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Detection of Cypermethrin at Ultra Low Concentrations via Surface Enhanced Raman Spectroscopy

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Abstract – As the World population increases, the main motivation of the agriculture industry becomes to obtain much more agriproducts from unit agriculture area, which hereby promotes the use of pesticides at the expense of harming nature and threatening human and animal health. Cypermethrin, which is a synthetic pyrethroid, is utilised as an insecticide in agriculture industry. While being highly toxic to bees and fish in nature, its gradual aggregation also gives rise to contamination of soil and grand water to a significant extent. Thus, its detection at even ultra low concentrations is of utmost importance, in terms of human and natural life's safety. Currently, several analytical methods such as gas chromatography, mass spectroscopy, and HPLC, are utilised in order to detect cypermethrin. These methods require expensive consumables and analysing durations are quite long. At this point, Surface Enhanced Raman Spectroscopy emerges as an effective alternative. In this method, metal nanoparticle structures are utilised in order to boost Raman Signals, which have low intensities. In this study, Ag Nanowire structures are used in order to detect cypermethrin pesticide at even ultra-low concentrations. Cypermethrin solutions from 10^{-3} M to 10^{-10} M are detected via Raman Spectroscopy, in a very short duration with regard to analytical methods and without the need to almost any consumables.

Keywords – Pesticide, Detection, SERS, Raman, Spectroscopy

I. INTRODUCTION

In modern agriculture, the use of pesticides is increasing day by day, since it leads to a significant increase in yearly product yields [1]. Unfortunately, these chemicals aggregate in soil and ground water, which serves as a threat to human and animal health, and as well as to natural life. Thus, monitoring these chemicals is of utmost concern and there is quite a large number of studies dealing with the detection of pesticides. Analytical techiques such as liquid chromatography/mass spectroscopy (LC/MS) [2], high performance liquid chromatography (HPLC) [3], enzyme-linked immunosorbent assay (ELISA) [4] are utilised for detection of cyphermethrin. However, these methods require expensive consumables, relatively longer analysing durations and also on-site analysis is not possible since analysing instruments are not mobile.

At this point, Surface Enhanced Raman Spectroscopy becomes a robust alternative since it requires very limited number and amount of consumables and short analyse durations.

Because of its nature, Raman spectroscopy was not a good alternative when dealing with materials in low concentrations. However, in 1974 Fleischman et. al. observed the Raman spectrum of pyridine on roughened Ag electrode surface, with a higher cross section [5]. This phenomenon opened a new track for Raman Spectroscopy since it enables detection of materials at even ultra low concentrations. In this method, novel metals such as Ag, Au, Cu are utilised as nanostructures in order to create plasmonic hot spots to enhance the naturally-low Raman Signals [6].

Today, there is quite a literature dealing with utilisation of nanostructures for detection of pecticides via Surface Enhanced Raman Spectroscopy. Tang et. al. synthesized Au nanorod-coated Fe_3O_4 microspheres and utilised these nanostructures in order to detect pesticides via SERS method [7]. Fernandez et. al. utilised dendrimer-based gold nanostructures for pesticide detection by SERS method in ground water [8]. Kim et. al. synthesized gold nanofinger sensors in order to detect pesticide residues in ground water and apple skin [9]. Zhu et. al. deposited silver ($AgNO_3$) nanoparticles on low-cost paper filters in order to detect pesticide residues on various peels by SERS method [10]. Leung et. al. synthesized SERS active silver nanorods in order to detect cypermethrin residues via SERS method by a handheld Raman spectrometer [11].

In this study, $AgNO_3$ nanowire SERS substrates were synthesized, they were characterized via Scanning Electron Microscopy (SEM), Energy Dispersive Spectrum (EDS), and X-Ray Diffraction (XRD) methods. Afterwards, they were utilised in order to detect cypermethrin solutions varying from 10^{-3}M up to 10^{-10}M. The obtained Raman spectrums revealed that silver nanowires are good candidates for detecting of cypermethrin via SERS method.

