



Detecting Water Contaminants Using Colloidal Silver Nanocubes as Liquid Substrate of Surface-Enhanced Raman Scattering

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ABSTRACT

Raman spectroscopy is an effective tool for detecting pollutants in water. The technique becomes even more powerful when combined with surface-enhanced Raman scattering (SERS). In this work, tri-sodium phosphate (Na_3PO_4) was detected in water in low concentrations as a pollutant using surface-enhanced Raman scattering technique. Colloidal silver nanocubes (AgNCs) were synthesized and characterized to be used as a liquid SERS substrate for detecting the pollutant in water. The excitation source used for illuminating samples was a CW 532nm Nd:YAG laser. The samples were detected with and without SERS technique to see the effect of the technique. The Na_3PO_4 concentrations of the detected samples were 0.05, 0.1, 0.5, and 1M. The AgNCs were examined by Field Emission Scanning Electron Microscopy (FE-SEM), Atomic Force Microscope (AFM), and X-ray Diffractometer (XRD). Almost all the vibrational mode spectra of the pollutant were detected by the normal Raman test, with varied peak intensities based on the pollutant concentrations. After using AgNCs colloid as SERS substrate, samples showed a discernible increase in the Raman signal. After analyzing the Raman signal intensities of the pollutant in all SERS samples, the maximum value of the analytical enhancement factor (AEF) was found to be 11.75, at the lowest phosphate concentration (0.05M) which indicates that SERS has higher efficiency with lower concentrations.

Keyword: Raman spectroscopy, hotspots, silver nanoparticles, AEF, SERS.

INTRODUCTION

One of the issues facing the world as a result of rapid industrialization is water pollution, which is extremely dangerous for the environment. Organic and inorganic pollutants harm the aquatic system (Shakir *et al.*, 2024a; Al-Sarraj *et al.*, 2019; Al-Sarraj *et al.*, 2014). As a result, monitoring water contaminants is of utmost importance to ensure its safety. Because of its quick detection of chemical and microbiological contaminants, non-contact, low sample preparation requirements, and non-invasive sampling, Raman spectroscopy has shown itself to be a more effective method for identifying water pollution. (Gowen *et al.*, 2012; Harz *et al.*, 2009). However, Raman spectroscopy has a very low sensitivity since, typically inelastically scattering occurs only in one photon out of 10⁸ photons that incident. Also, the probability of fluorescence compared to the probability of Raman scatter 1 in 10³-10⁵ vs 1 in 10⁷-10¹⁰. So, there was a need for enhancing the weak Raman signal. Surface-Enhanced Raman scattering (SERS) is a technique that enhances the typically weak Raman signals by adsorbing molecules to be detected on a metal or metal nanoparticle surface that has been roughened (Hidayah *et al.*, 2021). It is presently the most effective Raman technique for detecting very low concentrations of substances. In Raman scattering, a laser stimulates the molecular vibrations of the molecules. A molecule experiences a charge motion induced by one of its vibrations, resulting in the creation of a dipole (P) inside it. The magnitude of P is directly proportional to the molecule's polarizability (α), as well as the strength of the electric field (E) that induces it. As shown in Equation (1) (Freudiger *et al.*, 2008):

