

# Colorimetric Determination of Diazinon in Environmental Water Samples Based on Sensitive Localized Surface Plasmon Resonance of Silver Nanoparticles

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**ABSTRACT:** *Determination of organophosphorus pesticide diazinon (DZ) in water was described based on localized surface plasmon resonance of citrate-capped silver nanoparticles (CC-Ag NPs) in this study. The surface plasmon resonance band was scanned by UV-visible spectrophotometer and Transmission Electron Microscopy (TEM) was employed to reveal the interaction, surface characteristics, and particle size. With adding DZ to the CC-Ag NPs, it was adsorbed onto silver nano-spheres in an aqueous solution and the color of the silver nanoparticles changed from light yellow to orange or brown depending on DZ concentration. As a result of aggregation, the absorption peak of silver nanoparticles around 393 nm decreased and a new peak appeared in 520 nm. The wavelength and intensity shifts were characteristic of the pesticide structure and concentration, respectively. The interaction between the sensor and the pesticide was a result of the soft metal surface binding to the soft sulfur atom of the pesticide. Under optimized conditions, a linear relationship between DZ concentration and the absorbance ratio of  $A_{520}/A_{393}$  and the limit of detection was found in the range of 2- 80  $\mu\text{M}$  and 0.12  $\mu\text{M}$ , respectively. The present method has good repeatability reproducibility and good stability. The proposed method was used for real water samples and the results are in good agreement with other methods of analysis.*

**KEYWORDS:** *Silver nanoparticles; Localized surface plasmon resonance; Diazinon; Colorimetric sensor; Environmental contaminants.*

## INTRODUCTION

Pesticides are chemicals that control insects, weeds, fungi, and other pests that destroy crops and include a large number of compounds like fungicides, nematocides, insecticides, molluscicides, rodenticides, herbicides,

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and plant growth hormones. Pesticides are spread in the environment with the aim of controlling undesired living species. The use of these compounds may pose risks to human health and the environment because their toxicity is not always specific to the target organisms [1]. In recent years, Organophosphorus Pesticides (OPs) containing a thiophosphoryl (P-S) functional group is generally used as insecticides for agricultural applications. They exhibit a high level of toxicity due to disabling of the central nervous system by irreversibly binding to acetyl cholinesterase. Continual application of OPs compounds in farmlands worldwide has led to their presence as the residual not only in agricultural products but also has resulted in their seepage into underground water sources which is causing significant problems [2,3]. Diazinon (Fig. 1) is used in agriculture to control insects on fruits, vegetables, nuts, and field crops as an organophosphorus insecticide. It has been widely used to control soil and foliage insects and pests on a wide range of crops. Diazinon (DZ) is also used to control mange mites, ticks, lice, and biting flies on sheep, cows, pigs, goats, and horses [4]. When DZ is used on farms can be stable for weeks or even months depending on the soil environment. Due to the high solubility of DZ in water, it moves through soils and contaminates groundwater. Consequently, it may be present in surface or well water as a result of run-off and movement through the soil from areas where DZ is used in farming [5].

Although OPs have relatively short lives to decompose, they remain in the soil and environment and are leached into groundwater, which is a matter of great concern and increases the importance of identifying and measuring them. Conventional analytical methods (including gas chromatography, high-performance liquid chromatography, capillary electrophoresis, and mass spectrometry) have been effectively used for the analysis of pesticides in contaminated samples [6,7]. However, they impose certain limitations such as time-consuming sample preparation, process complexity, and the requirement of expensive instrumentation and highly skilled personnel [8]. Hence, there is a need to develop quick, cheap, and portable methods for pesticide sensing. Localized Surface Plasmon Resonance (LSPR) is a new method which attracted the attention of many scientists in recent decades. LSPR refers to the collective oscillation of electrons on the metallic nanoparticles (NPs) excited by the incident

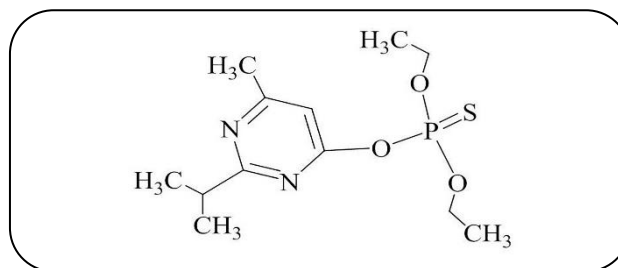


Fig. 1: Chemical structure of diazinon

photons at the resonant frequency [9]. The optical properties, especially the plasmonic properties, of noble metal nanostructures are used in the development of a new class of optical sensors in modern chemistry.

