بسم الله الرحمن الرحيم

MONA MAGHRABY

شبكة المعلومات الجامعية

التوثيق الالكتروني والميكروفيلم

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شبكة المعلومات الجامعية

التوثيق الإلكتروني والميكروفيلم

جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

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Study on Pesticide Residues in Food using Molecular Imprinting Technique

Ph.D.Thesis

Submitted to

Chemistry Department-Faculty of Science- Ain Shams University For The Degree of Doctor Philosophy (Ph.D.) In Science (Chemistry)

By

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M. Sc. In Chemistry (2016)

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Approval Sheet

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A Thesis for

Ph.D. Degree of Science in Chemistry

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ACKNOWLEDGEMENT

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Many thanks and Praise be to great Allah most gracious who shined my way and Supported me with patience and perseverance to fulfill this humble work.

My special thanks to my family for giving me inspiration, confidence and patience throughout the period of investigation and many thanks for my husband for his efforts and support for me to complete my thesis.

I wish to express my deep gratitude to Prof. ***Dr. Ayman Helmy Kamel,*** *Prof. Of Analytical Chemistry, Faculty of science, Ain- shams University for his Supervision, guidance, useful criticism and his efforts to fulfill this work.*

Many thanks to ***Dr. Amr Ali*** *lecture in inorganic chemistry; Faculty of science, Ain- shams University for his sharing in supervision, kind unfailing help throughout this work.*

Finally, deep thanks and gratitude to all my colleagues in the Faculty of Science, Ain Shams University escpicially for their valuable advice, continuous encouragement, cooperation and kind assistance.

Nashwa shable abdalla

Published Papers

molecules

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Article

All Solid-State Poly (Vinyl Chloride) Membrane Potentiometric Sensor Integrated with Nano-Beads Imprinted Polymers for Sensitive and Rapid Detection of Bispyribac Herbicide as Organic Pollutant

Nashwa S. Abdalla [1], Maha A. Youssef [2], H. Algarni [3], Nasser S. Awwad [4] and Ayman H. Kamel [1,*]

Abstract: All-solid-state potentiometric sensors were prepared by using polyaniline (PANI) as the solid contact material. A film of PANI (thickness approximately being 0.25 µm) was deposited on a solid substrate (carbon screen printed platform). The PANI layer was subsequently coated with an ion-selective membrane (ISM) containing uniform-sized molecularly imprinted nanoparticles to produce a solid-contact ion-selective electrode (SC/ISE) for bispyribac herbicide (sensor I). In addition, aliquat 336 was also used as an ion exchanger in plasticized PVC membrane (sensor II). The proposed sensors revealed a remarkably improved sensitivity towards bispyribac ions with anionic slopes of -47.8 ± 1.1 ($r^2 = 0.9995$) and -44.4 ± 1.4 ($r^2 = 0.9997$) mV/decade over a linear range 1.0×10^{-2}–8.6×10^{-6} M, 1.0×10^{-2}–9.0×10^{-6} M and detection limits of 1.33 and 1.81 µg/mL for sensors I and II, respectively.Selectivity of both sensors is significantly high for different common pesticides and inorganic anions. The potential stability of the SC/ISEs was studied using chronopotentiometry. Electrochemical impedance spectrometry was used to understand the charge-transfer mechanisms of the different types of ion-selective electrodes studied. The impedance response of the electrodes was modelled by using equivalent electrical circuits. The sensors were used for a direct measurement of the bispyribac content in commercial herbicide formulations and soil samples collected from agricultural lands planted with rice and sprayed with bispyribac herbicide. The results agree fairly well with data obtained using HPLC method.

Keywords: bispyribac sodium; solid-contact ISEs; screen-printed; molecularly imprinted polymers; organic pollutant

polymers

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Article

Novel Solid-State Potentiometric Sensors Using Polyaniline (PANI) as A Solid-Contact Transducer for Flucarbazone Herbicide Assessment

Ayman H. Kamel [1], Abd El-Galil E. Amr [2,3,*], Nashwa S. Abdalla [1], Mohamed El-Naggar [4], Mohamed A. Al-Omar [2], Hamad M. Alkahtani [5] and Ahmed Y. A. Sayed [5]

Abstract: Novel potentiometric solid-contact ion-selective electrodes (SC/ISEs) based on molecularly imprinted polymers (MIPs) as sensory carriers (MIP/PANI/ISE) were prepared and characterized as potentiometric sensors for flucarbazone herbicide anion. However, aliquat S 336 was also studied as a charged carrier in the fabrication of Aliquat/PANI/ISEs for flucarbazone monitoring. The polyaniline (PANI) film was inserted between the ion-sensing membrane (ISM) and the electronic conductor glassy carbon substrate (GC). The sensors showed a noticeable response towards flucarbazone anions with slopes of -45.5 ± 1.3 ($r^2 = 0.9998$) and -56.3 ± 1.5 ($r^2 = 0.9977$) mV/decade over the range of 10^{-2}–10^{-5}, 10^{-2}–10^{-4} M and detection limits of 5.8×10^{-6} and 8.5×10^{-6} M for MIP/PANI/ISE and Aliguat/PANI/ISE, respectively. The selectivity and long-term potential stability of all presented ISEs were investigated. The short-term potential and electrode capacitances were studied and evaluated using chronopotentiometry and electrochemical impedance spectrometry (EIS). The proposed ISEs were introduced for the direct measurement of flucarbazone herbicide in different soil samples sprayed with flucarbazone herbicide. The results agree well with the results obtained using the standard liquid chromatographic method (HPLC).

