) spliced between single mode optical fiber (SMF) to form Mach-Zehnder interferometer (MZI) structure and coated it with poly(vinyl alcohol) hydrogel to detect Ni^{2+}. Meanwhile, Kishore et.al. [2] have used hydrogel synthesized using tetraalkylammonium salts which is sensitive to Chromium. The hydrogel was coated on Fiber Bragg Grating (FBG). MZI and FBG structure are interesting since they are wavelength modulated so that measurement does not affect by loss comes from bending and connection. However, PCF-based MZI and FBG require complex fabrication technique. Another wavelength based optical sensor is intrinsic Fabry-Perot interferometer (FPI). FPI has been used for various sensor application such as temperature sensor [5], relative humidity sensor [6] refractive index sensor [7], hydrogen sensor [8] and displacement sensor [9]. FPI has also been used for heavy metal ion detection by using no-core fiber (NCF) spliced between SMF which was coated with

chitosan/polyacrylic acid (PAA) [10]. In this work, a simple optical sensor using FPI technique was studied. The FPI was formed by coating SMF with thin layer of chitosan. Since chitosan has ability to adsorbs various heavy metal ions, then properties of the sensor, which are sensitivity and response time to Pb^{2+}, Hg^{2+} and Ni^{2+}, were investigated. Thus, by obtaining the sensor properties to various heavy metal ions, further improvement can be done to reduce the sensor cross-sensitivity and improve sensor selectivity.

2. Methods

2.1. Sensing Principle

FPI can be realized by coating the end tip of fiber with thin layer chitosan. The two surfaces of chitosan layer serve as mirror, while layer thickness serves as cavity, as shown in Figure 1. Chitosan is natural biopolymer which is synthesized by deacetylisation of chitin. Chitosan has the ability to form complexes with metals. Its adsorption capacity for metal ion is higher than that of chitin since it contains amino group [11]. Chitosan has been used for heavy metal ion sensor using surface plasmon resonance (SPR) technique[12-13].

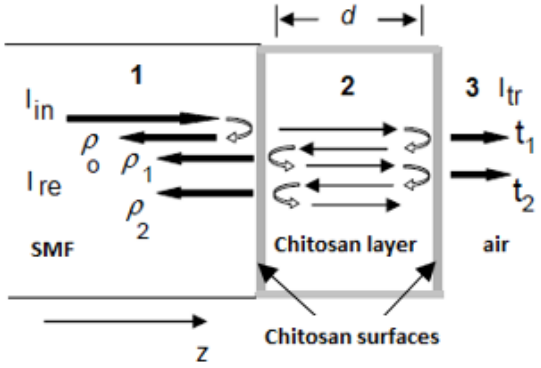

Figure 1. Chitosan layer-based FPI optical sensor

The phase of reflected light will change if the FPI cavity length, *d*, is change as determined by:

$$\varphi = \frac{4\pi n d}{\lambda} \quad (1)$$

where *n* is the effective refractive index of the optical fiber and λ is the light wavelength. As further effect, the power reflectivity will also change as determined by

$$R_{FP} = \left|\rho_{FP}\right|^2 \quad (2)$$

where

$$\rho_{FP} = \frac{\rho_{12} + \left[t_{12}t_{21} - \rho_{12}\rho_{21}\right]\rho_{23}\exp\left(-j\phi\right)}{1 - \rho_{21}\rho_{23}\exp\left(-j\phi\right)}, \quad (3)$$

ρ_{ij} and t_{ij} is the complex amplitude coefficient of the reflected and transmitted of the light propagates from region *i* to region *j*, as shown in Figure 1. The change of cavity length is resulted from the change of chitosan thickness when chitosan adsorbs heavy metal ions. Therefore, the change of reflected power indicates the presence of heavy metal ions in solution which in contact with the chitosan based FPI sensor.

2.2. Sensor Fabrication

Three sensors were fabricated by using SMF with core and cladding diameter of 9µm and 125µm, respectively which the tip was coated using chitosan to form Fabry-Perot interferometer. Prior to coating process, the chitosan solution was prepared by diluting 5g of chitosan powder with acetate acid with concentration of 1% and stirred it using magnetic stirrer for 3.5 hours at temperature of 90°C. Coating process was then conducted by dipping the fiber tip into chitosan solution for 10s and then it was dried

at room temperature for 2 hours. The coating process was repeated for 15 times to get sufficient thick layer. The fabricated sensors were then observed using optical microscope to measure the coating thickness. It was found that the thicknesses are 141.85 μm, 105.52 μm and 129.25 μm for sensor A, sensor B and sensor C, respectively.