II. Materials and Methods

Synthesis of the Ag Nanowires

The silver nanowires were synthesized by Sun’s method [12]. As the first step, 5 ml ethylene glycol (EG) was poured into three necked ballon and stirred at 400 rpm and at 160 °C for 20 minutes. After 20 minutes, it was flashed via Ar gas for 1 minutes. 0.25 mg of $AgNO_3$ solution, which was prepared in 5 ml EG was added to the solution dropwise and afterwards 1.56 gr of PVP, 100 microliters of NaCl, which was prepared in 10 ml EG was added to the solution. Later, the solution was left to stir at 400 rpm and at 160^o for two hours. At the end of two hours, the solution was taken to the ice bath to end the reaction. Later, 20 ml of acetone was added to the solution and centrifuged at 400o rpm for 30 minutes. Afterwards, the solution was centrifuged twice with distilled water at 4000 rpm for 30 minutes.

Characterization of the Ag Nanowires

SEM images of the Ag Nanowires were taken by a Hitachi Regulus 8230 Scanning Electron Microscope. As revealed by Fig. 1, Ag nanowires are in uniform shape with diameters at about 100 nm.

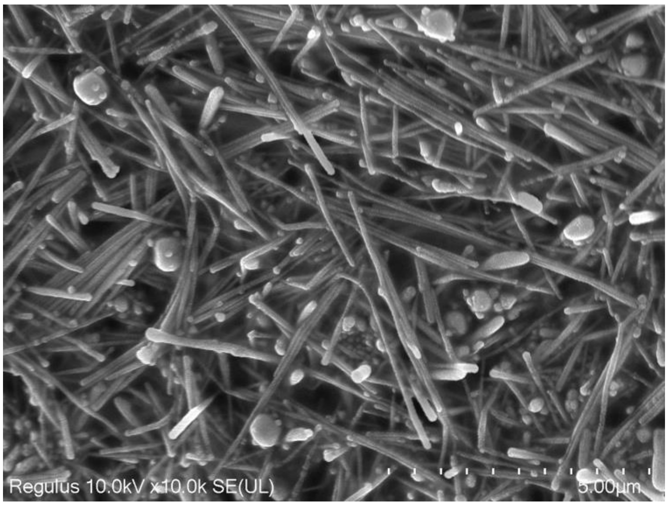

Fig. 1 SEM image of the Ag Nanowires.

The chemical composition of the Ag nanowires were verified by energy dispersive spectrum (EDS) method. The EDS spectrum belonging to the Ag nanowires is presented in Fig. 2. As the spectrum reveals, the structure is composed of Ag by 79.9 percent. The rest of the elements are Au, which is comes from the sputtering process to ensure conductivity for SEM imaging, C, which is from the carbon tape, Al, which is from the SEM stub material, and O and Cl from the synthesis process.

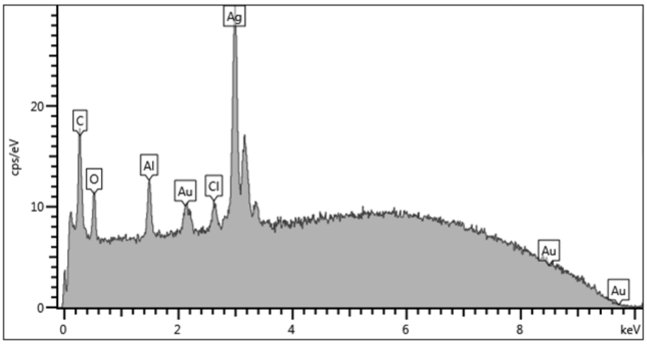

Fig. 2 EDS Spectrum of the Ag Nanowires.

The last step of the characterization process is X-Ray Diffraction spectrometry. The spectrum was obtained via Panalytical Empyrean XRD Spectrometer which utilises a Cu X-Ray tube at 45 kV and 40 mA. The spectrum was collected at 2theta of 5-90^0, the scanning speed was 2 ^{0}/min. The peaks located at 38.175^0, 44.370^0, 64.553^0, 77.537^0, and 81.691^0 belong to the Ag component, as confirmed by the JCPDS card number 04-004-2997, which verifies that the synthesis of nanowires is successful. The peaks labelled with asterix (*) symbol belongs to NaCl which was utilised during the synthesis process.