$$P = \alpha \cdot E \quad \dots\dots\dots (1)$$

The Raman radiation's intensity is connected to the magnitude of "P" induced in a molecule under the influence of "E". The degree of deformation in the electron cloud relative to the molecule's vibrational coordinates is measured by the polarizability of the molecule. This polarizability is directly linked to the induced dipole moment (Abdelsalam, 2011). To enhance the Raman signal, there are two ways: increase the polarizability or increase the amplitude of the electric field. Metallic nanostructures must be present for SERS to happen. Therefore, the interaction of light, molecules, and metallic nanostructure is necessary to fully describe SERS (Cortijo-Campos *et al.*, 2021). When incident laser light interacts with metal nanoparticles, it can excite localized surface plasmon resonances (LSPRs), which are oscillations created when a material surface has near-zero imaginary and negative real values for its dielectric constants. LSPRs are created due to the movement of material's conduction electrons driven by an electromagnetic field (Stiles *et al.*, 2008). These LSPRs generate intense, highly localized electromagnetic fields at regions called "hotspots," which are frequently nanogaps encircling the tips of metal nanostructures or between adjacent metal nanostructures (Meng and Tang, 2021; Khan *et al.*, 2019). When analyte molecules are located within or near these hotspots, their Raman scattering cross-sections are dramatically increased, leading to stronger Raman signals compared to the incident field (up to 100 times) (Le and Etchegoin, 2013). In this work, a liquid SERS substrate of Ag nanocolloidal will be used to enhance the Raman signal for detecting phosphates in water as a pollutant. This approach aims to improve the sensitivity and accuracy of detecting phosphates, which are significant contaminants in aquatic environments. By utilizing a silver nanoparticle-based substrate, the interaction between the nanoparticles and the phosphate molecules will boost the Raman signal, allowing for more effective monitoring of water quality.

EXPERIMENTAL

1- The preparation of the material to be detected

The chemical used as a contaminant is tri-sodium phosphate, (Na₃PO₄, 99%) offered for sale by Sabik, Inc. KSA, which was analytical purity level. Distilled water was used for dissolving the material in variable concentrations using the molarity equation below (Harvey, 2002):

$$M = (W \times 1000) / (V \times M.Wt.) \quad \dots\dots\dots (2)$$

Where M is the molarity (the concentration of the material in the solution) in (molar), W is the weight of the material in (g), V is the volume of the dissolved solution in (mL), and $M.Wt$ is the molarity weight of Na_3PO_4 in (g /mole) which is about 148 g /mol.

2- Synthesis of silver nanocubes (AgNCs)

The materials used for the preparation of AgNCs are: Silver nitrate ($AgNO_3$), ethylene glycol (EG), and Hydrochloric acid (HCl) were purchased from CDH, India, polyvinyl pyrrolidone (PVP) was purchased from SABIC, KSA, and de-ionized (DI) water.

A common approach used to produce silver nanocubes (AgNCs) was employed by Shakir *et al.*, (2024b). A 20 mL vial with 5 mL of EG is covered, and it is submerged in oil at $140^\circ C$ for an hour while being stirred. A quick addition of 1 ml of a 3 mM HCl solution in EG was made. Following ten minutes, 3 mL of a 94 mM $AgNO_3$ solution in EG and 3 mL of a 147 mM PVP solution were dropwise added to the stirring mixture. When the $AgNO_3$ solution was added, the hue turned pale yellow. The vial was then heated to $140^\circ C$ and covered.

3- Preparation of Na_3PO_4 samples for normal Raman scattering test

The preparation of the liquid pollutant samples involved dissolving Na_3PO_4 in distilled water at different concentrations at room temperature and atmospheric pressure. Four samples were prepared with various concentrations of the Na_3PO_4 : 0.05, 0.1, 0.5, and 1 M.

4- Preparation of Na_3PO_4 samples for surface – enhanced Raman scattering (SERS) test

Four liquid samples of Na_3PO_4 were prepared in the colloidal nanosilver instead of distilled water at the concentrations of 0.05, 0.1, 0.5, and 1 M at room temperature and atmospheric pressure.

5- Raman test

In the present configuration, backscattering was utilized, which is the primary configuration for Raman spectroscopy that has been employed many years ago. In this configuration, the sample is irradiated by laser, and the scattered light is reflected back into the detector; see Fig. (1A, 1B).

