

Detection of Chemicals using Fiber Optic Microfluidic Sensor

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Abstract

Sensors have been applied in various aspects and fields. The integration of innovative micro fluidic system in sensors offer a development of the device with better performance, highly reliable and easy to use. In this study, a fiber opti micro fluidic sensor was fabricated using dry film resist for potential chemical sensing. The device was investigated and evaluated on its performance in terms of sensitivity, reproducibility, response time and detection limit of two model chemicals, Nickel(II) Nitrate Hex hydrate and Cobalt(II) Sulphate Heptahydrate. Results obtained show that the micro fluidic fiber optic sensor produced satisfactory detection towards both of the chemicals in terms of sensitivity, repeatability and response time. The response time towards Nickel (II) Nitrate Hex hydrate and Cobalt (II) Sulphate Heptahydrate were 77 s and 101 s respectively. The detection limit of the device towards both Nickel(II) Nitrate Hex hydrate and Cobalt(II) Sulphate Heptahydrate was around 0.1 mol/dm³. This suggest that the fabricated micro fluidic fiber optic sensor to be reliable for chemical sensing.

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1. Introduction

The integration of sensors with microfluidic system has become more popular nowadays. These integrated sensors provide miniaturized platforms with many favorable properties, such as reduced sample volume, decreased processing time, low cost analysis and low reagent consumption [1]. Microfluidic devices have large surface-to-volume ratio which is suitable to be applied for on-site testing.

Small volume detection within microfluidic environments have typically been based on optical measurements. Optical detection is well suited for most microfluidic systems because most substrate materials have favourable optical characteristics that are the most sensitive. Emission based optical techniques are divided into fluorescence and chemiluminescence-based detection.

The advancement of low-loss optical fibre happened in the mid-1970s primarily for the telecommunication

industry and created Momentous development in the field of sensing applications. Optical fiber is the most common transducing platforms in optical sensor technology. This optical method provides many advantages such as they can be miniaturized, have multiplexing capabilities and can combine rapid response times with high sensitivity for analyte evaluation. Several schemes based on the label-free methods for chemical sensing have been developed [2, 3]. In this work, a fiber optic sensing on microfluidic platform is proposed for potential chemical sensing.

2. Material and Methods

Material

Preparation of chemical samples solutions. Nickel (II) Nitrate Hexahydrate and Cobalt(II) Sulphate Heptahydrate powder were added to distilled water to obtain a 2.5 M Concentration solution.

Methods

Fabrication of micro fluidic system. AutoCAD was used to design the microfluidic channel which has 500 μm and 12 mm width and length respectively. Later, the design was printed using high-resolution printer to prepare photomask. Next, microscope glass slides (25.4 mm x 76.2 mm) which was used as the substrate, was sonicated using 5% detergent solution for 1 minute and rinsed with distilled water, acetone, methanol and isopropanol thoroughly. Then, substrates were dehydrated at 200°C in the oven. The procedure was followed by lamination process, mask alignment and exposure and finally development and hard baking. [4, 5].

A ST multimode fibre pigtail from Ingellen Technology (China) as the transduction platform. The fibre core and cladding diameters were 62.5 μm and 125.0 μm respectively. Initially, the multimode pigtail was cut using a fibre cleaver (FC-6RS, Sumitomo). Then, the thin plastic coatings of the bare fibres were stripped off with a fibre stripper. Once the cleaving process was finished, the fibres were cleaned with a Kim wipe soaked in ethanol. The fibres were then inserted and secured in placed on the dry film resist (DFR). Fibre alignment was performed by measuring the transmittance output from the input multimode pigtail.

Performance Evaluation of micro fluidic system. The completed fiber optic microfluidic sensor was evaluated on sensitivity, response, reproducibility and detection limit on nickel and cobalt solution using UV VIS JAZ Spectrometer.

