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DETECTION OF PESTICIDES (CLOTHIANIDIN) BY CALIX[4]ARENE CUSTOMIZED GOLD NANOPARTICLES FROM DECOMPOSED PLANT MATTER

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Abstract

This work focuses on the detection of the pesticide from the soil, water and the plant materials by the help of para- sulphonato calix[4]arene modified gold nanoparticles. Work has been reported of this kind with other pesticides, but no work has been reported for the detection of clothianidin. In this paper, we report the preparation of Para Sulphonato Calix[4]arene modified Au Nanoparticles (pSC4 – Au Nps) and their application as colorimetric sensors for the detection of Clothianidin, which is widely used pesticide in developing countries.

1. Introduction

The environmental harm that this pesticide causes is often exacerbated due to the practice of applying the pesticides by foliar spraying or direct application to the surface of the soil. Wind-drift, leaching, and run off can cause the migration of a large fraction of the pesticide out of the desired zone of activity and into surface waters and direct contact with birds, animals and humans resulting in to toxicity into them. The Environment Protection Agency (EPA) and other environment agonists have filed the petition against the use of this pesticide. Despite of the toxic effects of the pesticide against the environmental factors and urgent action to stop the chemical, it is being marketed freely and being used on large scales in USA and Germany.
Clothianidin, (*E*)-1-(2-chloro-1, 3- thiazol-5-yl-methyl) -3-methyl-2-nitroguanidine, is a neonicotinoid used in systemic insecticide. This compound is highly effective in controlling hemipterous insects as well as coleopterous, thysanopterous, and certain lepidopterous pests.

The continuous use of this pesticide has led to the destruction of many colonies of bees in last few years and the testing of the dead bees showed that 99% of them had clothianidin built up. This occurs due to accumulation of clothianidin in the bodies of bees at the time of pollination and due to wind drift. Also this develops concerns over the cattle and birds eating seeds as they forage through fields planting with seeds treated with clothianidin as even only 1 or 2 corn seeds could result in developmental and reproductive harm in them. Also the signs of ingestion of this compound are among other things, labored breathing.

In the town of Stockton, 200 cattle just suddenly died as a result of acute interstitial pneumonia, a disease characterized by labored breathing where the creature eventually goes into shock and dies. Corn, is the common feed of cattle. Clothianidin is toxic to aquatic animals as well. In the last two years there have been 2 major die offs of fish in the Big Eau Pleine Reservoir. One of the major sources of the problem has been cited as clothianidin runoff resulting in choking algae blooms that suck all the oxygen out of the water. The killing this fish is not necessarily lack of oxygen, but rather asphyxiation occurring due to the presence of Clothianidin in the soil run off in the water. Though pesticides are used to control the peats and increase the crop production, but if they destroy the birds, bees and other aquatic animals then, it rather disturbs the environmental food chain and also reduces the rate of pollination due to reduced number to mediators.

This has induced an immediate need for the detection of the clothianidin from the soil and the Food products. To day, numerous techniques related to HPLC, LCMS and Gas Chromatography has been employed. However, these techniques employ tedious and lengthy time analysis, expensive instruments and highly trained experts. So some simple, cost effective and in situ method which permits easy detection of such pesticides is a real need at this point.

Colorimetric detection helps in easy detection of analytes by naked eye. Noble metal nanoparticles like gold and silver permit excellent Plasmon assimilation and so a variety of colorimetric sensor based noble metal nanoparticles have been developed. The efficient designing of colorimetric sensors can be done using appropriate organic compounds as ligands to modify noble metal nanoparticles. The introduction of organic compounds to the metal nanoparticles results in host- guest interaction, also some channeling structures can be positioned in between the metal nanoparticles and analytes, resulting in change in colour and UV- Vis Spectroscopic results due to aggregation of noble metal nanoparticles and the analytes.

Calix[4]arene is a supramolecule that has inner cavity of diameter 3 A˚ and are mostly hydrophobic in nature but the sulphonato calix[4]arene is water soluble and are strongly hydrophilic due to (SO_3^-) heads occupying the upper rims of the calixarene moiety. This hydrophilicity of moiety helps it to combine with the pesticide dissolved in water. Where as considerable accurate monitoring of the host molecule by metal nanoparticles helps in the selective and efficient colorimetric detection of pesticide through visible colour change.

2. Experiment

Microwave assisted synthesis of Au Nanoparticles

All the glass wares were thoroughly cleaned with freshly prepared 3:1 (HCl: HNO_3) and then rinsed with double distilled water before use. To synthesize microwave assisted Au nanoparticles, the reaction was carried out in a sealed vessel. 0.1 mM of 3 ml Au solution was prepared and mixed with 2 ml of 13 mM of sodium citrate and allow sustainable heating at 80 ^{0}C at power up to 150 W for 2 min. the colour changes from pale Yellow to Burgundy or Pink. Then cool for 15 min and use for the reaction.