A CW Nd: YAG laser model: MGL-111-532-100 mW. The laser provided monochromatic light at 532 nm with second harmonic generation, and an output power range of 0-100 mW. The wave selector and the detector in the present spectroscopic system were combined in a high-resolution spectrometer from ocean optics (HR2000 High-resolution Spectrometer, Florida, USA) with a spectral resolution of 2 cm^{-1} . In the field of Raman spectroscopy, the Raman-scattered light signal of interest is typically much weaker than the excitation light. Therefore, selecting optical filters that offer a high signal-to-noise ratio is essential. A band-pass filter (BPF) supplied by optolong optics Co. Ltd., Yunnan, China, is placed at the entrance of the laser beam to transmit only a specific wavelength region of the excitation source's electromagnetic wave (532 nm), a dichroic beam splitter (DBS), supplied by nano macro optics Co., Ltd, Guangdong, China, positioned at 45° to the laser light path to direct the path of the excitation beam toward the sample, and then pass the backscattered Raman radiation from the sample toward the detector. Dichroic mirrors used in Raman spectroscopy should have a high reflectance of over 95% at the laser line and high transmittance of over 95% for the Raman signal. A notch filter (NF) 532-12 NNF provided by iridian spectral technologies Ltd., Canada, was also used for blocking out intense Rayleigh scattered radiation that could otherwise interfere with the detector's readings. A collimating lens with a focal length of 5cm was utilized to collect and focus the beam inside the sample, along with two concave mirrors on both sides of the sample to collect dispersed rays into the sample, and one plane mirror behind the sample to reflect the scattered rays back to the detector. Additionally, an optical microscope was employed to focus the passing rays to the detector, finally, a fiber optic cable was used to transmit the obtained Raman signal to the detector.

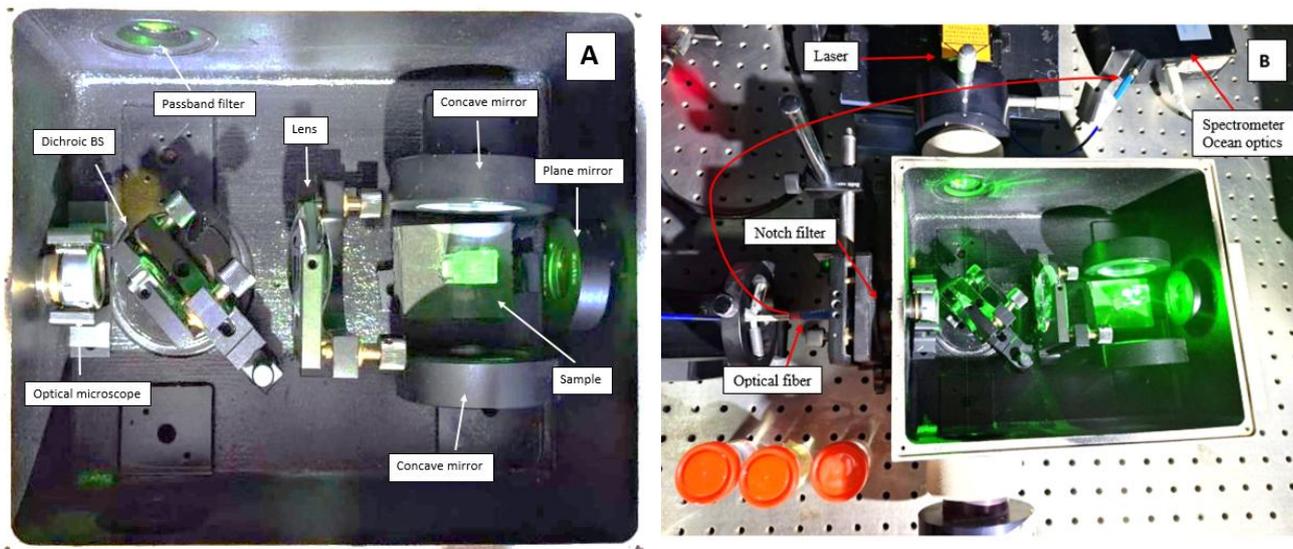


Fig.1. A: The probe of Raman spectroscopic system. B: the whole Raman spectroscopic system.