3. Results and Discussion

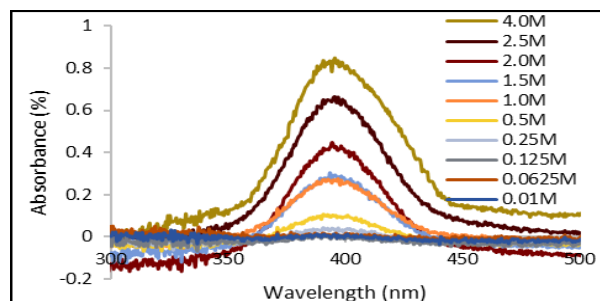
Determination of suitable wavelength

Initially, the suitable wavelength to measure Nickel and Cobalt solution was determined. Figure 1(a) and 1 (b) show the peak absorbance were at 392 nm and 515 nm wavelength for Nickel(II) Nitrate Hex hydrate and Cobalt(II) Sulphate Heptahydrate respectively. These recorded wavelengths at peak absorbance were similar to previous findings for nickel [6] and Cobalt (II) ions [7]. Hence, the results obtained for the microfluidic sensor developed produced satisfactory detection at the appropriate wavelength values as reported by previous workers.

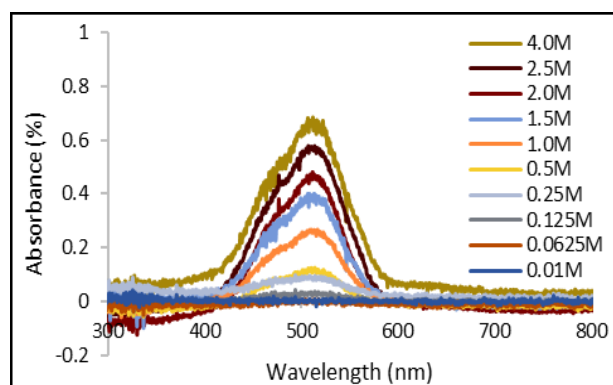
Detection limit

Next, the samples were prepared and tested in various concentrations for investigating the detection limit of the device. Detection limit is the value whereby further

decrease in concentration of samples does not cause a significant decrease in absorbance value. Figure 2a and 2b show absorbance against concentration plots for both of the chemicals.



(a) Nickel(II) Nitrate Hex hydrate



(b) Cobalt(II) Sulphate Heptahydrate

Figure 1: Absorbance graph of different concentrations for both chemicals

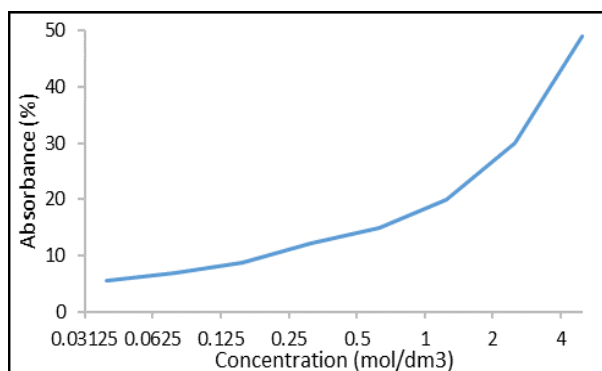
For Nickel(II) Nitrate Hexahydrate, when the concentration was decreased from 0.125 mol/dm³ until 0.05 mol/dm³, no significant change on the absorbance was observed (Figure 2a). Hence, the detection limit of the system towards Nickel(II) Nitrate Hex hydrate was found to be around concentration of 0.1 mol/dm³. Meanwhile, from Figure 2(b), small difference in absorbance value for Cobalt(II) Sulphate Heptahydrate was observed between concentration of 0.0625 to 0.125 mol/dm³, thus, the detection limit towards Cobalt(II) Sulphate Heptahydrate was also approximately 0.1 mol/dm³. In this case, the detection limit is described in terms of concentration of the chemicals. These values of concentration of 0.1 mol/dm³ are the lowest amount that the microfluidic device can be detected since further decrease of concentrations does not result in any significant changes of absorbance. This value is much higher than the WHO (World Health Organization) guideline value for the safe level of nickel in drinking water, which is 70 $\mu\text{g/L}$. In terms of number of mole per cubic decimeter, it is around 1.19×10^{-6} mol/dm³. Furthermore, Kim et al. [8] has determined that the guidance value of cobalt for fresh water environment is at 8 $\mu\text{g/L}$, which is around 1.36×10^{-7} mol/dm³. Therefore,

