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Detection of Napropamide by microwave resonator sensor using a carbon nanotube – polypyrrole-chitosan layer

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ABSTRACT

This paper presents the design and fabrication of a proximity coupled feed disk resonator coated with multi walled carbon nanotubes (MWCNTs) and polypyrrolechitosan (PPy-CHI) layers as a napropamide sensor. Computer Simulation Technology (CST) microwave studio was used to obtain the best design of the disk resonator and feed line position in a 5 GHz resonant frequency. Also, MWCNTs-PPy-CHI layers were coated on the disk resonator using electric field deposition, and the chemical interaction between the sensing layer and napropamide was investigated via a Fourier transform infrared spectroscopy (FTIR). The evaluation of the system was performed using different concentrations of commercial napropamide and pure napropamide at room temperature (25 °C). The experimental results proved that the proximity coupled feed disk resonator that was coated with MWCNTs-PPy-CHI layers was simple, fast (Measurement- time=5 seconds), accurate (as low as 0.1 ppm), and low cost; it also has the potential to be produced as a portable instrumentation system for detecting napropamide in water and soil.

1. Introduction

The detection of napropamide contamination has a considerable effect on human safety and preservation of our environment. Napropamide is among the most hazardous environmental contaminants and have noticeably increased over the last century. Napropamide [N, N-diethyl-2-(1-naphthalenyloxy)-propionamide] is a non-ionizable [1] and selective systemic amide pesticide used to control a variety of annual grasses and broad-leaved weeds in tobacco and kenaf fields [2-3]. Few methods have been reported concerning the detection of napropamide in soil and water. Most of them are chromatographic methods such as high-performance liquid chromatography (HPLC) in tandem with diode array detection [4], mass spectrometry (MS) [5], or gas chromatography (GC) [6]. Some researchers have tried to find alternative methods, which has led to the

development of some photo luminescencent strategies. The native fluorescence of napropamide was used by Stangl and Niessner in their studies dealing with the use of cloud-point extraction with surfactants [7]. Later, Pulgarin developed a method based on fluorescence detection in a sodium dodecyl sulfate (SDS) medium buffered at a pH of 7.2 [8]. Additionally, the method proposed by Tang was based on a supramolecular interaction between napropamide and β cyclodextrin in order to form an inclusion complex, which significantly enhanced the fluorescence intensity [9]. In order to increase the selectivity, Salinas demonstrated the viability of a chemical deoxygenation micelle-stabilized room-temperature phosphorimetry for napropamide analysis in soil [10]. These methods are accurate and have been employed as standard methods. However, these methods are not practical for field application because they are time-consuming, expensive and bulky.

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Various chemical and electrical CNT-based sensors have been developed using technology such as infrared, laser, microwave, electrical capacitance, ultrasound, etc. In the past two decades, a number of researchers have employed a carbon nanotube in microwave measurement methods for the sensing application; these include the work of Chopra [11] to detect gas molecules, Hee [12] to sense biomaterials, and Dragoman [13] to make a nano mass sensor. Although the microwave CNT-based electromagnetic resonator sensor applied in gas detection has advantages such as independency of higher-contact requirements and short recovery time (less than 10 minutes) [14-15], it has its own drawbacks. The carbon nanotubes on the top of the resonator are physically coated using conductive epoxy. This method is easy to apply, but the liquid samples which are prepared in solvent cannot be measured because the conductive epoxy dissolves. Moreover, polymers cannot be applied with carbon nanotubes. Hence, the development of a microwave measurement method using a carbon nanotube and a

polymer as a new napropamide detection sensor for further application is considered in this paper.

2. Material and methods

The schematic general layout of the sensor system is shown below in Figure 1 and gives an overall view of the system. The setup consists of a proximity coupled feed disk resonator coated by MWCNTs-PPy-CHI, a coaxial connector, a coaxial cable and a Vector Network Analyzer (VNA). In this work, the coated MWCNTs- PPy-CHI at the top of the resonator acts as a sensing layer. The chemical interaction between the sample under testing and the sensing layer results in a significant difference in the permittivity of the disk resonator and affects the resonant frequency of the disk resonator. The signal power from a Vector Network Analyzer (VNA) is connected to the feedline of the disk resonator using a coaxial connector. After coupling the power through substrate, the disk resonator will resonate; then, by monitoring the sharp dip of the insertion loss (S11) using VNA, changes in the resonant frequency of resonator will be determined.