The aqueous solutions of normal Raman and SERS samples were added individually into glass cuvettes with a volume of 3 mL and dimensions of (10 x 10 x 45) mm. Samples were separately illuminated by a CW Nd:YAG laser of wavelength of 532 nm and a power of 70 mW at the sample and an integration time of 9 ms. In all cases, the spectral resolution was adjusted to 2 cm^{-1} . Each sample was irradiated with the laser for 10 seconds. Results were compared with the typical spectrum of the material.

RESULTS AND DISCUSSION

The results and the characterizations of the AgNC have been verified for colloidal nano silver. As well as, the Raman test for normal and SERS samples with various concentrations have been demonstrated and discussed. Fig. (2) displays AFM images of the AgNC nanoparticle size distribution. Ultrasonography was used to break up the agglomeration in the silver nanocubes prior to AFM examination of the samples. AgNCs were found to have an average particle size of 115 nm, and the image shows that the cluster formations of nanosilver in the sample's topographic distribution are uniform.

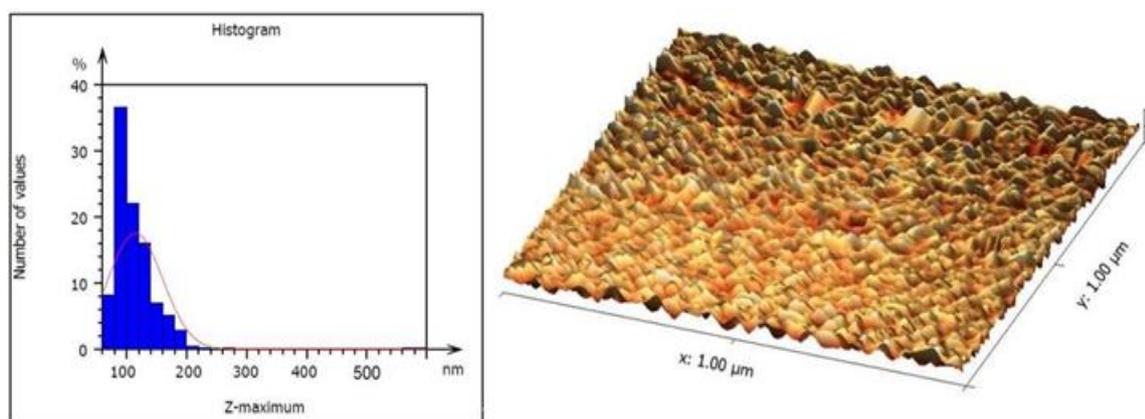


Fig. 2:

AFM-3 dimensional images and granularity cumulation distribution charts of silver nanocubes.

AgNCs' dimensions and form were investigated. The presence of AgNCs was evident based on the FE-SEM observation. As seen in Fig. (3), FE-SEM images revealed AgNCs with

approximate sizes between 50 and 200 nm. The nanocubes seem to be agglomerated and clustered on top of each other forming hotspots. It was believed that hotspots were the cause of the significant increase in signal strength needed for single-molecule detection. (Garcia-Leis *et al.*, 2013; Kumar, 2012).