Among these noble nanometals, gold and silver nanoparticles are the most extensively considered due to their unique optical properties connected with this phenomenon [10, 11]. Upon interaction of light and metal nanoparticles, free electrons of NPs undergo a collective coherent oscillation with respect to the positive metallic lattice. As a result, the metal NPs display bright intense colors and corresponding specific extinction bands in their UV-Vis spectra, when metal nanoparticles are dispersed in the aqueous phase, the solution shows a distinctive color attributed to their small size, and they exhibit a strong UV-Vis extinction band and display different bright colors. For example, in gold nanoparticles (Au NPs) or silver nanoparticles (Ag NPs), when surface resonance bands of noble metal nanoparticles are exposed to electromagnetic radiation, electrons on the surface can absorb light and the color of the solution appears red and yellow, respectively [12]. The color changes of a solution in the presence of other targets can be spectrometrically monitored and used as an analytical signal for the detection of chemical species. Au NPs are the most stable nanoparticles that are chemically inert, but Ag NPs have become more popular among researchers due to their higher extinction penetration coefficient and lower price [13,14]. AgNPs also tend to excel in SPR-based applications due to their large enhancement of near fields, which can be an order of magnitude greater than those of AuNPs. For example, LSPR of Ag NPs has successfully investigated for the determination of some heavy metals like Fe<sup>3+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Al<sup>3+</sup> [15-18]. LSPR of Ag NPs was also studied for the determination of some pesticides, some toxins, pharmaceuticals and several biologically important compounds [19-26].

In this research, we developed a fast sensitive method for the determination of DZ in water by localized surface plasmon resonance of silver nanoparticles. In summary, DZ was added to the solution of citrate-capped silver nanoparticles (CC-Ag NPs), color of the solution changed from light yellow to orange or brown, depending on DZ concentration. The absorbance spectra of the CC-Ag NPs solution before and after adding DZ are measured. Wavelength shift is characteristic of the structure and concentration of DZ. Also, by performing the necessary experiments, the effective parameters were investigated. After the optimization of the parameters affecting the interaction between plasmonic Ag NPs and DZ pesticide, this method was used to measure it in real water samples. A benefit of the described Ag NPs is that they allow real-time detection with the naked eye, without sample pre-treatment.

## EXPERIMENTAL SECTION

### Materials

All chemicals used were of analytical grade. Silver nitrate ( $\text{AgNO}_3$ ), sodium borohydride ( $\text{NaBH}_4$ ), tri-sodium citrate dehydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ), sodium chloride ( $\text{NaCl}$ ), sodium hydroxide ( $\text{NaOH}$ ), hydrochloric acid ( $\text{HCl}$  37%), Ethanol ( $\text{C}_2\text{H}_5\text{OH}$  100%), DZ ( $\text{C}_{12}\text{H}_{21}\text{N}_2\text{O}_3\text{PS}$ ) were purchased from the Sigma Aldrich Company and were of analytical grade. Milli-Q water was used in the synthesis process and solution preparation. Stock solution of DZ was prepared in ethanol and standard solutions of DZ with different concentrations were prepared by dilution of the stock solution.

### Methods

Synthesis of CC-Ag NPs: Colloidal silver nanoparticles were prepared following a procedure, previously reported [1]. Briefly, 18.50 mL of milliQ water were placed in an Erlenmeyer flask. To the flask, 0.50 mL of  $1.0 \times 10^{-2}$  M silver nitrate, 0.50 mL of  $1.0 \times 10^{-2}$  M of sodium citrate tribasic were added and stirred. To this solution, 0.50 mL of  $1.0 \times 10^{-2}$  M sodium borohydride was added and gently stirred. The final concentration of Ag NPs by Ag atoms is  $2.5 \times 10^{-4}$  M.