Concentration (ml/dm ³)	Average of absorbance (%)	Standard deviation	Standard error
1.0M	5.5568	0.0489	0.0244
1.5M	6.8504	0.0710	0.0355
2.0M	9.7827	0.0903	0.0451
2.5M	12.1745	0.1270	0.0635

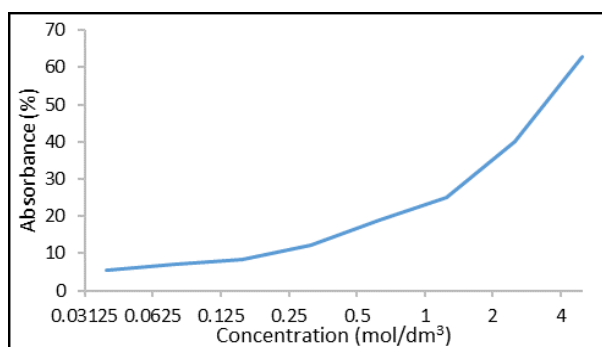
the microfluidic device is unable to provide a satisfactory detection limit towards the analyte of interested according to WHO standard.

Repeatability and reproducibility

For repeatability and reproducibility study, the sample was injected and flushed out from the microfluidic sensor via microfluidic channel for four times for each of the concentrations of the chemicals. The consistency of the peak absorbance value was analyzed.



(a) Nickel(II) Nitrate Hexahydrate



(b) Cobalt(II) Sulphate Heptahydrate

Figure 2: Peak absorbance value against concentration for both chemicals

Table 1: Standard deviation and standard error of the absorbance readings for Nickel (II) Nitrate Hexahydrate at different concentrations

Table 2: Standard deviation and standard error of the absorbance readings for Cobalt (II) Sulphate Heptahydrate at different concentrations

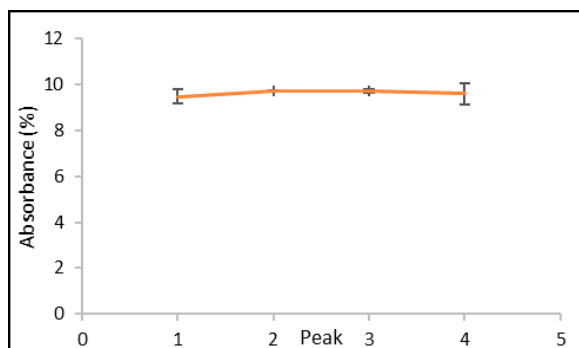
Concentration (ml/dm ³)	Average of absorbance (%)	Standard deviation	Standard error
1.0M	5.6211	0.1107	0.0554
1.5M	7.0801	0.1115	0.0557
2.0M	9.3368	0.1142	0.0571
2.5M	14.2462	0.2600	0.1300

Table 1 and Table 2 show the standard deviation and standard error of the absorbance value obtained for different concentrations of both chemicals. The lower value of the standard error in this criterion shows good repeatability. This means that the absorbance values obtained each time the sample is added do not differ much to the absorbance values obtained when the sample is removed.

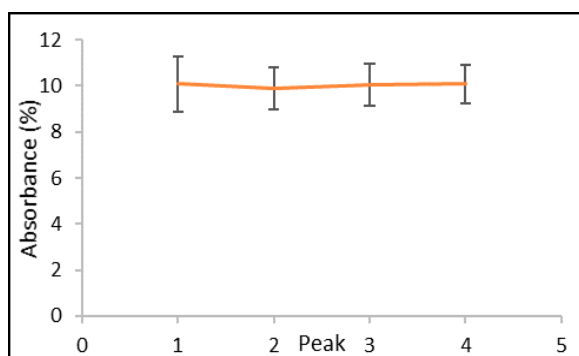
For Nickel (II) Nitrate Hex hydrate, all the standard errors at every concentration are less than 0.1. This indicates that the readings of absorbance are similar and nearly the same for each of the concentration, every time when the sample is removed and re-added. For Cobalt (II) Sulphate Heptahydrate, the standard error at different concentration are less than 0.1, except for the highest concentration which is recorded as 2.5 mol/dm³. There is also no significant difference in peak values.