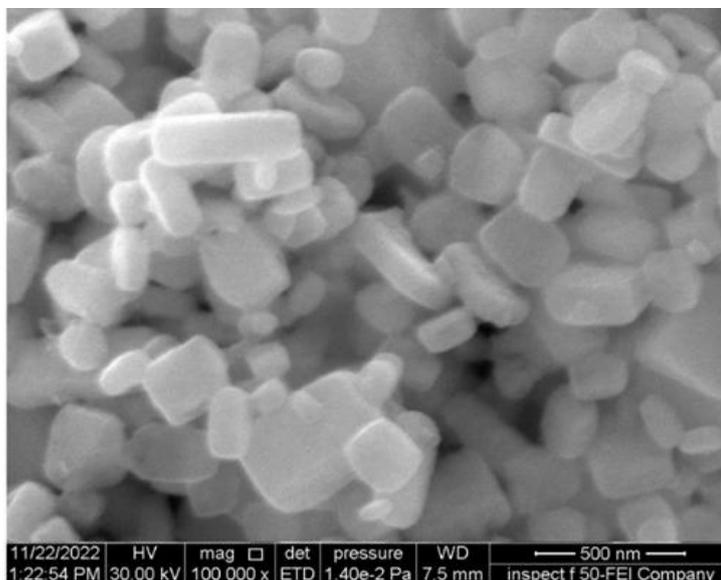


Fig. 3: FE-SEM image of AgNCs showing the aggregated nanoparticles which form hotspots.

The X-ray diffraction pattern of AgNCs showed some interesting diffraction peaks at about 38° , 64.4° , and 77.5° . These peaks closely resemble planes (111), (220), and (331), which are crystals of pure silver. These prominent peaks in the planes, as shown in Fig. (4), imply that the nanosilver is highly crystalline.

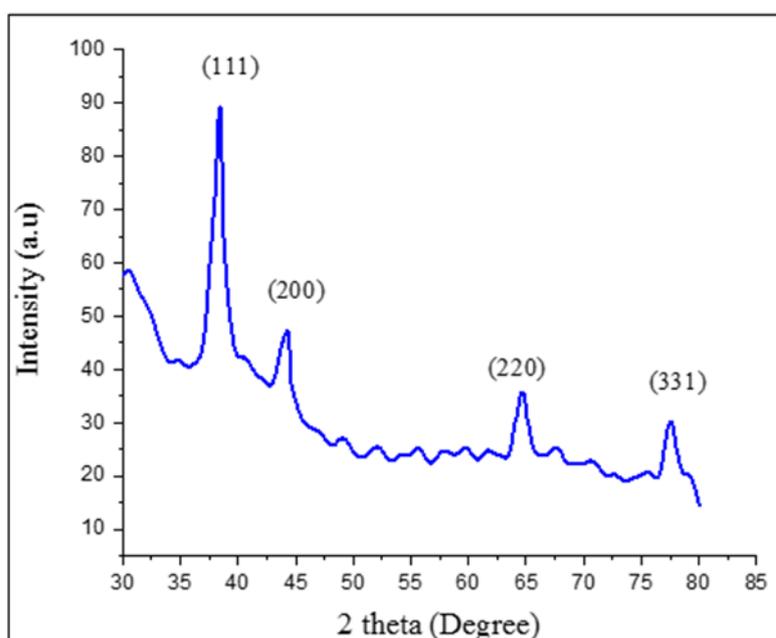


Fig. 4: X-ray diffraction patterns of the AgNCs that have been synthesized.

Based on the data presented in Fig. (5), the 532 nm laser used in the Raman measurement is appropriate because AgNCs have an absorption spectrum of 200 nm; therefore, it is not near the absorbance region that generates fluorescence.

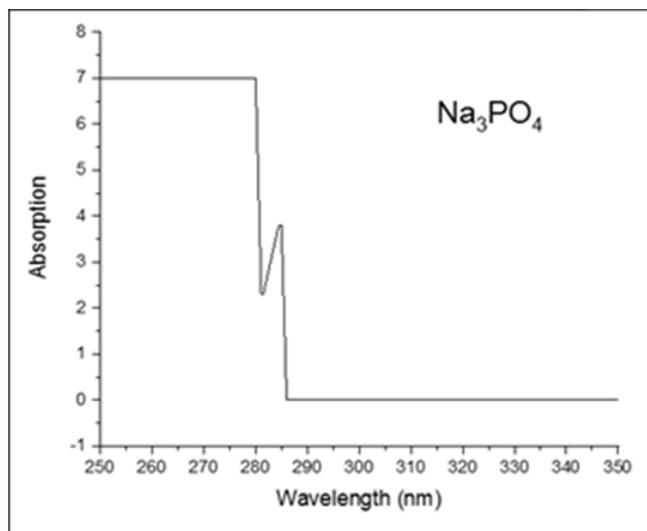


Fig. 5: UV-Vis absorption spectra of tri sodium phosphate.