Keywords: Solid-contact ion-selective electrode; conducting polymer polyaniline (PANI); flucarbazone herbicide; molecularly imprinted polymers (MIPs)

polymers

MDPI

Article

Tailor-Made Specific Recognition of Cyromazine Pesticide Integrated in a Potentiometric Strip Cell for Environmental and Food Analysis

Nashwa S. Abdalla [1], Abd El-Galil E. Amr [2,3,*], Aliaa S. M. El-Tantawy [4], Mohamed A. Al-Omar [2] Ayman H. Kamel [1] and Nagy M. Khalifa [2,3]

Abstract: Screen-printed ion-selective electrodes were designed and characterized for the assessment of cyromazine (CYR) pesticide. A novel approach is to design tailor-made specific recognition sites in polymeric membranes using molecularly imprinted polymers for cyromazine (CR) determination (sensor I). Another sensor (sensor II) is the plasticized PVC membrane incorporating cyromazine/tetraphenyl borate ion association complex. The charge-transfer resistance and water layer reached its minimal by incorporating Polyaniline (PANI) solid-contact ISE. The designed electrodes demonstrated Nernstain response over a linear range 1.0×10^{-2}–5.2×10^{-6} and 1.0×10^{-2}–5.7×10^{-5} M with a detection limit 2.2×10^{-6} and 8.1×10^{-6} M for sensors I and II, respectively. The obtained slopes were 28.1 ± 2.1 (r^2 = 0.9999) and 36.4 ± 1.6 (r^2 = 0.9991) mV/decade, respectively. The results showed that the proposed electrodes have a fast and stable response, good reproducibility, and applicability for direct measurement of CYR content in commercial pesticide preparations and soil samples sprayed with CYR pesticide. The results obtained from the proposed method are fairly in accordance with those using the standard official method.

Keywords: cyromazine (CR); solid-contact ISEs; screen-printed; molecularly imprinted polymers (MIPs); polyaniline (PANI)

International Journal of Environmental Research and Public Health

MDPI

Article

Modified Screen-Printed Potentiometric Sensors based on Man-Tailored Biomimetics for Diquat Herbicide Determination

Ayman H. Kamel [1,*], Abd El-Galil E. Amr [2,3,*], Nashwa S. Abdalla [1], Mohamed El-Naggar [4], Mohamed A. Al-Omar [2] and Abdulrahman A. Almehizia [2]

Abstract: Screen-printed platforms integrated with molecularly imprinted polymers (MIP) were fabricated and characterized as potentiometric sensors for diquat (DQ). The synthesized MIP beads were studied as sensory carriers in plasticized poly(vinyl chloride) membranes. The sensors were constructed by using poly(3,4-ethylenedioxythiophene) (PEDOT) as solid-contact material to diminish charge-transfer resistance and water layer potential. Conventional ion-selective electrodes (ISEs) with internal filling solution were used for comparison. The designed electrodes showed near Nernstian slopes of 28.2 ± 0.7 (r^2 = 0.999) over the concentration range of 1.0×10^{-6}–1.0×10^{-2} M with the limit of detection 0.026 µg/mL over the pH range 4.2–9.0. The electrode exhibited good selectivity for diquat cations over a large number of organic and inorganic cations. The sensor was successfully introduced for direct measurement of diquat content in commercial pesticide preparations and different spiked potato samples. The results showed that the proposed electrode has a fast and stable response, good reproducibility, and applicability for direct assessment of diquat content. The proposed potentiometric method is simple and accurate in comparison with the reported HPLC methods. Besides, it is applicable to turbid and colored sample solutions.

Keywords: diquat dibromide (DQ) solid-contact ISEs; poly(3,4-ethylenedioxythiophene) (PEDOT); screen-printed; molecularly imprinted polymers (MIPs); organic pollutant

ABSTRACT

Abstract

This thesis entitled with "Study on Pesticide Residues in Food using Molecular Imprinting Technique" includes five chapters.

Chapter one:

This chapter is included three parts: Part (I) contains Background on pesticides residues in food, Part (II) Background on Potentiometric Sensors and Part (III) Background on Molecularly Imprinted Polymers (MIPs.