Fig. 1. The schematic general layout of the sensor system

2.1. Characterization of raw wastewater

The proposed sensor consisted of two layers of low-cost flame retardant (FR-4) substrate with a dielectric constant ε_r of 4.3, a loss tangent tan $\delta\varepsilon$ of 0.025 and a thickness of 1.53 mm. The structure of the sensor is as follows: the disk resonator was placed over the first layer, and then the first layer was placed on top of the second layer which had a feedline. The 50 Ω SMA connector was placed between these two layers. The proximity coupling method was chosen to feed the disk resonator as it allows for the coating of the disk resonator separately as well as in the final fabrication of the sensor; the sample undergoing the test had no interaction with the feedline. The operating resonant frequency of 5 GHz for the disk resonator was employed based on proven performance from reported works [14-15] and the acceptable size of the disk. The diameter of the circular disk resonator was calculated by equation number 1. [16]

$$f_{0} = \frac{1.8412C_{0}}{2\pi\varepsilon_{r}r\left\{1 + \frac{2h}{\pi\tau\varepsilon_{r}}\left(\ln\frac{\pi r}{2h} + 1.7726\right)\right\}^{\frac{1}{2}}}$$
(1)

where C_0 is the speed of light in free space, f_0 is resonant frequency, r is the radius of the circular disk, ε_r and h are the relative dielectric constant and thickness of the substrate, respectively.

2.2. Electromagnetic simulation

The microwave resonator sensor in this work consisted of two separate layers, a disk resonator layer and a feedline layer. An accurate design for a disk resonator and feedline with different substrate materials can be achieved using appropriate simulation software. The Computer Simulation Technology (CST) microwave studio software was used for simulation of the disk resonator and feedline in this work. It used the full-wave analysis in its computations of the parameters that were analyzed. The design specifications were the resonant frequencies (5 GHz) with an input resistance of 50Ω . Two small holes were designed in the feedline substrate and disk resonator substrate for better

alignment of the two layers. Figure 2 illustrates the simulated feedline and disk resonator as well as their dimensions.



Fig. 2. A) Simulated feedline and disk resonator, B) Dimensions of the feedline, C) Dimensions of the disk resonator

2.3. Chemicals and materials

Polypyrrole (PPy) is a conductive organic polymer which can be formed by oxidation of the pyrrole monomer. Chemical and electrochemical oxidations are two common ways to prepare a number of pyrrole rings as a polypyrrole. PPy plays an important role in electronic devices and drug delivery, and it also can be used as a chemical sensor [17]. Sensing metal and non-metal ions like Hg²⁺ and fluoride ions are good examples of the capability of PPy as a sensing material [18]. Chitosan is a polysaccharide which is commercially produced from chitin. Chitin is the structural element in the exoskeleton of crustaceans and is commonly produced from crabs, shrimp, and the cell walls of fungi. The unique properties of chitosan make it an attractive bio material for many researchers in different applications such as agriculture, horticulture, environment, sensing devices, and biomedical applications. Chitosan film is a stable material against various surfaces with basic pH conditions due to its pH dependent solubility. There are many studies using chitosan (CHI) to detect glucose [19] and phenol [20]. Recently, polypyrrole-chitosan(PPy-CHI) were used as a sensing layer in many studies, including the work of Sadrolhosseini to detect iron ions in biodiesel [21] and Abdi to detect mercury and lead ions [22-23].

2.4. Coating of carbon nanotube- polypyrrole - chitosan layer

Pristine carbon nanotubes (CNTs) are insoluble in most solvents. This means that they are difficult to evenly disperse in a liquid matrix such as polymers. To make nanotubes more easily dispersible in liquids, it is necessary to physically or chemically attach certain molecules, or functional groups, to their sidewalls without significantly changing the nanotubes' desirable properties. In this work, sodium dodecylbenzene sulfonate (SDBS) were used to modify the MWCNTs. The fabrication process of coating the MWCNTs started with solving 0.1 grams of SDBS in 10 cc of deionized-water at room temperature (25 °C). After solving SDBS, 0.001 gram of MWCNTs was added to the mixture and left for 24 hours. The following day, the mixtures were left in sonicate for 6 hours. 1% acetic acid was used to solve chitosan powders and after 24 hours, the mixture was stirred with a magnetic stirrer. After the chitosan completely dissolved in the acetic acid, pyrrole was added to the solution and the whole mixture was stirred continuously for 2 minutes at room temperature. Then, this mixture was added to the MWCNTs and SDBS solution and stirred with a magnetic stirrer for several minutes. To avoid the occurrence of unwanted corrosion during the coating process, a thin layer (50 nm) of gold was coated on the top

of the disk resonator using a sputter coater Bal-Tec Sd005. The electropolymerization of pyrrole was completed via the electrochemical deposition process. A potentiostat (Model: PS 605, USA) was used to coat the MWCNTs-PPy-CHI layer as a sensing layer on the gold layer of the disk resonator. The voltage of the potentiostat was set at 1.2V and a saturated calomel electrode (SCE) was used as a reference while a carbon rod and indium-tin oxide (ITO) glass were used as counter and working electrodes, respectively.