Raman test results

The careful preparation and testing process ensured that the data was reliable and accurate. Raman test results for phosphates showed symmetric stretching modes (ν_1) at 956 and 857 cm^{-1} , a symmetric bending mode (ν_2) at 430 cm^{-1} , asymmetric stretching modes (ν_3) at 1069 and 1158 cm^{-1} , and the bending mode (ν_4) at 567 cm^{-1} as shown in Fig. (6) (Frost *et al.*, 2013a; Frost *et al.*, 2017b). The Raman intensity increases with increasing phosphate concentration in the solution. Regarding SERS groups, all SERS samples showed a discernible increase in the Raman signal; see Fig. (7).

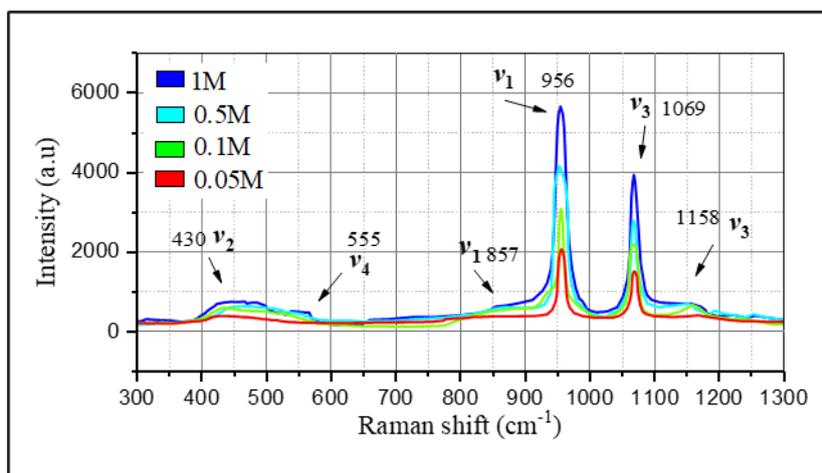


Fig. 6: Normal Raman spectra of Na_3PO_4 in aqueous solutions with variable concentrations.

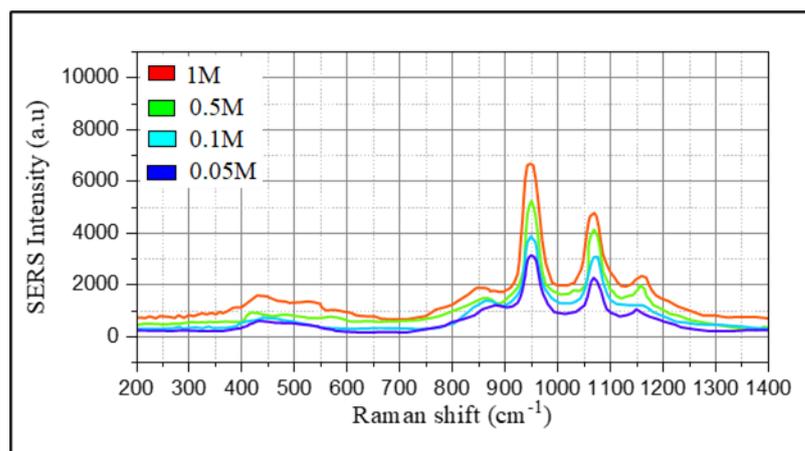


Fig. 7: SERS Raman spectra of Na_3PO_4 in AgNC colloid solutions with variable concentrations.

