

**DETECTION OF ORGANOPHOSPHATES USING
SILVER NANOPARTICLES AND MOLECULARLY
IMPRINTED POLYMER (MIP)**

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DETECTION OF ORGANOPHOSPHATES USING SILVER NANOPARTICLES AND MOLECULARLY IMPRINTED POLYMER (MIP)

by

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Certificate

This is to certify that the thesis entitled “**Detection of Organophosphates using Silver Nanoparticles and Molecularly Imprinted Polymer (MIP)**” submitted by **Ms. Shalini Shikha** to the Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy, is a record of the original bonafide research work carried out by her. She has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.

Prof. Sudip K Pattanayek

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Abstract

The organophosphates such as phorate, chlorpyrifos, malathion, etc are used to control weeds, pests, insects, or mosquitoes. The use of various pesticides as fumigants to repel insects and pests causes harm to the environment. The presence of various pesticides in the food chain as residual amounts causes harm to human health. In addition, a large number of pesticides present in effluent coming out of the pesticide industries go into the water bodies contaminating drinking water. The detection and control of pesticides are of paramount importance for human health and safety. Various traditional techniques are available for detecting pesticide molecules, but these techniques require sophisticated instruments, a technical workforce, and large capital investments. To overcome these issues, researchers have been trying to develop sensors that may be more efficient for the on-site detection of pesticides. One of the major components of the sensor is the sensing substrate for the selective detection of pesticide residues. An in-depth understanding of the interaction of pesticides with suitable sensing molecules is required to achieve such a kind of sensor substrate.

It is envisaged that a solution capable of changing its color on its interaction with pesticides can be a good candidate for an onsite detection platform. The concentration of pesticides in many real solutions is low, and the development of a platform containing a specific functional group, which is capable of giving very good adsorption from the solution is of paramount importance. We have used two broad methods- (i) silver nanoparticles based system giving change in color and (ii) molecularly imprinted polymers based substrate with a specific interaction.

The literature lacks an in-depth understanding of the interaction of sulfur-containing organophosphates in solution and on the surface with a suitable sensing molecule. Herein, the interaction of three organophosphates, namely phorate, chlorpyrifos, and malathion containing the P=S group with borohydride stabilized silver nanoparticles, was analyzed in solution. On mixing the pesticides with uncapped nanoparticles, the chlorpyrifos and malathion do not show a significant visual response, however, phorate shows a significant color change. The observed colorimetric changes are corroborated with UV-visible absorption studies, changes in particle size, and zeta potential. The silver and sulfur (Ag/S) complex is formed and the degradation of phorate happens through S-CH₂ linkage. The orientations of phorate near silver nanoparticles are discussed from the adsorption energy calculation using density functional theory.

In a real sample, interfering substances like metal ions may interfere with this type of interaction. The salts studied are sodium chloride (NaCl), potassium permanganate (KMnO₄), magnesium sulfate (MgSO₄), nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), and trisodium citrate (Na₃C₆H₅O₇). The effect of these salts on the interactions of pesticides with borohydride stabilized silver nanoparticles are analyzed. Only oxidizing salts potassium permanganate and nickel (II) nitrate hexahydrate can affect the color of solutions. The oxidation/degradation of pesticides happens in the presence of Ag nanoparticles only.

The substrate based on molecularly imprinted polymers with a specific functional group is expected to give the required specificity and adsorption. To determine the best chemical functionality, we have studied the adsorption of two organophosphates, phorate, and malathion, on four different chemical functionalized surfaces. The four different functionalized surfaces are obtained by modifying the silica surface with four different silane coupling agents, namely n-propyltrimethoxy silane (PTMS), octyltrimethoxy silane (OTMS), 3- (trimethoxysilyl) propyl methacrylate (TMSPMA) and 3- (triethoxysilyl) propionitrile (TESPN). A diffusion-controlled kinetic model is developed with a surface phase concept. The model is fitted to the real-time adsorption data of phorate, and malathion over various substrates obtained using QCM-D. The results show that TMSPMA functionalized surface has uniform adsorption of pesticides. The adsorption is explained through molecular interactions. A reasonably strong binding with a possibility of reversible binding of phorate and malathion on TMSPMA functionalized surface is observed.

Next, MIP is synthesized using the sol-gel technique using 3- (trimethoxysilyl) propyl methacrylate (TMSPMA) as a functional monomer. The well-characterized MIP was used for detecting phorate and malathion in a silica-quartz crystal of QCM-D. The real-time adsorption studies of pesticides on MIP surfaces show their significant binding with the respective pesticide used as a template molecule. The specificity and repeatability experiments indicate that the developed MIP is highly selective for the studied pesticides. The given study provides insight into the underlying interaction capabilities of the given pesticides with the synthesized substrate.