The colloidal solutions of Ag NPs were covered with aluminum foil and kept under  $4^\circ\text{C}$  [27]. A standard solution of 1000 mg/L was prepared from DZ pesticide. CC-Ag NPs were prepared following a procedure above

and they with light yellow color were achieved ( Fig. 2.a) Then of defined volume (3 to 120  $\mu\text{L}$ ) of DZ solution was added to 2.50 mL aliquot of CC-Ag NPs solution and after adjustment of pH and ionic strength, final volume reached to 5 mL. UV-visible spectroscopy was used to characterize the changes in the LSPR band with the addition of pesticide.

### Instrumentation

Synthesized nanoparticles of Ag were characterized using UV-visible absorbance spectroscopy and transmission electron microscopy (TEM). Absorption spectra were recorded on an Agilent 8453 UV-visible spectrophotometer. TEM images were acquired using Philips EM208 transmission electron microscope operating at 80 kV accelerating voltage. All pH measurements were made by using a Metrohm 744 pH-meter equipped with a combined pH glass electrode.

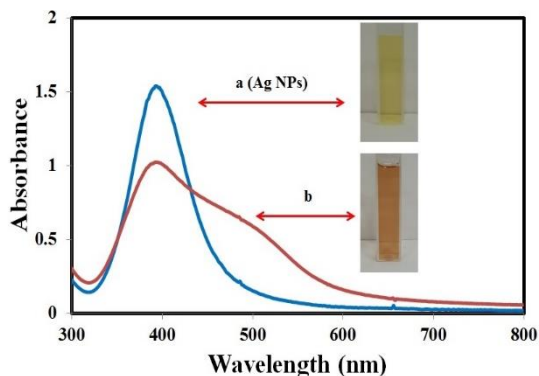
## RESULTS AND DISCUSSION

### Aggregation of Ag NPs

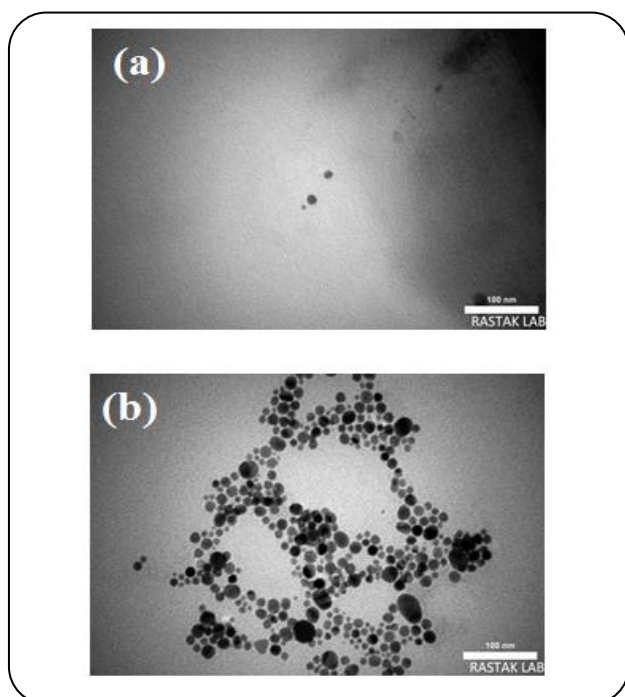
The characteristic LSPR band for Ag NPs arises at 393 nm (Fig. 2. a). Stability of silver nanoparticles decreased due to interaction of DZ and the surface of CC-Ag NPs and color of the solution changed from light yellow to red consequently, that depends on DZ concentration. As a result of aggregation, LSPR peak of silver nanoparticles around 393 nm decreases and a new peak appears around 520 nm (Fig. 2. b) In fact the aggregation of NPs making changes in the LSPR of plasmonic NPs as clearly observed by a color change to the naked eye.