From the spectra, we noticed that the presence of AgNCs with the pollutant improved the Raman signal. AgNCs can be considered to play a major role in improving the Raman signal. (Kumar, 2012). Also, it is evident that as the pollutant concentration rises, the intensity of Raman signal does too; see Fig. (8). The reason for this is that more pollutant molecules are coupled to AgNCs, resulting in enhanced Raman scattering and a stronger Raman signal (Frost *et al.*, 2013a; Frost *et al.*, 2013b).

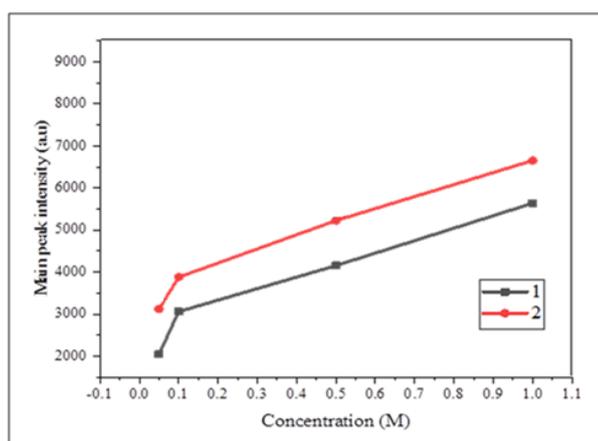


Fig. 8: Concentrations of Na_3PO_4 versus main Raman peak intensities.

Pollutant molecules that are dissolved in Ag nanocolloidal interact with "hotspots". The Raman signal increases as the electromagnetic field gets stronger. It is important to remember that the colloidal AgNCs were intentionally designed to aggregate and create hotspots. The Raman signal is simultaneously enhanced by the electromagnetic (EM) and chemical (CM) mechanisms that make up the SERS effect. The local increase in an electric field near the nanoparticles caused by localized surface plasmon resonances (LSPR) affects electromagnetic enhancement. (Shakir *et al.*, 2024a). Charge-transfer interactions between the nanoparticles' surface and the molecules' electronic states cause the CM, which also causes an increase in Raman signals. Therefore, the EM is dependent on the surface plasmon resonance (SPR), while the CM is determined by the Raman-active molecule and its interaction with the surfaces of nanoparticles. (McLellan *et al.*, 2006).

One of the most crucial parameters used to assess a substrate's ability to boost the Raman signal for SERS applications is the determination of the SERS analytical enhancement factor

(AEF) (McLellan *et al.*, 2006). Signal intensity and analyte concentration are combined in this analytical method of signal enhancement.

The analytical enhancement factor of an analyte is:

$$AEF = ISERS \times CNRS / (CSERS \times INRS)$$

Where; INRS is the Raman intensity without SERS technique, ISERS is the SERS intensity, CNRS is the analyte concentration in the normal Raman, and CSERS is the concentration of the analyte in the SERS liquid substrates (Shakir *et al.*, 2024b).

The AEF against various Na_3PO_4 concentrations was plotted in Fig. (9), where it showed a non-linear rise in AEF as the pollutant's content decreases. The maximum phosphate AEF value was 11.75, at the lowest phosphate concentration (0.05M). This means that SERS has higher efficiency with lower concentrations. When molecules are present in trace amounts, the electric field of the target molecule located in the hot spot will rise locally, enhancing the SERS signal and thus raising the AEF. The aggregation of the silver nanoparticles plays a main role in the enhancement factor value, where the strength of the local electromagnetic field (a hotspot) determines the AEF (Maher, 2012). The properties of metal nanoparticle colloid depend on how the metal and molecules interact with each other. This interaction affects the overlap of the SPR bands and laser source, which can vary based on the size and edges of the nanoparticles. This difference is primarily responsible for differences in AEF. However, the SERS substrate was in a liquid form and the pollutant's molecules were moving there, so it was difficult to identify the hotspots with precision. Thus, the signal enhancement value is affected by unstable hot spots in the liquid substrate (Hidayah *et al.*, 2021; McLellan *et al.*, 2006).

