Rapid detection of permethrin in treated wood biology essay

Science, Biology

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Abstract

Background

A novel optical sensor for the rapid and direct determination of permethrin preservatives in treated wood was designed. The optical sensor was fabricated from the immobilization of 2, 6-dichloroquinone-4-chloroimide (Gibbs Reagent) in Nafion-sol gel hybrid film and the mode of detection was based on absorption spectrophotometry. Physical entrapment was employed as a method of immobilization

Results

The sensor gave a linear response range of permethrin between 2. 56–383. 00 µM with detection limit of 2. 5µM and demonstrated good repeatability with relative standard deviation (RSD) for 10 µM at 5. 3 %, 100 µM at 2. 7 % and 200 µM at 1. 8 %. The response time of the sensor was 40 second with an optimum response at pH 11.

Conclusions

However, validation study of the optical sensor against standard method HPLC showed that the permethrin sensor tends to overestimate the permethrin concentration. Thus, the sensor is useful for rapid screening of wood/treated wood products before detail analysis using tedious procedure is performed.

Keywords

2, 6-Dichloroquinone-4-Chloroimide, permethrin, nafion, sol-gel, optical sensors

Background

Preservatives have been widely used in wood preservation process, agriculture, chemical, and polymer technology to protect various products against decay by biodegradation [1]. The choice of preservative to protect a product, such as wood-based materials and vegetables is based on the chemical properties of the preservative [2]. Usually consist of a mixture of preservatives between chemicals that act as anti-fungal spoilage and insect repellent. In general, a preservative used must have the appropriate level of toxicity to prevent spoilage from molds and insects from attacking wood or vegetable [3]. In the past, preservative such as lindane, dieldrin, aldrin and chlorpyrifos are widely used. At this point these chemicals are largely replaced with pyrethroid group of preservative such as permethrin and cypermethrin [4].

Until now, the quality of permethrin treatment preservative in wood and vegetable matrix was analyzed using gas chromatography (GC), liquid chromatography (LC), immunology and electronic nose [5-8]. These instrumental methods can normally determine permethrin concentrations in wood/vegetables according to the specifications set by standard procedures that associates with the effectiveness of prevention of pest attack that causes biodegradation. Gas chromatography (GC) and liquid chromatography (LC) are techniques that cannot be used for in situ determination of permethrin and in addition the sample also requires an extraction step, which very often is time consuming. The use of electronic noses could only detect permethrin qualitatively, i. e., whether it is presence or absence in a sample.

In this study, an optical chemical sensor for the detection of permethrin preservative in treated wood has been developed. The new chemical sensor concept is based on the reaction between permethrin and 2, 6-dichloroquinone-4-chloroimide reagent (Gibbs reagent). Gibbs reagent has been reported to give a clear color change and very stable when reacted with permethrin [9]. Gibbs method is a standard method used for the detection of phenol [10]. It is based on the condensation reaction between dichloroquinone-4-chloroimide with phenol compounds that do not have a successor group to form a compound of the 2, 6-dichlorophenol. The reaction takes place in an alkaline medium at pH 9. 4 of borate buffer. For the determination of phenol in the range of ppm, 2, 6-dichlorophenol compounds give absorption at a wavelength of 595 to 630nm. In addition, such factors as temperature, pH and the presence of other compounds such as sulfide, reducing agent and tiocresol found to affect the reaction. Gibbs reagent structure shown in Figure 1. Until now there is not been reported reaction between permethrin with Gibbs reagent. A optical sensor is fabricated to detect permethrin by using 2, 6-dichloroquinone-4-chloroimide reagent immobilized in a nafion and sol-gel silicate hybrid membrane. The performance of the chemical sensor was validated with standard methods for the analysis of permethrin in treated wood.

Results

UV-Vis Studies

The absorption spectrum of Gibbs reagent immobilised in the hybrid film nafion/sol-gel silicate is shown in Figure 3. The absorption increase was due

to the complex formation of permethrin-Gibbs when Gibbs reagent immobilized in the film reacts with permethrin where the yellow color has changed to a blue color.

Effect of nafion-sol gel ratio

The effects of varying the ratio of nafion/sol-gel silicate on the chemical sensor response are shown in Figure 4.

Effect of pH

Figure 5 shows the effect of pH toward buffer solution in the pH range from 1. 0 to 14. 0 on the chemical sensor response. Optimal chemical sensor response was found at pH 11. 0.