The TEM images show the spherical geometry of all Ag NPs before and upon the addition of DZ to the solution of CC-Ag NPs (Fig. 3). Aggregation of silver nanoparticles by adding DZ was also confirmed by the TEM images.

The sensitivity of DZ toward the NPs was found to rely of its structure and can be explained based on several theories. OP pesticides are esters of phosphoric acids and their derivatives. The general structure of an OP pesticide comprises the central phosphorus (P) atom and the characteristic thiophosphoryl (P=S) or phosphoryl (P=O) group. According to the structure of diazinon that has thiophosphoryl (P=S), interaction between Ag NPs and diazinon can be explained in terms of hard-soft acid-base (HSAB) theory [28,29]. In accordance with this theory,



**Fig. 2:** UV-visible spectrum of the plasmonic nanoparticles and color of silver nanoparticles in the absence (a) and presence (b) of  $48 \mu\text{M}$  diazinon.



**Fig. 3:** TEM mages of Ag NPs in the absence (a) and presence (b) of  $48 \mu\text{M}$  diazinon.

soft acids interact more strongly with soft bases while hard acids interact more strongly with hard bases. The surface atoms on the Ag are acting as soft acids, while the sulfur (S) atoms in the DZ are acting as soft bases. When DZ is added to the NPs solution, it acts as a ligand that binds via S atoms with the NP surface [30,31].

#### Optimization of assay condition

Early experiments have been done to determine optimized conditions in the assay. We have examined the

effect of reaction time, ionic strength concentration and pH in the assay on the aggregation of citrate capped silver nanoparticles.

#### Effect of reaction time

In this study, nanoparticle stability in the presence of diazinon was measured by monitoring changes in LSPR using UV-visible spectrometry. The absorbance ratio of  $A_{520}/A_{393}$  was used as the analytical signal [32]. Reaction time or in other words time interval between addition of DZ to solution of CC-Ag NPs and absorbance measurement is critical parameters in the assay that must be optimize to enhance the sensitivity of the method. (Fig. 4) shows the changes of the absorbance ratio of CC-Ag NPs colloid after different times over the range of 20-160 seconds. The results showed that signal of plasmon intensity reaches a maximum in 110 seconds then remains constant. Thus, a 110 second time interval was selected for subsequent studies.

#### Effect of ionic strength

Due to the high surface area to volume ratio in plasmonic NPs, the LSPR frequency is sensitive to the refractive index of the surrounding medium. Any change in the environment including surface adsorption and desorption of chemical agents, aggregation and the medium refractive index will shift the LSPR frequency and result in a colorimetric change that can be utilized as optical signals for detection. Effect of sodium chloride on aggregation of silver nanoparticles was explored because ionic strength of reaction media has a critical role on aggregation of Ag NPs. (Fig. 5) shows the changes of the absorbance ratio of the colloidal silver nanoparticles by various concentrations of NaCl over the range of 0-16 mM. It has been found with increasing NaCl concentration, the absorbance ratio ( $A_{520}/A_{393}$ ) was increased, because sodium chloride can constrict the electrical double layer of capping citrate ions [33]. According to the results, 6 mM was selected as optimum electrolyte concentration for subsequent investigations.

#### Effect of pH

The pH value of sensor solution is an important variable that affects on aggregation of silver nanoparticles, the effect of pH was investigated in the range of 3.0-10.0. As shown in (Fig. 6) pH=8.0 is an optimum selection due to high stability of Ag-citrate complex. In  $\text{pH} \leq 2.5$ , Ag NPs

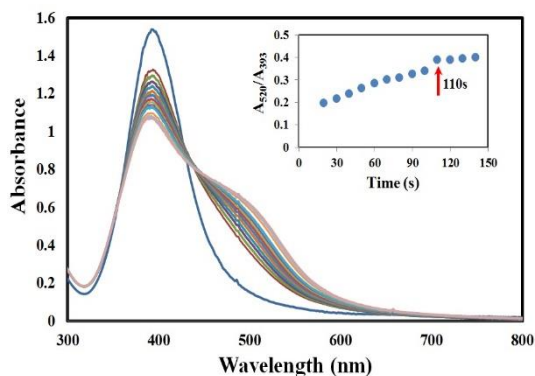


Fig. 4: Effect of time on aggregation of silver nanoparticles in the presence 48  $\mu\text{M}$  diazinon, 6 mM NaCl and pH = 8.