2.3. Characterization

Solution of Pb, Hg and Ni was prepared with various concentration. The first step in solution preparation was making stock solution which is solution with concentration of 1000ppm for each heavy metal ion. To make 1000ppm of Pb^{2+} solution, 2.512g of $Pb(NO_3)_2$ was diluted in 0.1l of distillated water. Meanwhile, to obtain 1000ppm of Ni^{2+} solution and Hg^{2+} solution, 0.314g of $Ni(NO_3)_2$ and 0.117g of HgCl was used, respectively. After the stock solution ready, the next step was mixing some volume of the stock solution with distilated water to get lower concentration. Solution with concentration of 0.1ppm to 1ppm with increment of 0.1ppm were made for each heavy metal ions.

To obtain sensitivity of the sensors, the change of output intensity of light reflected from the sensor as the sensor immersed in various solution concentration was observed. 1310nm light from optical light source was launched to the sensors that was dipped in heavy metal ion solution through one of the output part of 1×2 optical splitters. The input part of the splitter was connected to the sensor, while other output part of the splitter was connected to optical power meter (OPM) to measure the reflected light intensity, as shown in Figure 2. The light intensity was measured until the intensity shown in the OPM was stable which indicates that the sensor has reach its steady state. The time required to reach steady state was recorded as time response of the sensors. Then, the solution was removed and replaced by solution with higher concentration. The process was repeated for 10 solutions for each heavy metal ion. Sensor A, B, and C were characterized in Pb^{2+}, Hg^{2+} and Ni^{2+} solution, respectively. After characterization was done, the element composition of chitosan layer was analysed using scanning electron microscope (SEM) to obtain the amount of heavy metal ions that was adsorbed by the chitosan.

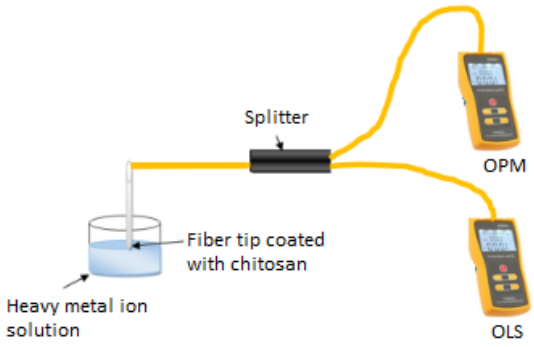

Figure 2. Characterization set up for sensitivity determination

3. Result and Discussion

3.1. Sensitivity

The intensity of reflected light was plotted against concentration of heavy metal ion solution to obtain sensitivity of the sensors correspond to each heavy metal ions as shown in Figure 3. It is shown that for all heavy metal ion samples, the intensity decreases as solution concentration increases as indicated by negative gradient. As shown in Equation (3), the reflected intensity of FPI sinusoidally depends on cavity length. Therefore, the increase of certain range of cavity length will results in increasing reflected intensity and other range will result in decreasing intensity. In FPI formed by Chitosan layer, the increase of cavity length is occurred due to adsorptions of heavy metal ions by the Chitosan.

The sensor sensitivity to Pb^{2+}, Hg^{2+} and Ni^{2+} are -0.177dBm/ppm, -0.215dBm/ppm and -0.1445dBm/ppm, respectively. Clearly, the sensitivity to Hg^{2+} is the highest among others. The SEM-EDX examination confirmed the results. It is shown that the amount of Hg^{2+} that was adsorbed by the Chitosan layer is the highest compared to Pb^{2+} and Ni^{2+}, as tabulated in Table 1. Since the Chitosan

adsorb more to Hg^{2+}, then small change of Hg^{2+} concentration results in high change of cavity length which further results in the high change of reflected light intensity. The results also agree well with the work done by Babel [14] which showed that adsorption of Chitosan to Hg^{2+} is the highest compared to that of other heavy metal ions. The other factor that also affect the sensitivity is the atomic radius of the heavy metal ions. When chitosan adsorbs ions with high radius, then the thickness of chitosan will change more rapid then when it adsorbs ions with lower radius. From Table 2, it is shown that Hg has the highest atomic radius compared to Pb^{2+} and Ni^{2+}.