2.5. Transform infrared spectroscopy (FT-IR)

One piece of the coated disk resonator without exposure to the contaminant (as a reference) and two pieces of the coated disk resonator exposed with 100 ppm solution of commercial napropamide and pure napropamide were tested by FTIR spectroscopy. The FTIR spectra of samples were recorded over the range of 4000-400 cm⁻¹ by a Bruker VECTOR-22 spectrophotometer (Bruker Optics Inc., Germany). The results from the FTIR spectroscopy of the commercial napropamide and pure napropamide applied on the coated disk resonator were compared with the results of the reference to define the chemical interaction between the applied materials with the MWCNTs-PPy-CHI layer.

2.6. Final fabrication of microstrip disk resonator sensor

To fabricate the final shape of the disk resonator, a rectangular plastic cover with a 5 mm thickness was attached to the top of the disk resonator as a liquid holder. The centre of the liquid holder was drilled around the disk resonator to allow interaction between the sensor and the liquid being tested. Four nuts and bolts were attached to the plastic cover on the top of the disk resonator and plastic glue was applied to insure there would be no liquid leakage in the sensor system. The schematic configuration design of the two layer microstrip disk resonator as a probe is shown in Figure 3.

The performance of the fabricated two layer microstrip disk resonator was measured using the Anritsu 37347D vector network analyzer to validate the design parameters after coating and is shown in Figure 5.



Fig. 3. The schematic configuration design of a two layer microstrip disk resonator

3. Results and discussion

3.1. Results of disk resonator

A comparison between the simulation and experimental results of the return loss (S_{11}) obtained by the disk resonator is shown in Figure 6. The simulated and measured return losses of the resonator at a resonant frequency of 5.003 GHz were -57.2 dB and -50.513 dB, respectively. The resonant frequency of the disk resonator after coating and

fabrication should be determined for the calibration of a sensor system. Based on experimental results, the return loss and center of the resonant frequency were 4.931025 GHz and -44.5107 dB, respectively. This change occurred due to the coating of extra materials and the plastic cover. To improve the accuracy, this experiment was iterated and the data of 1600 points were collected in the frequency range of 4.915 GHz to 4.945 GHz as plotted in Figure 7.



Fig. 5. The performance of the fabricated two layer microstrip disk after coating



Fig. 6. Simulated and measured return loss (S_{11}) of circular patch antenna



Fig. 7. Measured return loss and resonant frequency of coated and fabricated disk resonator.

3.2. Results of FTIR spectra

The FTIR spectra of the disk resonator exposed with napropamide and reference spectra (spectra of the resonator without exposure to contaminants) are presented in Figure 8. The spectra of the sample with napropamide indicated shifts in frequencies from 1530 cm⁻¹ to 1527 cm⁻¹ (C=C benzonic form), 1455 cm⁻¹ to 1452 cm⁻¹ (C-C band stretch) 1156 cm⁻¹ to 1147 cm⁻¹ (S=O bond), 663 cm⁻¹ to 675 cm⁻¹ (C-H deformation vibration of the ring), and 596 cm⁻¹ to 606 cm⁻¹ (Alkynes). The electronic bond perturbation of the C-O group suggested that there was a direct interaction between this functional group, possibly by an H-bond formation with a certain functional group of the napropamide. The changes in the frequencies of the C-H and N-H groups were probably due to a chargetransfer mechanism between the functional groups of napropamide and the functional groups on the PPY-CHI layer.

The FTIR spectra of the disk resonator with exposure to commercial napropamide and reference spectra are presented in Figure 9. The spectra of the sample with commercial napropamide indicated shifts in frequencies from 1645 cm⁻¹ to 1625 cm⁻¹ (C=C benzonic form), 1279 cm⁻¹ to 1265 cm⁻¹, and 775 cm⁻¹ to 770 cm⁻¹ (C-H deformation vibration of the ring). The results of the FTIR spectra suggested that there was a direct interaction between the functional groups of commercial napropamide and the functional groups on the PPY-CHI layer.