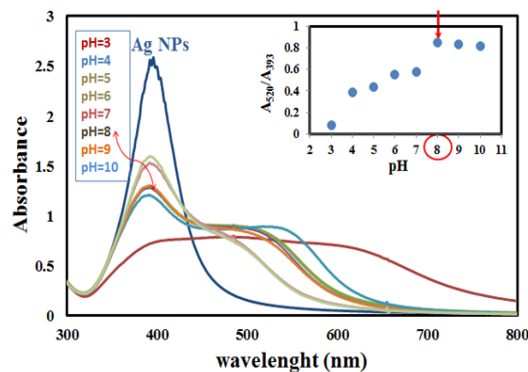


Fig. 6: Effect of pH on aggregation of silver nanoparticles in the presence 48  $\mu\text{M}$  diazinon and 6 mM NaCl. Dark blue spectrum belongs to AgNPs in absence of diazinon.

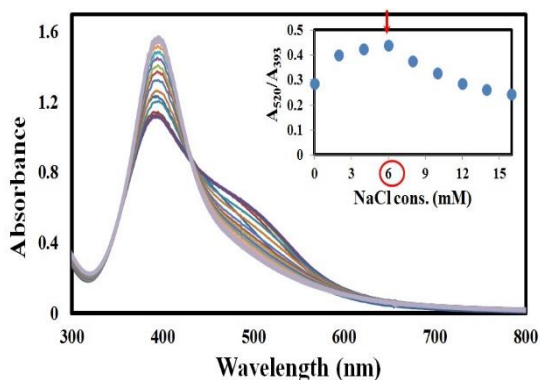


Fig. 5: Effect of NaCl concentration on aggregation of silver nanoparticles in the presence 48  $\mu\text{M}$  diazinon and pH = 8.

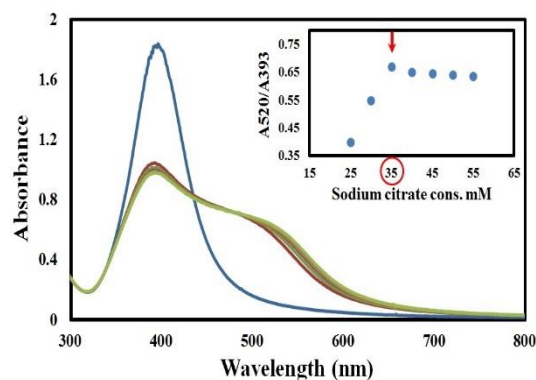


Fig. 7: Effect of citrate concentration on aggregation of silver nanoparticles in the presence 48  $\mu\text{M}$  diazinon and 6 mM NaCl.

are unstable and with raising pH from 3 to 8, stability of Ag NPs is increased by step by step deprotonation of citric acid. In basic solutions ( $\text{pH} \geq 8.0$ ), citrate becomes more negative and electrostatic repulsion between CC-Ag NPs enhanced and aggregation is lowered [34].

#### Effect of the tri-sodium citrate concentration

Effect of sodium citrate concentration on the plasmon absorbance intensity of the silver nanoparticles was studied. It was observed that the concentration of added sodium citrate within the range of 25 mM to 65 mM had significant effect on the plasmon absorbance and aggregation of silver nanoparticles. A concentration of 35 mM of sodium citrate was chosen as optimum (Fig. 7).