Effect of reagen concentration

The effect of Gibbs reagent loading on the permethrin-Gibbs complex formation was studied by measuring the intensity of the complex formed at a wavelength of 670 nm. Gibbs reagent concentrations studied were in the range of 0-2 M and permethrin concentration used was 25 µM, 50 µM and 100 µM in buffer solution at pH 11. 0 (Figure 6).

Leaching studies

The effect of leaching of Gibbs reagent on the response of optical sensors in buffer pH 11. 0 containing permethrin for various immobilization matrices are shown in Figure 7.

Kinetic studies

Figure 8 shows the time taken by an optical sensor to respond to permethrin in concentration of 100 µM.

Dynamic range

The linear response range of the optical sensor was of 0-150 µM of permethrin (R2= 0. 9900) (Figure 9). The value of the detection limit is 2. 50 µM

Reproducibility studies

Reproducibility for Gibbs reagent immobilized in the hybrid film sol-gel/nafion refers to the measurement performed using different sensors of the same batch. Reproducibility study was performed at three different concentrations of permethrin: 10. 0 µM, 100. 0 µM and 200. 0 µM as shown in Figure 10.

Sensor life time studies

From Figure 11, it appears that for the two-month study period (60 days), the permethrin optical sensors yielded RSD values of 4. 86 % and 2. 76 % respectively for dark and bright environments indicating that the immobilized Gibbs reagent was stable for the study period of 60 days.

Validation and recovery studies

Validation studies of the permethrin sensor was performed by comparing the analysis of treated wood sample spike with permethrin using sensor and also standard method such as HPLC (Table 1). The permethrin sensor developed here gave recovery values much higher than that of HPLC method, i. e. at the range of 120 -130 %.

Discussion

In this study, TEOS was used as starting material for the preparation of sol-gel silicate for the immobilisation of Gibbs reagent. It is known that the material properties of sol-gel silicate matrix such as surface area, pore size and distribution are influenced by many factors. Among these are the pH and the ratio of silica to water between important parameters during the preparation of the sol-gel silicate. Nafion is a polymer having hydrophobic backbone fluorocarbon but cation converter is characteristically hydrophilic and this makes it to have the character of medium hydrophobic [11]. This properties help in containing reagent dye in the film and reduce leaching. Therefore, in this study nafion mixed with sol-gel silicates to form organic-inorganic hybrid material was used to immobilise Gibbs reagent. In addition, the nature of this hybrid material can overcome the cracking problem commonly experienced by the sol-gel film of pure silicate [11-13].

There has been no report on the reaction of Gibbs reagent with permethrin. Dacre (1971) had reported that the reaction of Gibbs reagent with phenol but it is not specific [14]. Reactions of any phenolic compounds of no spare converter at the ortho position with Gibbs reagent is thus named Gibbs reaction. The mechanism of the reaction is substitution and it depends on the reactivity of the substituents at the ortho position and the group substituents in the phenolic compounds. The same reaction will occur for the primary, secondary and tertiary amine compounds where the reaction is in alkaline condition. Thus, it is expected that the Gibbs reagent will form a complex with permethrin at the ortho position in the vanilil (Figure 2) functionality as reported by El-Ragehy (2002), for the compound mequitazine [15]. The absorption spectrum of Gibbs reagent immobilised in the hybrid film nafion/sol-gel silicate is shown in Figure 3. The absorption increase was due to the complex formation of permethrin-Gibbs when Gibbs reagent immobilized in the film reacts with permethrin where the yellow color has changed to a blue color.

The use of hydrophobic hybrid and high porosity material to immobilize the hydrophilic Gibbs reagent and prevents leaching of soluble chemical from the sensor film. The effects of varying the ratio of nafion/sol-gel silicate on the chemical sensor response are shown in Figure 4. It was found that lower optical response occurred when pure silicate sol-gel matrix material used for immobilization of Gibbs reagent. This behavior may be due to the nature of the hydrophilic silicate film which couldn’t withstand excessive Gibbs reagent loaded into the matrix material [16]. Hybrid material with a ratio of