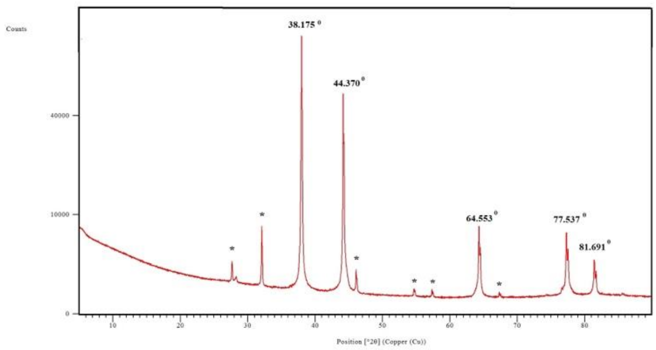

Fig.3 XRD Spectrum of the Ag Nanowires

SERS Experiments

For SERS experiments, cypermethrin solutions at varying concentrations from 10^{-3} to 10^{-10} were prepared. For each concentration, 100 microliters of Ag nanowire and 100 microliters of cypermethrin were mixed in an eppendorf and the mixture was vortexed for obtaining a homogeneous solution. Afterwards the mixture belonging to each concentration was dropped onto seperate ITO glasses and left to ambient environment to dry.

As the first step the Raman spectrum of the powder form of cypermethrin was obtained. The resulting spectrum is displayed in Fig. 4. The peaks located at 662 cm^{-1}, 1002 cm^{-1}, 1165 cm^{-1}, 1208 cm^{-1}, and 1625 cm^{-1} are characteristic Raman bands as verified by the literature [13,14]

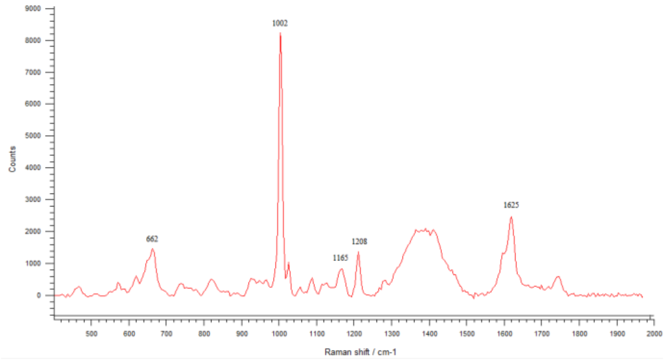

Fig. 4 Powder cypermethrin's Raman spectrum.

After the drops were dried, their Raman spectra were obtained via Renishaw In-Via Raman Spectrometer, by utilising a 785 nm laser.

For SERS experiments, the characteristic Raman bands located at 662 cm^{-1} and 1002 cm^{-1} were selected. The reason for this preference is their distinction to each other and their visibility at even ultra low concentrations.