#### Analytical figures of merit

The Limit of Detection (LOD), linear range, reproducibility, sensitivity and selectivity of the method

were evaluated under the values optimized above. The LOD for DZ was calculated using the following Eq. 1:

$$\text{LOD} = 3s_b / m \quad (1)$$

where,  $s_b$  is the standard deviation of the blank and is constant for the blank solution used for the nanoparticle preparation and absorbance measurement and  $m$  is the slope of the calibration curve with various concentrations of DZ [35]. Calibration plot was constructed using DZ concentrations and the absorbance ratio ( $A_{520}/A_{393}$ ) data of sensor (Fig. 8a). As the concentration of the DZ increases, the absorbance ratio ( $A_{520}/A_{393}$ ), corresponding to the change in plasmon of the Ag NPs is increased. Under the specified experimental conditions, LOD obtained for the determination of diazinon, was 0.12  $\mu\text{M}$ . Also the calibration curve for diazinon was linear from 2.0-80.0  $\mu\text{M}$  with a squared correlation coefficient ( $R^2$ ) of 0.9917 and equation of  $(A_{520}/A_{393}) = 0.0115 [\text{diazinon}] + 0.0522$



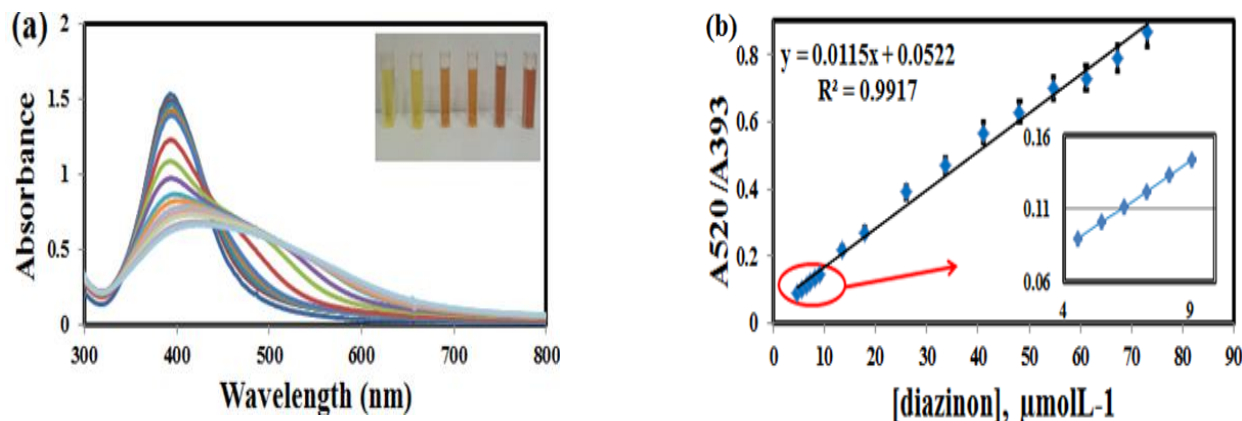


Fig. 8: (a) A typical absorption spectra of Ag-NPs (0.25 mM) in presence of different concentration of diazinon (2-80  $\mu\text{M}$ ) (b) Calibration curve of LSPR signal for DZ under optimum conditions.

(Fig. 8b). Relative standard deviation for a 48  $\mu\text{M}$  standard solution of DZ was achieved 1% ( $n=10$ ).

The selectivity of the Ag NP sensor toward DZ is evaluated using the unique wavelength shifts in Ag NPs upon addition of other OP pesticides. The selectivity of the developed method was evaluated by determination of DZ in the presence of common OP pesticides e.g. malathion, fenthion, ethion and parathion. DZ concentration was measured in absence and in presence of equimolar concentration of each of interference pesticides at 50  $\mu\text{M}$ . Relative error in DZ content was less than 1.5% in presence of interference pesticides. This selectivity arises from distinct difference of LSPR wavelengths of them from 520nm (LSPR signal of DZ). Thus, the procedure is very selective for determination of DZ. The performance of the developed method was compared with some of the figures of merit of the some spectrophotometric methods reported for the determination of DZ. As it can be concluded from the data presented in Table 1, the developed method provides comparable results with other previously reported method.