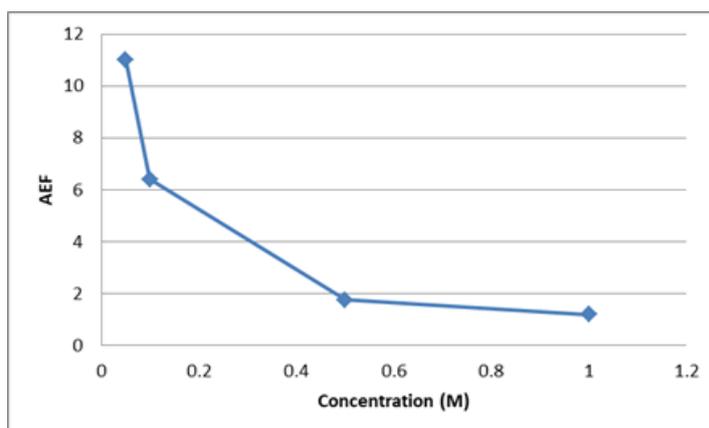


Fig. 9: AEF against Na_3PO_4 concentration.

CONCLUSIONS

From this work we can conclude that it is important to ensure that the wavelength of the laser source used for Raman measurement is not within the absorption region of the detected substance to prevent fluorescence. AgNCs is a good liquid SERS substrate for detecting inorganic pollutants in water. As the concentration of pollutants in the sample rises, the Raman intensities of the peaks in the spectra also rise. The aggregation of the AgNCs is important for creating the hotspots for better detection and higher efficiency. Finally, it was found that with lower concentrations, SERS is more effective.

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الكشف عن ملوثات المياه باستخدام مكعبات الفضة النانوية الغروية كركيزة سائلة لتشتت رامان المعزز بالسطح

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قسم الفيزياء/ كلية العلوم للبنات/ جامعة بغداد/ بغداد/ العراق

الملخص

تعد تقنية رامان للتحليل الطيفي أداة فعالة للكشف عن الملوثات في الماء. وتصبح هذه التقنية أكثر قوة عند دمجها مع تقنية تشتت رامان المعزز بالسطح (SERS). في هذا البحث، تم الكشف عن مادة ثلاثي فوسفات الصوديوم (Na_3PO_4) في الماء كملوث بتركيز منخفضة باستخدام تقنية تشتت رامان المعزز بالسطح. وقد تم تحضير مكعبات الفضة النانوية الغروانية (AgNCs) لاستخدامها كركيزة سائلة لهذه التقنية للكشف عن الملوثات في الماء. كان مصدر الإثارة المستخدم لإضاءة العينات هو ليزر Nd:YAG 532nm CW. تم الكشف عن العينات باستخدام تقنية التشتت رامان المعزز بالسطح وبدونها لمعرفة تأثير التقنية. كانت تراكيز Na_3PO_4 للعينات 0.05 و 0.1 و 0.5 و 1 مولاري. كما تم فحص AgNCs بواسطة المجهر الإلكتروني الماسح (FE-SEM) ومجهر القوة الذرية (AFM) ومقياس حيود الأشعة السينية (XRD). تم الكشف عن جميع أطيف الوضع الاهتزازي للملوث تقريباً بواسطة اختبار رامان العادي، مع كثافات ذروة متفاوتة بناءً على تراكيز الملوث. عند استخدام محلول الفضة النانوية المكعبة الشكل كركيزة SERS سائلة، أظهرت النتائج زيادة ملحوظة في إشارة رامان لجميع العينات. كما وجد ان القيمة القصوى لمعامل التعزيز التحليلي بلغت 11.75 وذلك عند أدنى تركيز للعينات والبالغ 0.05 مولاري مما يشير الى ان تقنية SERS تكون أكثر كفاءة عند التراكيز الواطئة للملوثات.

الكلمات الدالة: مطيافية رامان، النقاط الساخنة، دقائق الفضة النانوية، عامل التعزيز التحليلي، تقنية تشتت رامان المعزز.