Synthesis of pSC4 – Au Nps with Pesticide

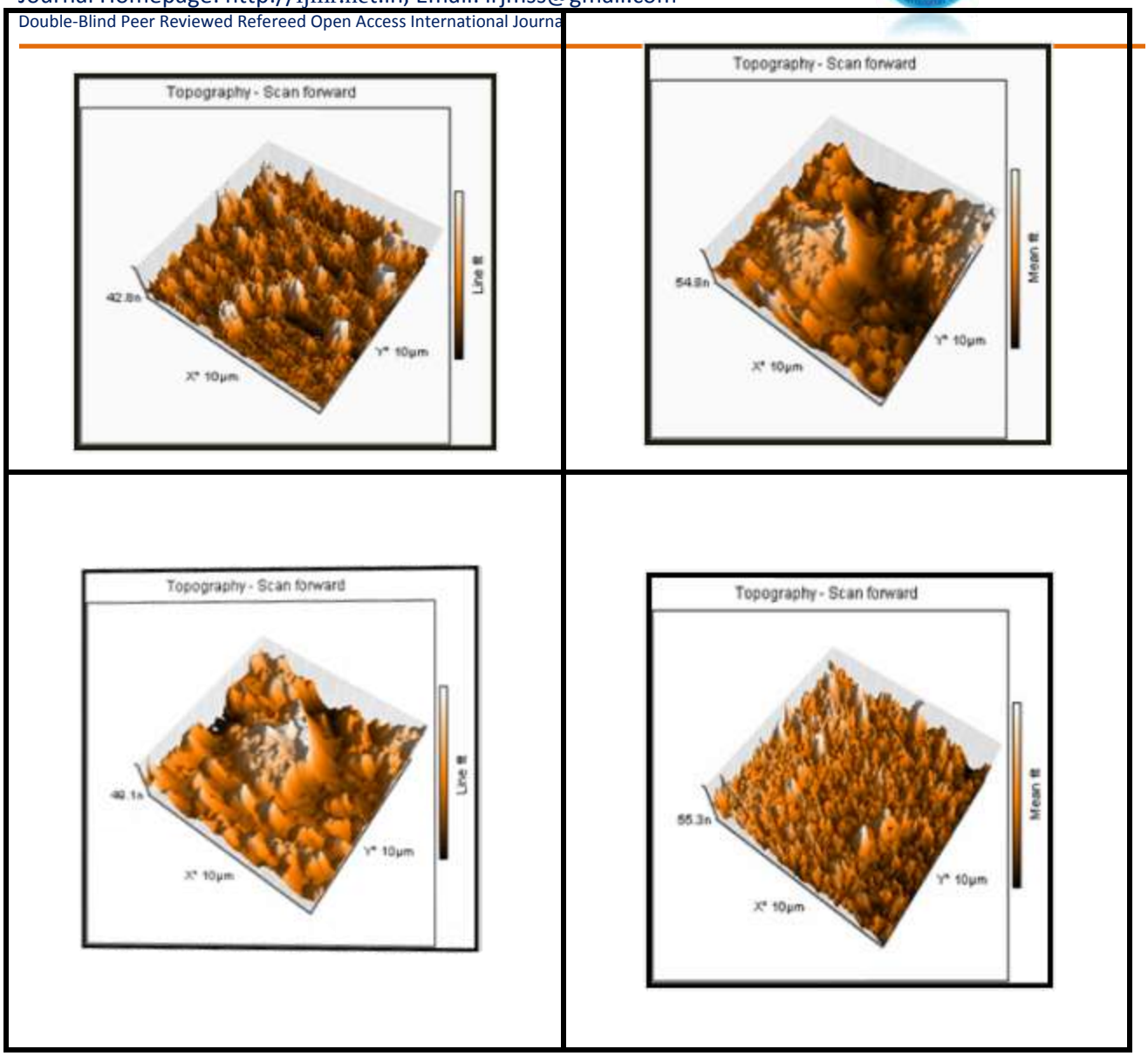
Clothianidin dissolved in water was taken in different dilutions of 5 ppm, 10 ppm, 50 ppm, 100 ppm, and 250 ppm. The reaction was performed with different dilutions taking 2 ml of each solution and by adding up of equal proportion of 2 ml of Au NPs and 2 ml of Para – Sulphonato Calixarene. The reaction mixture was allowed to stand for some time and the colour change was obtained from red to blue.

3. Results and Discussion

Spectral Characterizations

By reacting 1 ml of 0.1 mM Au Nps with 1 ml of 0.1 mM of Para Sulfonato calix[4]arene solution, at room temperature for 5 min and 10 min respectively, the pSC4 – Au Nps were obtained in water and were characterized by AFM and FTIR Spectroscopy.