3.3. Results of disk resonator to detect napropamide and commercial napropamide

To evaluate the sensing capability of the proposed sensor system, one mL of 100 ppm napropamide solution was dropped on the centre of the disk resonator and left for 24 hours at room temperature (25 °C) to dry. The return losses of the resonator were obtained and the disk resonator was washed with deionized water. After 24 hours, the experiment was repeated and the collected results were compared as shown in Figure 10. The resonant frequency of the disk resonator shifted (3.1875 MHz) after applying 100 ppm of napropamide. This change in resonant frequency indicated that the disk resonator can detect napropamide due to the interaction between the sensing layer and the napropamide. After washing the disk resonator with deionized water, the resonant frequency shifted back to near the original value. Different concentrations of napropamide (0.1 ppm, 0.5 ppm, 1 ppm, 5ppm, 15ppm, 25ppm, 50ppm and 100 ppm) and 1 mL of toluene as a zero ppm of napropamide were tested to characterize the sensitivity of the disk resonator coated by a MWCNTs-PPy-CHI layer and is shown in Figure 11.



Fig. 8. The FTIR spectra of disk resonator with applying napropamide and reference spectra



Fig. 9. The FTIR spectra of disk resonator with applying commercial napropamide and reference spectra

The above mentioned experimental setup and procedure was repeated with 100 ppm of commercial napropamide solution and a 3.375 MHz change in the resonant frequency obtained (Figure 12). The resonant frequency shift of the antenna for 100 ppm of commercial napropamide was bigger than 100 ppm of napropamide. The change in the resonant frequency was caused by a change in the dielectric

constant of the MWCNTs-PPy-CHI sensing layer after chemical interaction with the applied material on the resonator. The commercial napropamide includes napropamide and the extra chemical materials which may interact with the sensing layer and make a difference in the total dielectric constant of the sensing layer. Different concentrations of commercial napropamide (0.1 ppm, 0.5 ppm, 1 ppm, 5ppm, 15ppm, 25ppm, 50ppm and 100 ppm) and 1 mL of toluene as a zero ppm of commercial napropamide were tested to characterize the sensitivity of

the disk resonator coated by a MWCNTs-PPy-CHI layer and is shown in Figure 13.



Fig. 10. The comparison of return losses of disk resonator faced with air, 100 ppm napropamide and after washing



Fig. 11. Resonant frequency of disk resonator shift versus different concentrations of N napropamide



Fig. 12. The comparison return losses of disk resonator faced with air, 100 Ppm commercial napropamide and after washing.



Fig. 13. Resonant frequency of disk resonator shift versus different concentrations of commercial napropamide.

As shown in Figure 13, the resonant frequency of the disk resonator showed higher values of resonant frequency shift with an increase in the concentration of commercial napropamide. For 0.1 ppm of commercial napropamide, 7.5 KHz in resonant frequency shift was obtained as an ability

of this sensor system to detect small concentration of commercial napropamide.

3.3. Results of testing coated layer by atomic force microscopy

An Atomic Force Microscopy (AFM) is a high-resolution scanning method for imaging any type of sample including polymers and composites without any special sample preparation or vacuum environment. AFM enables imaging and measuring in three dimensions: x, y, and z (normal to the sample surface), with resolution in the x-y plane ranging from 0.1 to 1.0 nm and 0.01 nm in the z direction. In this work, AFM imaging was used to ensure the successful coating of the MWCNTs-PPy-CHI layer on the gold layer of the disk resonator. Four small pieces of the disk resonator that were coated with MWCNTs-PPy-CHI via electrochemical deposition were cut and scanned by AFM. As can be clearly seen in Figure 14, polypyrrole and chitosan were sticking on the carbon nanotubes which were successfully coated on the surface of the disk resonator.



Fig. 14. AFM imaging of disk resonator after coating MWCNTs-PPy-CHI by electrochemical deposition

4. Conclusions

In the current work, the design and development of a proximity coupled feed disk resonator coated with MWCNTs- PPy-CHI as a napropamide sensor were presented. The detailed design, analysis, construction, simulation, and testing of the proximity coupled feed disk resonator was presented. Napropamide and commercial napropamide are pesticides which were investigated by a sensor system in this work. The experimental results of different concentration of napropamide and commercial napropamide showed this sensor system was capable of detecting small amounts of napropamide. A portable and wireless design of a proximity coupled feed disk resonator coated with a MWCNTs- PPy-CHI layer are recommended for future work.

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