40%: 60% (v/v) sol-gel and nafion showed optimal response. Increasing of nafion content higher than 60% (v) in the matrix film will reduced the intensity of the optical sensor response. The film thickness of chemical sensor is calculated based on weight of coated layer of nafion/sol-gel silicate immobilized with reagents Gibbs. The film thickness for nafion/sol-gel silicate ratio 40: 60 (v/v) is estimated in the range of 4-5 µm. The decrease in sensor response is due to the reduction of porosity of silicate sol-gel film when nafion content increased in the hybrid material and also with the increased hydrophobic properties. Therefore, it has affected the amount of Gibbs reagent immobilized in nafion/sol gel silicate hybrid network. When the hybrid material porosity decreased, the amount of immobilized reagents Gibbs also reduced. Similar observation was also reported by Miao and Tan (2001) in which porosity reduction hybrid chitosan/sol-gel silicate causes the amount of immobilized horseradish peroxidase enzyme reduced led to poor sensor response [13]. Reduction of chemical sensor response also may be due to increased hydrophobic properties of the hybrid material. This increases the difficulty of permethrin diffusion into the transducer containing Gibbs reagents. As a result, weak response obtained. Figure 5 shows the effect of pH toward buffer solution in the pH range from 1. 0 to 14. 0 on the chemical sensor response. Optimal chemical sensor response was found at pH 11. 0. Therefore, the buffer at pH 11. 0 was selected for use in further studies. This is similar to the results reported by Palacio (1979) in his analysis of the colorimetric method of determination of capsaicin in using vanadium oksitrichloride [17]. The effect of Gibbs reagent loading on the permethrin-Gibbs complex formation was studied by measuring the intensity

of the complex formed at a wavelength of 670 nm. Gibbs reagent concentrations studied were in the range of 0-2 M and permethrin concentration used was 25 µM, 50 µM and 100 µM in buffer solution at pH 11. 0. At all permethrin concentrations, the intensity of the absorption of permethrin-reagent complex reached maximum at the concentration of Gibb reagent of 1. 0 M as shown in Figure 6. Thus, this concentration of 1. 0 M Gibbs reagent has been used as a condition for determination of permethrin using the chemical sensor. The effect of leaching of Gibbs reagent on the response of optical sensors in buffer pH 11. 0 containing permethrin for various immobilization matrices are shown in Figure 7. From immersion time of 0-5 min, Gibbs reagent leaching was 1%, 80% and 90% respectively for films nafion/sol-gel silicate, pure silicate sol-gel and pure nafion. The composition of the 40% sol-gel and 60% nafion demonstrated almost no leaching of sensor components. This is because the under this optimal mixture, there is a suitable hydrophobicity phase in the film to prevent leaching. Figure 8 shows the time taken by an optical sensor to respond to permethrin in concentration of 100 µM. The response time was fast for an optical sensor, which is about 40 seconds to reach steady-state response. This shows that properties of reagent do not change when the Gibbs reagent immobilized in sol-gel/nafion hybrid matrix. The linear response range of the optical sensor was of 0-150 µM of permethrin (R2= 0. 9900) (Figure 9). The value of the detection limit is 2. 50 µM. This response range is somewhat lower than that of permethrin using non-immobilised Gibbs reagent (2. 56–383. 00 µM), this is the result of the more restricted movement of permethrin through the hybrid polymeric matrix when compared with reaction at the

liquid phase. Reproducibility for Gibbs reagent immobilized in the hybrid film sol-gel/nafion refers to the measurement performed using different sensors of the same batch. Reproducibility study was performed at three different concentrations of permethrin: 10. 0 µM, 100. 0 µM and 200. 0 µM as shown in Figure 10. However, the repeatability study could not be done due to the sensor could not be reused or regenerated. The RSD values for the fabrication of optical permethrin sensors are 5. 3 % (n = 10), 2. 7 % (n = 10) and 1. 8 % (n= 10) respectively for 10. 0 µM, 100. 0 µM and 200. 0 µM. According Alabbas (1989), numerous variations of the sensor response is caused by two factors, fabrication and operation of the sensor [18]. This includes the variation caused by the quantity and particle size sensor matrix which is then linked to variations produced by the immobilized reagent concentration on support material (transducer). However the main reason causing the poor response was more focused on sensor fabrication. The sensor life time studies were performed under two different conditions, namely bright and dark conditions at room temperature for a specified period of time. Two conditions were chosen to investigate any differences that might exist. From Figure 11, it appears that for the two-month study period (60 days), the permethrin optical sensors yielded RSD values of 4. 86 % and 2. 76 % respectively for dark and bright environments indicating that the immobilized Gibbs reagent was stable for the study period of 60 days. Validation studies of the permethrin sensor was performed by comparing the analysis of treated wood sample spike with permethrin using sensor and also standard method such as HPLC. The permethrin sensor developed here gave recovery values much higher than that of HPLC method, i. e. at the range of

120 -130 %. The RSD values under precision study for both method are < 10 % (n= 10). Statistical analysis of the data show that there is significant differences between the two methods of determining permethrin. This is the result of the less selective nature of the permethrin sensor where it was found to response slightly to the wood extracts even in the absent of permethrin.