Atomic Force Microscopic analysis



Here, the figures 1 (a) & (b) show the AFM images of the Au Nps and Para Sulfonato Calix[4]arene before addition of the Pesticide (Clothianidin). Here, the particle size is smaller and does not show any aggregation. Where as, the figures 1 (c) & (d) shows the AFM images of Au Nps and Para Sulfonato Calix[4]arene after addition of the Pesticide (Clothianidin). It shows increased particles size due to aggregation.

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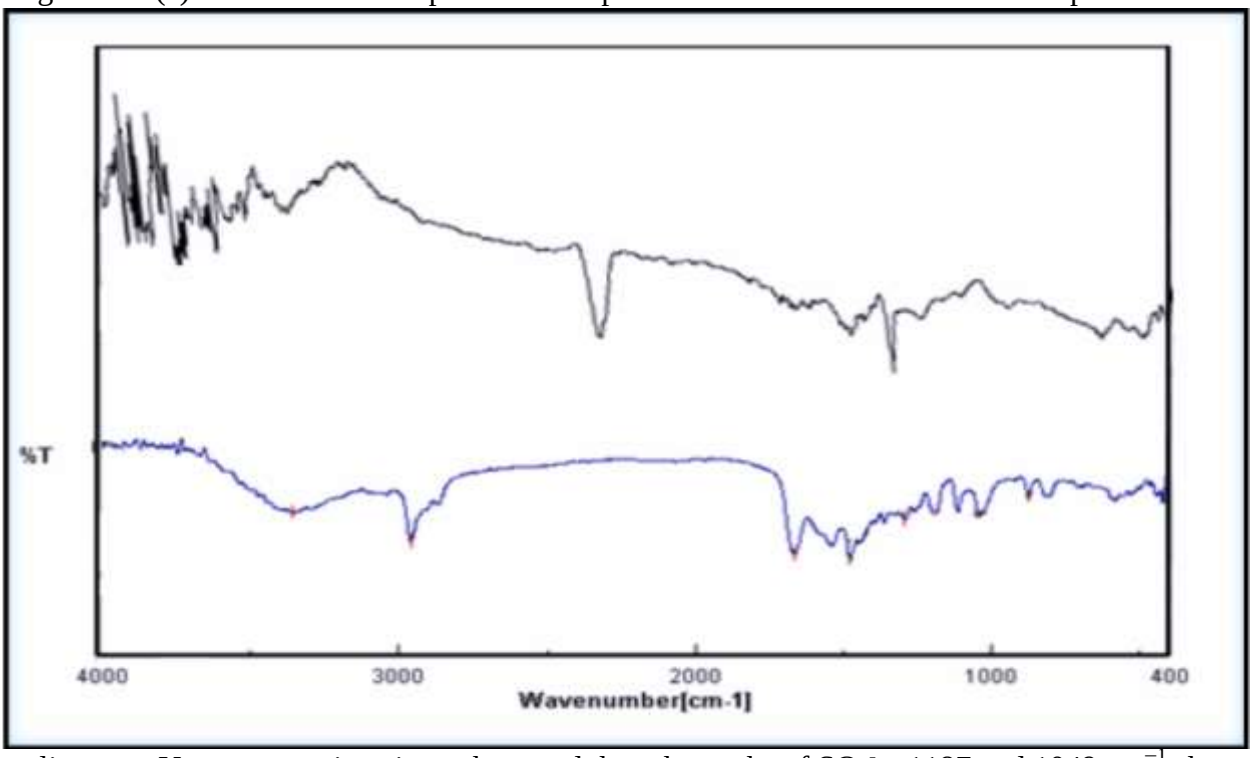
FTIR spectra analysis

Figure – 2 (a) shows the FTIR spectra of the para Sulfonato calixarene and Au – para Sulfonato



calixarene. Upon comparison it can be noted that, the peaks of SO_3^-at 1187 and 1049 cm^{-1} shown in pure *p*SC4 are shifted to 1178 and 1036 cm^{-1} in the graph of Au Nps + pSC4 which suggests that, the SO_3^- groups of pSC-4 coordinate with the gold atoms on the surface of Au NPs, when the pSC4 – Au Nps are formed.

The aggregation process occurs between clothianidin and para Sulfonato Calix[4]arene possibly either due to host – guest interaction or due to electrostatic interaction.
In the host – guest interaction, the clothianidin get bound into the cavity of para sulfonato calix[4]arene which undergoes aggregation.
As para – sulfonato calix[4]arene possesses an electron rich cyclic cavity of SO_3^- that can attract the positively charged NH^+ of clothianidin, which results in electrostatic interaction between NH^+ and SO_3^-.