The slight difference in repeatability of Cobalt (II) Sulphate Heptahydrate and Nickel (II) Nitrate Hex hydrate can be related to the solubility of the chemicals. The solubility of Cobalt (II) Sulphate Heptahydrate in water is 60.4 g/100 mL at temperature of 3 °C. As a comparison, Nickel (II) Nitrate Hex hydrate has a solubility of 243. g/100 mL in water when the temperature is 0 °C. The solubility of Cobalt (II) Sulphate Heptahydrate in water is relatively lower than Nickel (II) Nitrate Hex hydrate. The lower solubility will cause the chemical more difficult to soluble in water when the concentration is higher. At the concentration of 2.5 mol/dm³ for Cobalt (II) Sulphate Heptahydrate, in terms of molecular mass per 100 mL of water, is around 70.28 g/100 mL. This value is slightly higher than the solubility of this chemical. The chemical samples will not able to dissolve completely. Because of the undissolved chemicals, the absorbance value has higher chances of getting error and lower repeatability. Figure 3 and Figure 4 shows the error bar analysis for

Nickel (II) Nitrate Hex hydrate and Cobalt(II) Sulphate Heptahydrate respectively.



(a) Nickel(II) Nitrate Hex hydrate



(b) Cobalt(II) Sulphate Heptahydrate

Figure 3: Error bar analysis for the reproducibility of the microfluidic sensor for both chemicals

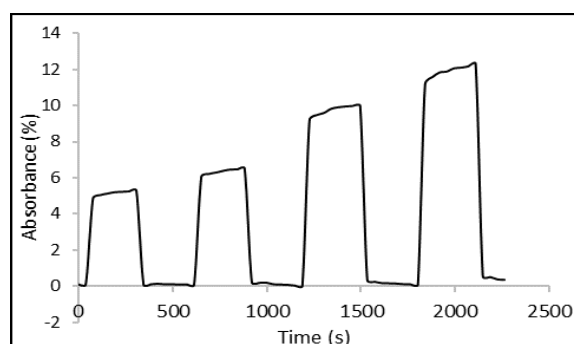
Figure 3 shows significant errors in most of the readings when repeated at other time except for Nickel(II) Nitrate Hex hydrate solution. This indicates that the readings obtained on the repeated experiments fluctuated. The deviation of the readings may be due to several possible reasons. First, the samples prepared might not have exactly the same concentration as in the original sample due to time factor. The sample was prepared by adding certain volume of stock sample in distilled water. The exact concentration might be slightly different from the desired concentration. With time, the molecules in the solution may experience dissociation and thus lead to discrepancy.

Moreover, some of the chemicals is not dissolved completely and will settle on the bottom of the container. This cause the concentration to be deviated from the specified concentration and affect the absorbance readings. In short, the microfluidic sensor has relatively higher repeatability and relatively lower reproducibility, towards the two chemicals tested.

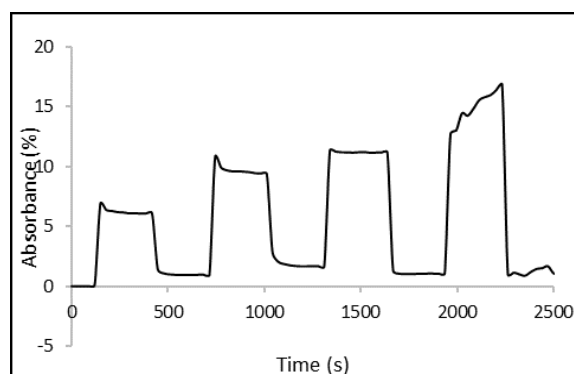
Response time

The output state of the sensors will not change instantly when the input parameter changes. The output state will change to a new state over a period of time. This time is termed as the response time. The response time is the time required for a sensor output to change from its previous state to a final stable state, after the input state changed.

Figure 4 shows absorbance versus time plots and the response time was determined by observing the time taken for the line on the graph to rise from the lower point to the saturated point. For each chemical, four tests were performed with four different concentrations and represented by the four peaks on the graph.