Conclusions

Optical chemical sensor using of 2, 6-dichloroquinone-4-chloroimide immobilized on nafion/sol-gel silicate film for the determination of permethrin in treated wood has been developed. The response of the optical sensor to permethrin is linear with response time of 40 s. The optical sensor for permerthrin showed sensitivity, good reproducibility and stability. However, validation study of the optical sensor against standard method HPLC shows significant difference between the two methods where the permethrin sensor tends to overestimate the permethrin concentration. This may be due to the slightly lack of selectivity of the sensor towards permethrin. We suggest that the sensor can be applied for rapid screening of wood/treated wood products before detail analysis using tedious procedure is performed.

Methods

Reagents and solutions

All chemicals used were of analytical grade. The deionized water was used throughout for solution preparations. Permethrin standard was purchased from Merck (Darmstadt, Germany). Permethrin stock solution (1200 µM) was

prepared by dissolving 0. 3 g permethrin powder in ethanol (99%) and diluted to 250 mL. Gibbs reagent was obtained from Fluka. Gibbs stock solution (9. 5 x 10-2 M) was prepared by dissolving 1g of the reagent in ethanol and diluted to 50 mL. Buffer solutions were prepared according to the methods from Handbook of Basis Tables for Chemical Analysis (Svoronos 1989).

Apparatus

Calibrated Perkin-Elmer, Model Lamda 35 Ultraviolet–visible Spectrophotometer was used. A calibrated Shimadzu HPLC, Model SPD-M10AVP with PDA detector, column used Gemini 5 lm C18 110A(250 mm 9 4. 6 mm 9 5 lm) brand Phenomenex, flow rate 1. 5 ml/min was used for validation. All glassware was calibrated according to the MS ISO/IEC 17025 requirement.

Procedure for HPLC Analysis

Before the sample solution was injected into the HPLC, extraction solution injected into the HPLC sample bottle using a syringe containing a nylon membrane which is used to protect the head from damage. Sample bottles are then arranged in a rack where the sample bottle using HPLC analysis carried out automatically. Ultraviolet detector type set at a wavelength of 260 nm. Injected sample volume of 20 µL. For the wood samples, the mixture of n-hexane and tetrahidofuran (THF) (95: 5, v/v) was used as mobile phase.

Measurement of the absorption spectrum

The absorption spectrum of chemical sensors based on the Gibbs reagent immobilization of layered hybrid film nafion/sol-gel silicate in the presence of permethrin (100. 0 µM) in buffer solution at pH 9. 0 was recorded using a spectrophotometer UV-Vis. For the effect of permethrin concentration on the sensor response, analyte concentrations of permethrin used is at 0. 0 µM to 150 µM. Absorption spectra for the sensor were recorded at wavelengths of 300-800 nm at interval of 1 min for 5 min.

Procedure for Evaluation of various parameters on optimum permethrin sensor response

For the purposes of assessing the effect of the nafion/sol-gel silicate, the ratio of 100: 0, 80: 20, 60: 40, 50: 50, 40: 60, 20: 80 and 0: 100 (v / v) was used and the film chemical sensor included. Nafion/sol-gel silicate hybrid solutions were prepared by mixing nafion (5% solution in a mixture of alcohol) and sol-gel silicate solution in an airtight bottle. Some nafion volume ratio of sol-gel silicate used is 100: 0, 80: 20, 60: 40, 50: 50, 40: 60, 20: 80 and 0: 100 (v / v). The mixture was stirred to produce a homogeneous solution and then left overnight at room temperature before use. Gibbs reagent concentration used is set at 2 M and pH of 9. 0 and permethrin concentration set at 100. 0 µM. Chemical sensor response recorded at the wavelength of 670 nm for 5 minutes. The effect of pH on the response of chemical sensors has been studied in the pH range of 1. 0-14. 0. Permethrin concentrations were determined at a concentration of 100. 0 µM. Gibbs reagent concentration used is set at 2 M. Chemical sensor response recorded at the wavelength of 670 nm for 5 minutes. In this study, the estimated load

stationary Gibbs reagent in the hybrid film nafion/sol-gel silicate used is in the 0 M to 2 M. Permethrin concentration used was 100 µM in buffer solution pH optimum. Chemical sensor response were recorded at a wavelength of 670 nm for 5 minutes. Gibbs reagent leaching effects studied by soaking the chemical sensor in buffer solution pH optimum for 0, 5, 15, 25 and 40 minutes before the evaluation of the performance of the chemical sensor response performed using 100. 0 µMpermethrin. Chemical sensor response recorded at the wavelength of 670 nm at intervals of 1 min for 5 minutes.