4. CONCLUSION

Water Soluble pSC4 – Au Nps were prepared successfully and were characterized by AFM, and FTIR Spectroscopy. Para Sulfonato Calix[4]arene – Au Nps can be successfully utilized as an innovative advancement for the detection of clothianidin allowing the analysis to be simpler, easier and faster by colorimetric assay down to the limit of 0.05 ppm concentration. With the great potential for the real time in – situ detection of clothianidin. The project can be helpful to the countries like India, USA, Canada, Singapore, Germany, Libia, France, etc, where the

environment agonists are protesting against the use of clothianidin as an insecticide in corn, mustard and rice fields.

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5. References

1. HIRAKAWA, Y., YAMASAKI, T., HARADA, A., IWASA, S., NARITA, H., & MIYAKE, S. (2018). Development of an Immunosensor Based on Surface Plasmon Resonance for Simultaneous Residue Analysis of Three Pesticides —Boscalid, Clothianidin, and Nitenpyram— in Vegetables. Analytical Sciences, 34(5), 533-539. doi: 10.2116/analsci.17p487
2. Pesticides Detection Using Acetylcholinesterase Nanobiosensor. (2016). Biosensors Journal, 5(1). doi: 10.4172/2090-4967.1000133
3. KITAMI, H. (2011). Simultaneous Determination of Oxine Copper, Thiamethoxam, and Clothianidin in River-Water by HPLC with UV Detection after Solid-Phase Extraction. BUNSEKI KAGAKU, 60(5), 427-432. doi: 10.2116/bunsekikagaku.60.427
4. ZHAO, H., JIA, Y., DING, M., SUN, D., & ZHAO, M. (2011). Analysis of organochlorine pesticides and pyrethroid pesticides in vegetables by gas chromatography-electron capture detection coupled with solid-phase extraction using multiwalled carbon nanotubes as adsorbent. Chinese Journal Of Chromatography, 29(5), 443-449. doi: 10.3724/sp.j.1123.2011.00443

5. Dejun Xiong and Haibing Li , 2008 Nanotechnology 19 465502; (http://iopscience.iop.org/09574484/19/46/465502)

6. Gaurang Patel and Shobhana Menon*, Received (in Cambridge, UK) 13th March 2009, Accepted 16th April 2009

7. Florent Perret, Adina N. Lazar and Anthony W. Coleman* , Received (in Cambridge, UK) 17th January 2006, Accepted 23rd February 2006 First published as an Advance Article on the web 10th March 2006

8. UNITED STATES ENVIRONMENTAL PROTECTION AGENCY; WASHINGTON, D.C. 20460 Office of Chemical Safety and Pollution Prevention; Date : 02 Nov, 2010.

9. Wenzhan Yang1 and Melgardt M. de Villiers; Department of Basic Pharmaceutical Sciences, School of Pharmacy, University of Louisiana at Monroe, Monroe, LA 71209

10. Dejun Xiong, Mingliang Chen and Haibing Li*Received (in Cambridge, UK) 22nd October 2007, Accepted 4th December 2007; First published as an Advance Article on the web 18th December 2007

11. The HGCA Barley Disease Management Guide 2011; Spring 2011.

12. MIAO-FAN CHEN, JENN-WEN HUANG, SUE-SUN WONG AND GOW-CHEN
13. Journal of Food and Drug Analysis, Vol. 13, No. 3, 2005, Pages 279-283
14. Exposure to Clothianidin Seed-Treated Canola Has No Long-Term Impact on Honey Bees; G. CHRISTOPHER CUTLER1 AND CYNTHIA D. SCOTT-DUPREE; Journal of Economic Entomology, 100(3):765-772. 2007

15. United States Environment Protection Agency. Pesticide Fact Sheet 2007, Office of Prevention, Pesticides and Toxic Substances – USA

16. FAO Specification and Evaluation for Agricultural Pesticides – CLOTHIANIDIN Form, Food and Agriculture organizations, The United Nations.
17. Residual Analytical Methods for the determination of Clothianidin in Plant Materials by LC-MS/MS Performed By, Bayer AG, Crop Protection Research Center, Federal Republic of Germany, 2001
18. Environmental Regulation of Nanotechnology: Some Preliminary Observations By Glenn Harlan Reynolds
19. Application and Health Effects of Pesticides Commonly Used in India By Manoj Kumar[1] and Ashok Kumar[2]; May 2007 Post Graduate Institute of Medical Education and Research (PGIMER), Chandigarh and DAV College, Dehradun, Uttranchal
20. Moldovan, R., Iacob, B., Farcău, C., Bodoki, E., & Oprean, R. (2021). Strategies for SERS Detection of Organochlorine Pesticides.

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