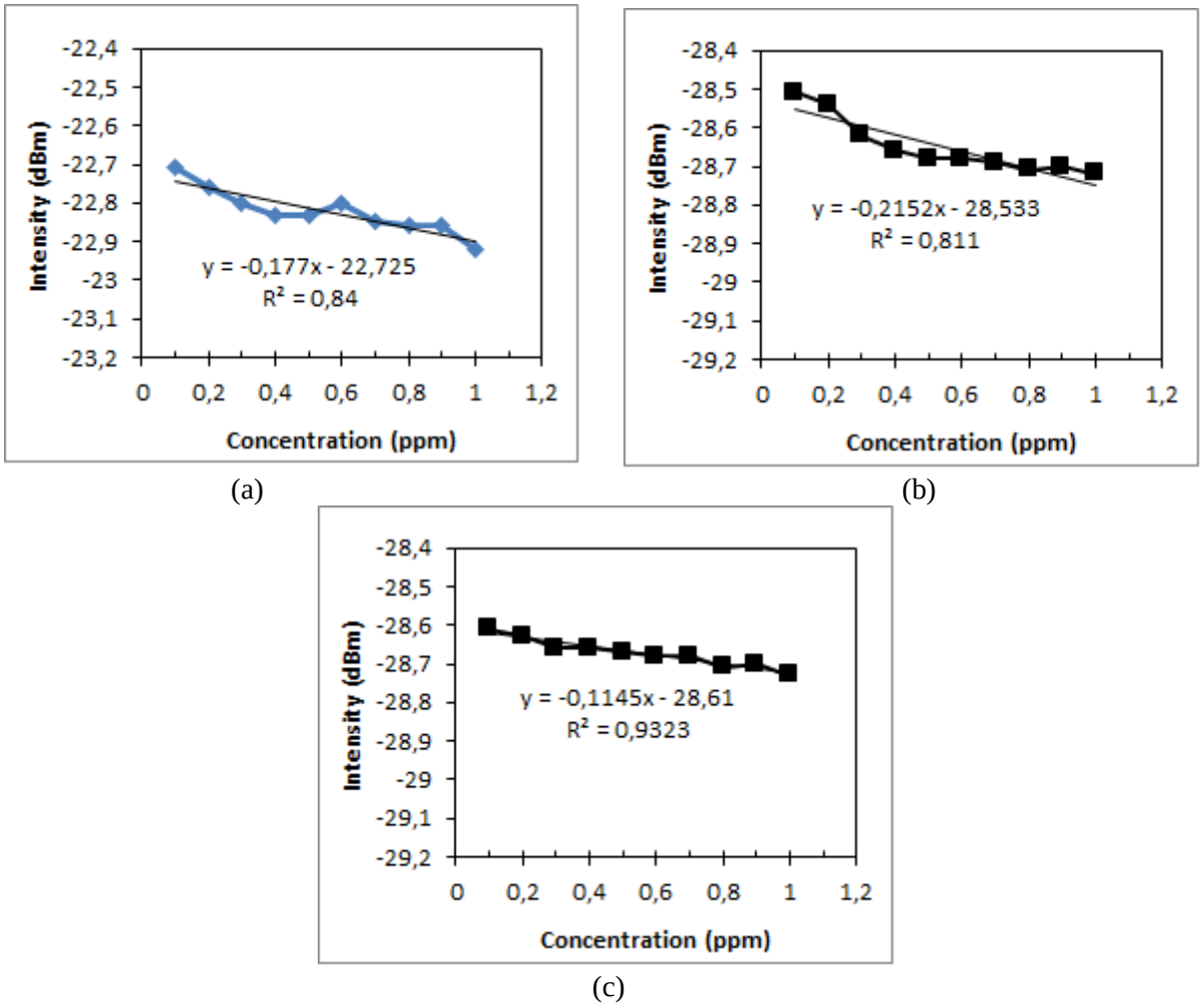

Figure 3. Reflected light intensity vs heavy metal ion concentration of Pb^{2+} (a), Hg^{2+} (b) and Ni^{2+} (c)

3.2. Response Time

Response time of the sensor is measured as the time taken to reach steady state during measurement. The intensity of the reflected light was measured for each solution concentration every five seconds and the results were plotted as shown in Figure 4. It is shown that the response to Hg^{2+} is more stable compared to Pb^{2+} and Ni^{2+}. At concentration of 0.1ppm, the sensor required 25s to reach stable condition. As the concentration increases, the sensor need longer response time. The results agree with experiment done by Ni & Bai [15] and Benavente [16] which showed that adsorption of Hg^{2+} requires less time to reach stable than that of Pb^{2+}. The fluctuation is the results of the kinetic of heavy metal ions adsorption which consist of two process which are the transport of ions from the bulk solution to the

surfaces of the chitosan and the attachment of ions to the active adsorption sites on the surfaces of the chitosan [15].