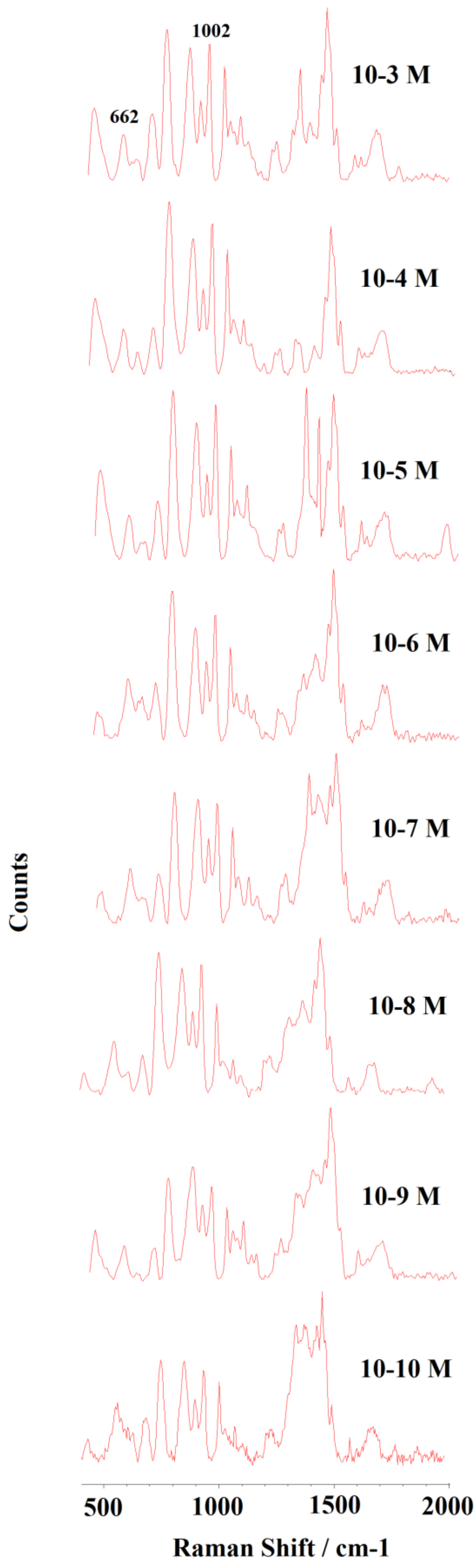

Fig. 5 SERS Spectra of cypermethrin solutions from 10^{-3} up to 10^{-10} M

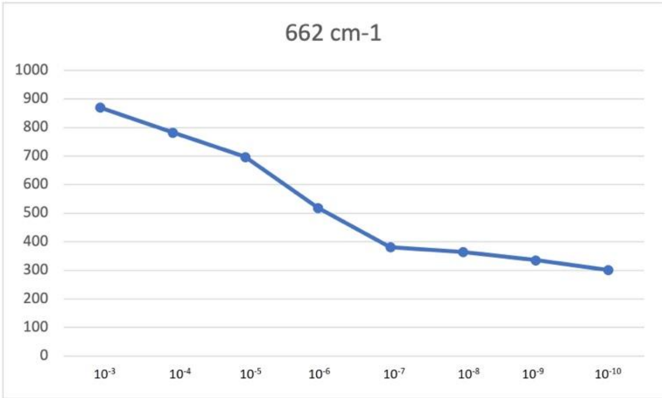

Fig. 6 Intensity vs. Molarity graph for 662 cm^{-1}.

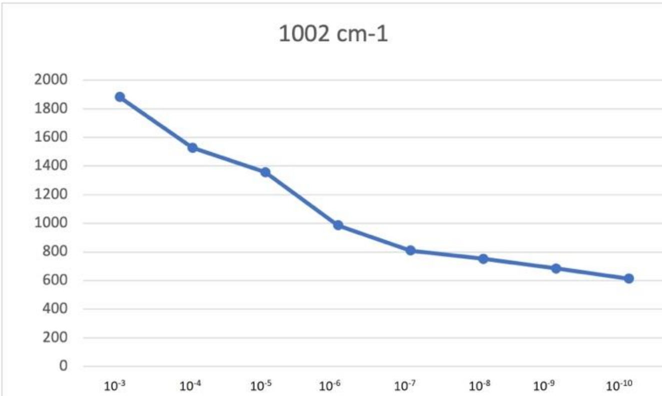

Fig. 7 Intensity vs. Molarity graph for 1002 cm^{-1}.

III RESULTS

Fig. 5 displays the SERS spectra belonging to the cypermethrin solutions from 10^{-3} M to 10^{-10} M. As the figure reveals, although the intensities of the peaks belonging to these Raman bands get weaker, their detection is still possible, at even ultra-low concentrations, verifying that the Ag nanowires are good candidates for detection of Cypermethrine at even ultra-low concentrations. Fig. 6 and Fig. 7 display the intensities of the characteristic peaks of cypermethrin located at 662 cm^{-1} and 1002 cm^{-1} respectively. As the graphs reveal, although the intensities of the characteristic peaks decrease as expected, Ag nanowires still boost the Raman signals and enable detection of cypermethrin molecules at even ultra low concentrations, even at 10^{-10} M.

IV DISCUSSION

As the results of the experiments reveal, Ag nanowires serve as a good candidate of substrate for detection of cypermethrin at ultra-low concentrations. The substrate nanostructure can be improved to study lower concentrations down to 10^{-14} – 10^{-15} M. To optimize the nanostructure in order to attain the detection of lower concentrations, different reaction conditions or novel metals can be utilised for further studies.

III. CONCLUSION

In this study, Ag nanowires were synthesized to be utilised as a SERS substrate. Cypermethrin solutions at concentrations varying from 10^{-3}M to 10^{-10} M were used as the analyte molecule for the SERS experiments. Evet at ultra-low concentrations, Ag nanowires enabled detection of cypermethrin, which makes this nanostrucuture an ideal candidate as SERS substrate.

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