सार

ऑर्गनोफॉस्फेट जैसे फोरेट, क्लोरपाइरीफोस और मैलाथियान आदि का उपयोग खरपतवार, कीट, कीड़े या मच्छरों को नियंत्रित करने के लिए किया जाता है। कीड़ों और कीटों को दूर भगाने के लिए विभिन्न कीटनाशकों के उपयोग से पर्यावरण को नुकसान होता है। खाद्य श्रृंखला में विभिन्न कीटनाशकों की अवशिष्ट मात्रा के रूप में उपस्थिति मानव स्वास्थ्य को नुकसान पहुंचाती है। इसके अलावा, कीटनाशक उद्योगों से निकलने वाले अपशिष्ट में मौजूद बड़ी संख्या में कीटनाशक पेयजल को दूषित करने वाले जलाशयों में चले जाते हैं। मानव स्वास्थ्य और सुरक्षा के लिए कीटनाशकों का पता लगाना और उनका नियंत्रण सबसे महत्वपूर्ण है। कीटनाशक अणुओं का पता लगाने के लिए विभिन्न पारंपरिक तकनीकें उपलब्ध हैं, लेकिन इन तकनीकों के लिए परिष्कृत उपकरणों, एक तकनीकी कार्यबल और बड़े पूंजी निवेश की आवश्यकता होती है। इन मुद्दों को दूर करने के लिए, शोधकर्ता ऐसे सेंसर विकसित करने की कोशिश कर रहे हैं जो कीटनाशकों के साइट पर पता लगाने के लिए अधिक कुशल हो सकते हैं। सेंसर के प्रमुख घटकों में से एक कीटनाशक अवशेषों के चयनात्मक पता लगाने के लिए सब्सट्रेट को सेंस करना है। इस तरह के सेंसर सब्सट्रेट को प्राप्त करने के लिए उपयुक्त संवेदी अणुओं के साथ कीटनाशकों की बातचीत की गहराई से समझ आवश्यक है।

यह परिकल्पना की गई है कि एक समाधान जो कीटनाशक के साथ अपनी बातचीत पर अपने रंग का पीछा करने में सक्षम है, ऑनसाइट डिटेक्शन प्लेटफॉर्म के लिए अच्छा उम्मीदवार हो सकता है। कई वास्तविक घोलों में कीटनाशकों की सांद्रता कम हो रही है, विशिष्ट कार्यात्मक समूह वाले प्लेटफॉर्म का विकास, जो घोल से बहुत अच्छा सोखना देने में सक्षम है, सर्वोपरि है। हमने दो व्यापक तरीकों का इस्तेमाल किया है- (i) सिल्वर नैनोपार्टिकल्स आधारित सिस्टम जो रंग में बदलाव देता है और (ii) विशिष्ट इंटरैक्शन के साथ आणविक रूप से अंकित पॉलिमर आधारित सब्सट्रेट।

समाधान में और सतह पर उपयुक्त संवेदी अणुओं के साथ सल्फर युक्त ऑर्गनोफॉस्फेट की बातचीत की गहन समझ में साहित्य का अभाव है। इस प्रकार, तीन ऑर्गनोफॉस्फेट, अर्थात् फोरेट, क्लोरपाइरीफोस, और मैलाथियान जिसमें पी = एस समूह होता है, बोरोहाइड्राइड स्थिर चांदी के नैनोकणों के साथ, समाधान में विश्लेषण किया गया था। कीटनाशकों को बिना ढके नैनोकणों के साथ मिलाने पर फोरेट रंग में महत्वपूर्ण दृश्य परिवर्तन दिखाता है। देखे गए वर्णमिति परिवर्तन यूवी-दृश्यमान अवशोषण अध्ययन, कण आकार में परिवर्तन और जीटा क्षमता के साथ पुष्टि की जाती है। सिल्वर और सल्फर (Ag/S) कॉम्प्लेक्स बनता है और फोरेट का क्षरण S-CH_2 लिंकेज के माध्यम से