(a) Nickel(II) Nitrate Hex hydrate



(b) Cobalt(II) Sulphate Heptahydrate

Figure 4: Dynamic response both chemicals at different concentration

Figure 4(a) was used to measure response time for Nickel (II) Nitrate Hexahydrate at wavelength 392 nm. From the graph, four readings of response time were recorded as 95 s, 77 s, 58 s and 77 s, for low concentration to high concentration respectively. From these readings, an average response time of 77 s was calculated for Nickel(II) Nitrate Hex hydrate. Figure 4(b) meanwhile is the graph of absorbance against time used to determine the response time of the microfluidic sensor towards Cobalt(II) Sulphate Heptahydrate at 519 nm wavelength. From the graph, four response time were obtained which are 89 s, 89 s, 60 s and 165 s respectively for low concentration to to high concentration, giving an average response time of 101 s.

Referring to the graph of absorbance against time for each of the chemicals, a similarity can be seen. The peak of the absorbance value increases when the concentration of the sample increases. When the concentration of sample is increased, there are more molecules for the light to absorb and emit when it passes through the chamber. The error during the experiment might be due to the inconsistency of the rate of adding samples to the microfluidic channel. This difference in rate of sample adding is difficult to control as the sample is added to the channel manually by pushing on piston of the syringe used.

The time taken using this microfluidic sensor is not as short as some of the integrated microfluidic sensor. However, it is still at satisfactory level as the time taken is not more than 5 minutes. For instance, when the optical sensing hybrid system changed from using cuvette to microfluidics [2], a reduction of response time from 100s to 4 s was recorded. Yu et al. [3] also recorded a response time of 2 minutes when utilizing a micro fluidic paper-based chemiluminescence biosensor for simultaneous determination of glucose and uric acid. Thus, the response time of 77 s and 101 s towards Nickel(II) Nitrate Hex hydrate and Cobalt(II) Sulphate Heptahydrate respectively shows that the microfluidic device is reliable to produce satisfactory rate of chemical sensing.

Sensitivity

A sensitive device is the device that will produce detectable output with minimal input. The sensitivity of the microfluidic sensor towards each of the chemicals was observed from the detection of the chemicals in low concentration within the detection limit. Figure 5 shows the response graph for the two chemicals with low concentration. From the graph, the absorbance value for both chemicals is similar. For Nickel(II) Nitrate Hex hydrate, the absorbance rose to the peak value at the faster rate compared to Cobalt(II) Sulphate Heptahydrate. This is shown by the steeper slope in the graph for nickel solution. This proved that the microfluidic device is more sensitive towards Nickel(II) Nitrate Hex hydrate compared to Cobalt(II) Sulphate Heptahydrate.

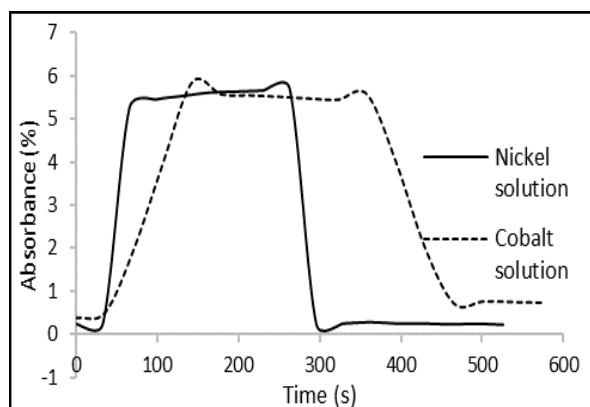


Figure 5: Comparison of dynamic response for both chemicals

4. Conclusion

A fiber optic microfluidic sensor has been tested on chemical detection using Nickel (II) Nitrate Hex hydrate and Cobalt (II) Sulphate Heptahydrate. The fabricated microfluidic fiber optic sensors exhibited good detection limit, reproducibility and also sensitivity. The response times for Nickel (II) Nitrate Hex hydrate and Cobalt(II) Sulphate Heptahydrate are 77 s and 101 s respectively. In short, the microfluidic fiber optic sensor fabricated using dry film resist provide a satisfactory and reliable detection towards both samples.

Acknowledgement

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Liew Mun Ngar graduated in BEng (Hons) Chemical Engineering in 2018 from Universiti Putra Malaysia and currently pursuing her career in company as engineer.



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