Analytical Performance of Permethrin Chemical Sensor

Sensor Response, Reproducibility and Repeatability Studies

After the optimization process is done, the optimal value is used in the study of the dynamic range of concentrations of permethrin. Permethrin concentration range studied was between 0. 0 µM to 500. 0 µM. pH and concentration of the reagent is at the optimum. Limit value detection (LOD) were also determined from the study of this dynamic range. For the analysis of chemical sensor repeatability, chemical sensor immersed in a solution of concentrated permethrin 10. 0, 100. 0 and 200. 0 µM and the absorption reading was recorded after 5 minutes. The same procedure is repeated using the analyte solution and a new film every time measurements until the readings in 10 different film derived. For the reproducibility analysis of the chemical sensors were known, the chemical sensor is dipped into the solution concentrated permethrin 10. 0, 100. 0 and 200. 0 µM and the absorption recorded after 5 minutes. Chemical sensor then regenerated using a buffer solution at pH 2. 0 before dipped in permethrin solution with

the same concentration. These steps are repeated until the reading for 10 measurements obtained.

Life-time studies

Life time studies performed to study the stability of this chemical sensor when stored for a certain period. The study was conducted using two different conditions of chemical sensors is stored in a volumetric flask wrapped in aluminum foil and placed in the refrigerator. Second, chemical sensors is stored in a volumetric flask that is not wrapped and placed at room temperature. The study was done using permethrin solution with concentration 50. 0 µM. Absorption graph plotted against time. Further analysis of the stability of the chemical sensor, a study was done for a period of 3 months. Chemical sensors constructed so that the sensor is stored in desiccator always be kept dry and stability are determined each week. For each measurement, three replicates of chemical sensors have been used. Permethrin concentration was set at 100. 0 µM. Chemical sensor response recorded at the wavelength of 670 nm for 5 minutes.

Validation and Recovery Studies

In this study the concentration of permethrin used is 50. 0 µM. Then permethrin solution is included in Kempas (Koompassia malaccensis) wood powder and Rubberwood (Heveabrasiliensis) powder. Reading response from optical sensor that developed has been taken. Then optic chemical sensor readings with wood extracts that contain permethrin taken. In addition, the optical chemical sensors developed were tested on the material preserved from the same group of pyrethroid such as cypermethrin in concentration

ratio of 1: 1. Optical chemical sensor readings to permethrin alone when compared with optical chemical sensor readings to mix permethrin with cypermethrin. The same procude apllied to other interference chemical such as sugar and deltamethrin. Recoveries of permethrin study sample were done by using wood samples. Sensors are calibrated with a solution of permethrin. Later known weight of wood samples crushed and added to a solution of permethrin was known concentration. Wood samples were also added to the buffer as control. Chemical sensor then is exposed to the wood sample. Permethrin response value, which can be added is determined by the equation, x= y-zwhere x is a real response permethrin concentration added to the wood samples while y is the response of wood samples measured and z is the response of wood samples measured before permethrin added. By extending the slope of the line on the graph cut the x-axis calibration, will be available real value permethrin concentrations in wood samples by xM. Percent recovery is calculated by formula,(x/y) x 100 = %yM is the actual concentrations of permethrin added to wood samples. Test analysis used to determine the analyte in the sample timber permethrin is the standard method of Australian/New Zealand Standard [19]. A total of 1g of wood powder were weighed and transferred into a 50 mL erlenmeyer flask. Then the solvent n-hexane solution of 15-20 mL inserted into the flask. Next the flask is covered with aluminum sheets and placed on an electric sieve. Wood powder immersed in the solvent n-hexane solution filtered for 30 minutes at a speed of 100 revolutions per minute. After 30 minutes, the wood powder is separated from the solvent extraction results through screening process by using a size 4 filter paper, extraction results put into 25

mL volumetric flask. N-hexane solution was added to the extraction yield up to level 25 mL. In this situation results permethrin analyte extraction from wood samples were available for analysis.

Competing interests

All authors declare that they have no competing interests

Authors' contributions

MNMA planned and carried out the sensor manufacturing, measurements and data production. LYH headed the scientific planning and evaluation of the project. MA provided scientific advices. All authors read and approved the final manuscript

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