Table 1. SEM-EDX results of the sensor A, B, and C

Sensor	Atomic element (%)		
	Ni	Hg	Pb
Sensor B	-	97,6	-
Sensor A	-	-	1,7
Sensor C	0,3	-	-

Table 2. Atomic radius of Pb, Hg and Ni

Heavy metal ion	Atomic radius (pm)
Hg^{2+}	171
Pb^{2+}	154
Ni^{2+}	149

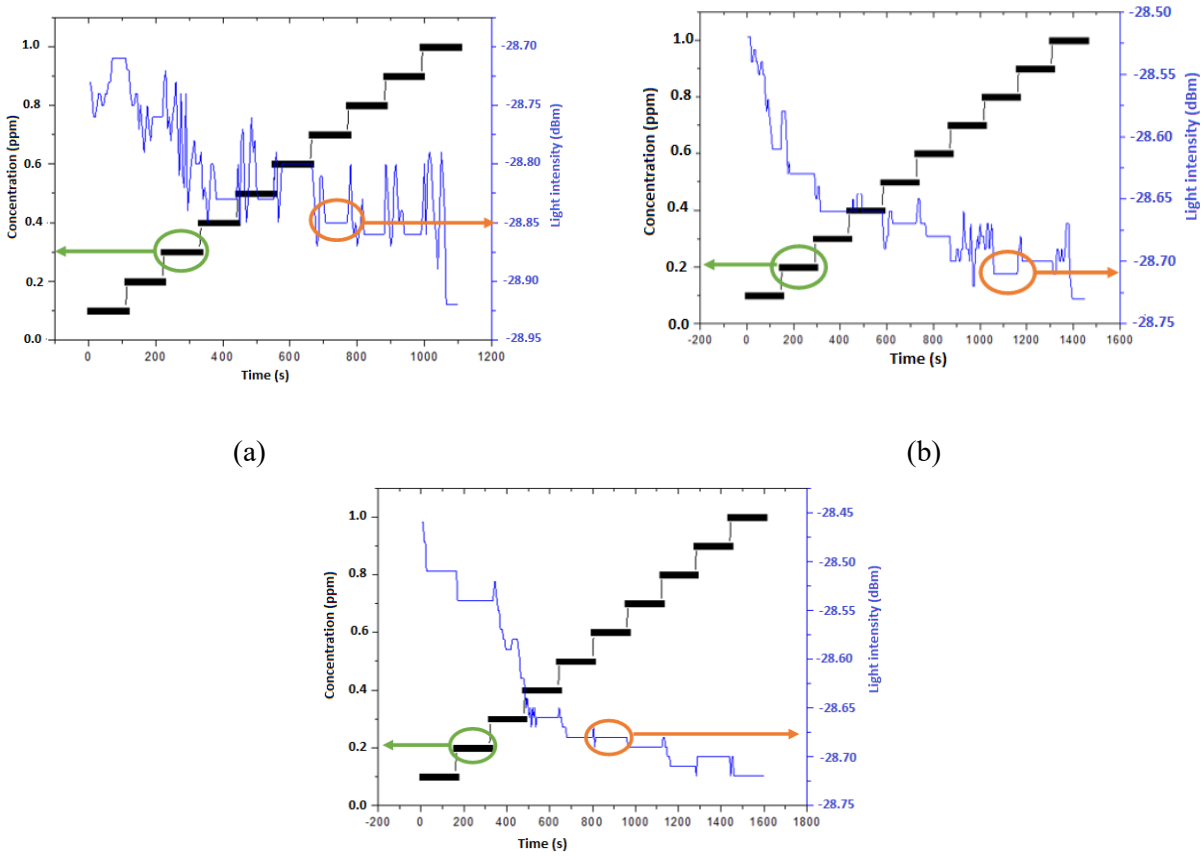

Figure 4. Response time of sensor A, B and C to Pb^{2+} (a), Hg^{2+} (b) and Ni^{2+} (c), respectively

4. Conclusion

Properties characterization of three optical sensors based on Fabry-Perot interferometer technique have been done. The interferometer was formed by coating thin layer of Chitosan on the tip of SMF. The results showed that the sensor was more sensitive to Hg^{2+} than to Pb^{2+} and Ni^{2+}. However, the sensitivity values of the three heavy metal ions are in the same order. Therefore, modification to chitosan should be made to increase sensor selectivity (increase sensitivity to a desired heavy metal ion while reduce sensitivity to other ions). Other technique to reduce cross-sensitivity is by considering a change of reflected light spectrum which can be observed using optical spectrum analyser (OSA).

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