Chapter two:

All-solid-state potentiometric sensors were prepared by using polyaniline (PANI) as the solid contact material. A film of PANI (thickness approximately being 0.25 μm) was deposited on a solid substrate (carbon screen printed platform). The PANI layer was subsequently coated with an ion-selective membrane (ISM) containing uniform-sized molecularly imprinted nanoparticles to produce a solid-contact ion-selective electrode (SC/ISE) for bispyribac herbicide (sensor I). In addition, aliquat 336 was also used as an ion exchanger in plasticized PVC membrane (sensor II). The proposed sensors revealed a remarkably improved sensitivity towards bispyribac ions with anionic slopes of -47.8 ± 1.1 (r^2 = 0.9995) and -44.4 ± 1.4 (r^2 = 0.9997) mV/decade over a linear range 1.0 × 10^{-2}–8.6 × 10^{-6} M, 1.0 × 10^{-2}–9.0 × 10^{-6} M and detection limits of 1.33 and 1.81 μg/mL for sensors I and II, respectively. Selectivity of both sensors is significantly high for different common pesticides and inorganic anions. The potential stability of the SC/ISEs was studied using chronopotentiometry. Electrochemical impedance spectrometry was used to understand the charge-transfer mechanisms of the

different types of ion-selective electrodes studied. The impedance response of the electrodes was modelled by using equivalent electrical circuits. The sensors were used for a direct measurement of the bispyribac content in commercial herbicide formulations and soil samples collected from agricultural lands planted with rice and sprayed with bispyribac herbicide. The results agree fairly well with data obtained using HPLC method.

Chapter three:

Screen-printed ion-selective electrodes were designed and characterized for the assessment of cyromazine (CYR) pesticide. A novel approach is to design tailor-made specific recognition sites in polymeric membranes using molecularly imprinted polymers for cyromazine (CR) determination (sensor I). Another sensor (sensor II) is the plasticized PVC membrane incorporating cyromazine/tetraphenyl borate ion association complex. The charge-transfer resistance and water layer reached its minimal by incorporating Polyaniline (PANI) solid-contact ISE. The designed electrodes demonstrated Nernstain response over a linear range 1.0×10^{-2}–5.2×10^{-6} and 1.0×10^{-2}–5.7×10^{-5} M with a detection limit 2.2×10^{-6} and 8.1×10^{-6} M for sensors I and II, respectively. The obtained slopes were 28.1 ± 2.1 (r^2 = 0.9999) and 36.4 ± 1.6 (r^2 = 0.9991) mV/decade, respectively. The results showed that the proposed electrodes have a fast and stable response, good reproducibility, and applicability for direct measurement of CYR content in commercial pesticide preparations and soil samples sprayed with CYR pesticide. The results obtained from the proposed

method are fairly in accordance with those using the standard official method.

Chapter four:

Novel potentiometric solid-contact ion-selective electrodes (SC/ISEs) based on molecularly imprinted polymers (MIPs) as sensory carriers (MIP/PANI/ISE) were prepared andcharacterized as potentiometric sensors for flucarbazone herbicide anion. However, aliquat S 336 was also studied as a charged carrier in the fabrication of Aliquat/PANI/ISEs for flucarbazone monitoring. The polyaniline (PANI) film was inserted between the ion-sensing membrane (ISM) and the electronic conductor glassy carbon substrate (GC). The sensors showed a noticeable response towards flucarbazone anions with slopes of -45.5 ± 1.3 (r2 = 0.9998) and -56.3 ± 1.5 (r^2 = 0.9977) mV/decade over the range of 10^{-2}–10^{-5}, 10^{-2}–10^{-4} M and detection limits of 5.8 × 10^{-6} and 8.5 × 10^{-6} M for MIP/PANI/ISE and Aliguat/PANI/ISE, respectively. The selectivity and long-term potential stability of all presented ISEs were investigated. The short-term potential and electrode capacitances were studied and evaluated using chronopotentiometry and electrochemical impedance spectrometry (EIS). The proposed ISEs were introduced for the direct measurement of flucarbazone herbicide in different soil samples sprayed with flucarbazone herbicide. The results agree well with the results obtained using the standard liquid chromatographic method (HPLC).

Chapter five:

Screen-printed platforms integrated with molecularly imprinted polymers (MIP) were fabricated and characterized as

potentiometric sensors for diquat (DQ). The synthesized MIP beads were studied as sensory carriers in plasticized poly (vinyl chloride) membranes. The sensors were constructed by using poly (3, 4-ethylenedioxythiophene) (PEDOT) as solid-contact material to diminish charge-transfer resistance and water layer potential. Conventional ion-selective electrodes (ISEs) with internal filling solution were used for comparison. The designed electrodes showed near Nernstian slopes of 28.2 ± 0.7 (r^2 = 0.999) over the concentration range of 1.0×10^{-6}–1.0×10^{-2} M with the limit of detection 0.026 μg/mL over the pH range 4.2–9.0. The electrode exhibited good selectivity for diquat cations over a large number of organic and inorganic cations. The sensor was successfully introduced for direct measurement of diquat content in commercial pesticide preparations and different spiked potato samples. The results showed that the proposed electrode has a fast and stable response, good reproducibility, and applicability for direct assessment of diquat content. The proposed potentiometric method is simple and accurate in comparison with the reported HPLC methods. Besides, it is applicable to turbid and colored sample solutions.

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