#### Detection of diazinon in water samples from the environment

Water samples from real environments such as tap water, underground water and river water, collected through Vard Avard area (Tehran province), were first filtered using syringe filters with a 0.22  $\mu\text{m}$  membrane, to which standard solutions of DZ at various concentrations were added and then analyzed using proposed method, in order to evaluate our colorimetric assay in real samples.

The analytical results are given in Table 2 in comparison with results obtained for the same samples analyzed by HPLC [41]. It is obvious that the observed concentration of DZ is close to that determined by HPLC and that the CC-Ag NPs detection system can be used for analysis of DZ in different water samples drawn from real environments. The results indicate good recoveries in the range of 97 to 101% in well water and 97 to 103% in tap water. Also the Relative Standards Deviations (RSD) of the method were found to be <4% in the real water samples. Repeatability and reproducibility of the proposed method were also evaluated as precision indicators. Three similar experiments were performed for the analysis of samples on the same day and on five consecutive days. The obtained RSD values for the intra-day and inter-day spiked samples were to be <2% and <3%, respectively. The accuracy of the method was further evaluated by comparing the results of tablets analysis with those of chromatographic reference method. According to the t-test at 95% confidence level, there is no significant difference between the colorimetric and chromatographic results. Thus, the procedure is suitable for the determination of the DZ in the in the sample type examined.

#### CONCLUSIONS

In this work, a colorimetric probe based on Ag NPs aggregation effect was developed for rapid and sensitive detection of diazinon. The presence of DZ induces the aggregation of silver nanoparticles through metal-ligand interaction and change in LSPR of Ag NPs, in an alkaline environment ( $\text{pH} \geq 8$ ). To improve the sensitivity of DZ detection, the experimental conditions including pH,

**Table 1: Comparison of Figures of Merit of the developed method with other reported spectrophotometric methods for determination of diazinon.**

Method	LOD( $\mu\text{M}$ )	RSD%	LDR( $\mu\text{M}$ )	Ref
Spectrophotometry	0.7	0.4	3.2-26.0	[36]
Spectrophotometry	0.34	1.2	1.2-50	[37]
spectrophotometry	1.7	1.5	-	[38]
spectrophotometry	0.33	3-6	1.1-75	[39]
Colorimetry	0.16	1-3	0.6-80	[40]
Localized surface plasmon peak	0.12	1	2-80	This work

**Table 2: Determination of diazinon in real water samples.**

Sample Type	Added ( $\mu\text{M}$ )	Found <sup>a</sup> ( $\mu\text{M}$ )	Recovery (%)	Reference Method ( $\mu\text{M}$ )
Tap water	-	ND <sup>b</sup>	-	ND
	25	24.3 $\pm$ 0.6	97.2	25.0
	50	50.6 $\pm$ 1.0	101.2	51.7
Well Water	-	ND	-	ND
	25	25.8 $\pm$ 0.8	103.2	24.9
	50	48.4 $\pm$ 1.1	96.8	50.4
River water	-	ND	-	ND
	25	24.0 $\pm$ 0.5	96.0	24.4
	50	49.1 $\pm$ 1.4	98.2	49.5

a: The results are mean of three measurements  $\pm$  standard deviation.

b: ND=not detected.

NaCl concentration and reaction time, were optimized. Under the optimal conditions, a linear relationship between absorbance ratio  $A_{520}/A_{393}$  and the DZ concentration in the range of 2-80  $\mu\text{M}$  with a regression coefficient  $R^2$  of 0.992 was obtained. A LOD of 0.12  $\mu\text{M}$  was also determined which was lower than Maximum Residue Limit (MRL) in agricultural and environmental water samples, regulated by the governments. The proposed colorimetric probe also showed very good selectivity for against other four OP pesticides (malathion, fenthion, ethion, and parathion). Besides, the detection of DZ based on the proposed colorimetric probe was also achieved in environmental water samples including tap water, well water, and river water with a recovery of 96–103% and a relative standard deviation less than 3%. As a consequence, due to its advantages of low cost, rapid detection, good selectivity, and high sensitivity, the proposed colorimetric probe can provide enormous potential for on-site detection of diazinon in environmental water samples.

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