होता है। चांदी के नैनोकणों के पास फोरेट के अभिविन्यास पर घनत्व कार्यात्मक सिद्धांत का उपयोग करके सोखना ऊर्जा गणना से चर्चा की जाती है। एक वास्तविक नमूने में धातु आयनों जैसे हस्तक्षेप करने वाले पदार्थ इस प्रकार की बातचीत में हस्तक्षेप कर सकते हैं। सोडियम क्लोराइड (NaCl), पोटेशियम परमैंगनेट (KMnO₄), मैग्नीशियम सल्फेट (MgSO₄), निकल (II) नाइट्रेट हेक्साहाइड्रेट (Ni(NO₃)₂·6H₂O), और ट्राइसोडियम साइट्रेट (Na₃C₆H₅O₇) नमक का अध्ययन किया जाता है। बोरोहाइड्राइड स्थिर चांदी के नैनोकणों के साथ परस्पर क्रिया पर इन लवणों के प्रभाव का विश्लेषण किया जाता है। केवल ऑक्सीकरण लवण पोटेशियम परमैंगनेट और निकल (II) नाइट्रेट हेक्साहाइड्रेट समाधान के रंग को प्रभावित कर सकते हैं। कीटनाशकों का ऑक्सीकरण/क्षरण केवल एजी नैनोकणों की उपस्थिति में होता है।

एक विशिष्ट कार्यात्मक समूह के साथ आणविक रूप से लगाए गए पॉलिमर पर आधारित सब्सट्रेट से अपेक्षित विशिष्टता और सोखना देने की उम्मीद है। सर्वोत्तम रासायनिक क्रियाशीलता का निर्धारण करने के लिए, हमने चार अलग-अलग रासायनिक क्रियात्मक सतहों पर दो ऑर्गनोफॉस्फेट, फोरेट और मैलाथियान के सोखने का अध्ययन किया है। चार अलग-अलग कार्यात्मक सतहों को सिलिका सतह को चार अलग-अलग सिलेन युग्मन एजेंटों के साथ संशोधित किया जाता है, अर्थात् n-propyltrimethoxy silane (PTMS), octyltrimethoxy silane (OTMS), 3- (trimethoxysilyl) propyl methacrylate (TMSPMA) और 3- (triethoxysilyl) propionitrile (टीईएसपीएन)। एक प्रसार नियंत्रित गतिज मॉडल एक सतह चरण अवधारणा के साथ विकसित किया गया है। परिणाम बताते हैं कि टीएमएसपीएमए कार्यात्मक सतह में कीटनाशकों का एक समान सोखना है। TMSPMA कार्यात्मक सतह पर फोरेट और मैलाथियान के प्रतिवर्ती बंधन की संभावना के साथ एक काफी मजबूत बंधन मनाया जाता है। इसके बाद, एमआईपी को एक कार्यात्मक मोनोमर के रूप में 3- (ट्राइमेथॉक्सीसिलिल) प्रोपाइल मेथैक्रिलेट (टीएमएसपीएमए) का उपयोग करके सोल-जेल तकनीक का उपयोग करके संश्लेषित किया जाता है। क्यूसीएम-डी के सिलिका-कार्बज क्रिस्टल में फोरेट और मैलाथियान का पता लगाने के लिए अच्छी तरह से चित्रित एमआईपी का उपयोग किया गया था। एमआईपी सतहों पर कीटनाशकों के वास्तविक समय के सोखने के अध्ययन टेम्पलेट अणु के रूप में उपयोग किए जाने वाले संबंधित कीटनाशक के साथ उनके महत्वपूर्ण बंधन को दर्शाते हैं। विशिष्टता और पुनरावर्तनीयता प्रयोगों से संकेत मिलता है कि विकसित एमआईपी अध्ययन किए गए कीटनाशकों के लिए अत्यधिक चयनात्मक है। दिया गया अध्ययन संश्लेषित सब्सट्रेट के साथ दिए गए कीटनाशकों की अंतर्निहित अंतःक्रिया क्षमताओं में एक अंतर्दृष्टि प्रदान करता है।

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List of Abbreviations

ACN	Acetonitrile
AFM	Atomic Force Microscopy
AgNP	Silver nanoparticles
AuNP	Gold Nanoparticles
CA	Contact angle
DFT	Density Functional Theory
DLS	Dynamic Light Scattering
EIS	Electrochemical Impedance Spectroscopy
EPA	Environmental Protection Agency
ESI	Electron Spray Ionization
FTIR	Fourier Transformed Infra-red (spectroscopy)
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
HRTEM	High-Resolution Transmission Electron Microscopy
LC	Liquid Chromatography
MIP	Molecularly imprinted polymer
MS	Mass spectrometry
NP	Borohydride stabilized silver nanoparticles
OPs	Organophosphates
OTES	Triethoxy(octyl)silane

List of Abbreviations

OTMS	Octyl trimethoxy silane
PTMS	n- propyl trimethoxy silane
QCM-D	Quartz crystal microbalance with dissipation
SAMs	Self-assembled monolayers
TESPN	3-(Triethoxysilyl) propionitrile
TMSPMA	3-(Trimethoxysilyl) propyl methacrylate
WHO	World Health Organization