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A Highly Sensitive Colorimetric Determination of Paraquat by Silver Nanoparticles

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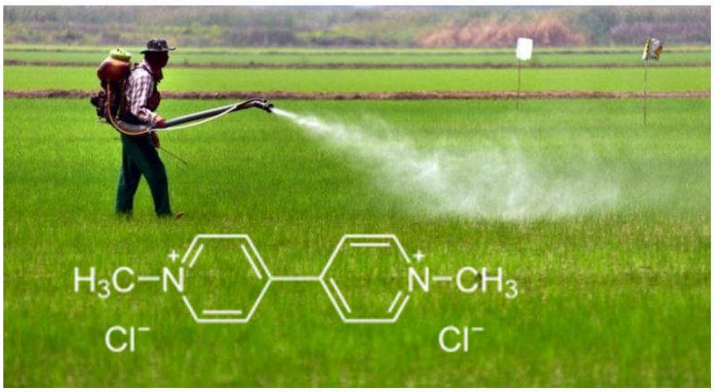
ABSTRACT

In this work, we describe a simple, selective and sensitive colorimetric method for the detection of Paraquat. In this approach, the synthesized silver nanoparticles (AgNPs) solution was stabilized by the citrate anions which repulsed and protected the AgNPs from aggregation. Paraquat was added to AgNPs solution and was incubated to react for 6 min. The resulting mixture color was changed. These processes were studied and characterized by UV-Vis spectroscopy. Several parameters such as size and concentration of nanoparticles, reaction time and pH of medium that governed the analytical performance of the method have been studied in detail and optimized. Paraquat could be selectively detected in concentration range from 0.1to 0.02µM with a limit of detection as 0.01µM. Some common ions such Mg^{+2}, Au^{+2}, Cd^{+2} and No_3^- showed no interference in the determination of Paraquat.

GRAPHICAL ABSTRACT



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1- Introduction

Paraquat is a chemical herbicide, or weed killer, that's highly toxic and used all over the world. It's also known by the brand name Gramoxone. Paraquat is one of the most common herbicides used today, but it can cause fatal poisoning when ingested or inhaled. It's primarily used to control weed and grass growth.[1]. The use of Paraquat has constituted a significant health risk [2, 3]. Therefore, determination of Paraquat residue is of great importance. Paraquat can be analyzed by different detection technologies, such as gas chromatography, gas chromatography tandem mass spectrometry, high performance liquid chromatography and so on[4, 5]. However, the apparatus used these technologies are very expensive, and in addition, the apparatus operation and analysis process are complicated. So it is necessary to attempt to explore an inexpensive and simple determination method of the Paraquat.

In the past decades, there has been rapid growth in nanotechnology researches. Nanotechnology deals with processes that take place on the nanometer scale, that is, from approximately 1 to 100 nm. In nanotechnology, the assembly of metallic nanoparticles has resulted in novel materials with interesting electronic, optical and chemical properties[6-9]. Among these metal nanoparticles, silver nanoparticles (AgNPs) have founded useful applications in chemical analysis [10-12]. Silver nanoparticles have unique optical, electrical, and thermal properties and are being incorporated into products that range from photovoltaics to biological and chemical sensors. In recent few years the use of AgNPs as sensing probe for the detection of important analyses base on aggregation of nanoparticles was dramatically increased. AgNPs can exhibit unusual chemical, physical, electrical and optical properties that are not likely in bulk materials. The optical properties of AgNPs have attracted scientists because of their applications as a colorimetric probe [13, 14]. AgNPs as colorimetric sensor or probe have been widely used for several analytes such as mutations[15], immunoglobulin G [16], mercury(II) ion[17], cartap[18] and melanine[19]. AgNPs provide high sensitivity for the detection because they exhibit characteristic surface plasmon resonance (SPR) absorption properties. The resonance frequency of this SPR is strongly dependent upon the size, shape, dielectric properties and local environment of the nanoparticles [20].In most of the cases, the use of AgNPs as chemical sensing can achieve by monitoring the changes in the color upon aggregation/dissociation processes. The color of AgNPs may range from red to purple, blue or almost black, due to the formation of aggregates [21-46]. In colloidal solutions, AgNPs are red in color because of the Mie absorption by their surface plasmon oscillation that peaks at 527 nm [47]. AgNPs have been induced to aggregate by the addition of molecule which presented of amine or thiol groups via non-covalent bonding [48-50]. The aggregation of AgNPs leads to the formation of a new absorption band at longer wavelengths as a result of color change from red to purple-blue depending on their particle size [51].The method is based on reduction of AgNO3 to AgNPs by the citrate anions[52-66].

2. Experimental

2.1-Materials and instrument

All chemical reagents were of analytical grade and were purchased from Merck (Germany).

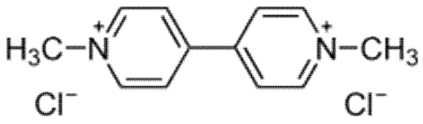

Fig. 1 Chemical structure of the Paraquat.

All solutions were prepared with deionized water. 1.0×10^{-4} mol L^{-1} of Paraquat as stock solution was prepared by dissolving 0.0171g of Paraquat (merck).

Standard solutions were prepared by dilution of the stock solution. UV-Vis spectroscopic measurement was performed by a Perkin Elmer lambda-25 spectrophotometer using a 3 cm of quartz cuvette. Measurement of pH was performed using a Metrohm 827 pH-meter with a combined glass electrode. All glassware and storage bottles were soaked in 10% $HNO_3$for an overnight and thoroughly rinsed with deionized water prior to use.

2.2-Preparation of AgNPs

Every glassware was cleaned in aqua regia (HCl: HNO3 = 3:1), rinsed with ultrapure water, and dried for three hours prior to use. (Caution: aqua regia is a very corrosive oxidizing agent, which should be handled with great care.) An aqueous solution of $AgNO_3$ (1 mM, 50 mL) was brought to be fluxing solution quickly with rapid stirring, and then 5 mL of a 38.8 mM trisodium citrate solution was added rapidly, which resulted in a change in solution color from light yellow to dark red within ~1 min. The resulting solution was boiled for an additional 30 min, allowed to cool to room temperature.

2.3-Colorimetric assays based on AgNPs aggregation

In order to determine Paraquat concentration by aggregation of AgNPs, a range of concentrations of Paraquat were prepared (0.02-0.09µM). Each Paraquat solution was added to 0.5×10^{-3}Mof AgNPs solution and the resulting mixtures were then allowed to react for 6 min. Subsequently, the absorbance changes were monitored by UV-Visible spectrophotometry. The incubation time and pH values were investigated on the aggregation of AgNPs. All of the experiments were done at room temperature.

3- Results and Discussion

In our experiment, AgNPs were formed by the direct reduction of AgNO3 using sodium citrate at a certain pH and ambient temperature. As illustrated in Fig.2, the microscopic characterization of the prepared AgNPs, such as Transmission Electron Microscope (TEM), showed that by the control of the experimental conditions, it was possible to synthesize highly dispersed AgNPs with an average size of 12nm.

The Plasmon absorption of AgNPs shows a single peak at 437nm (Fig.3). The presence of Paraquat in AgNPs formation can lead to decrease its intensity

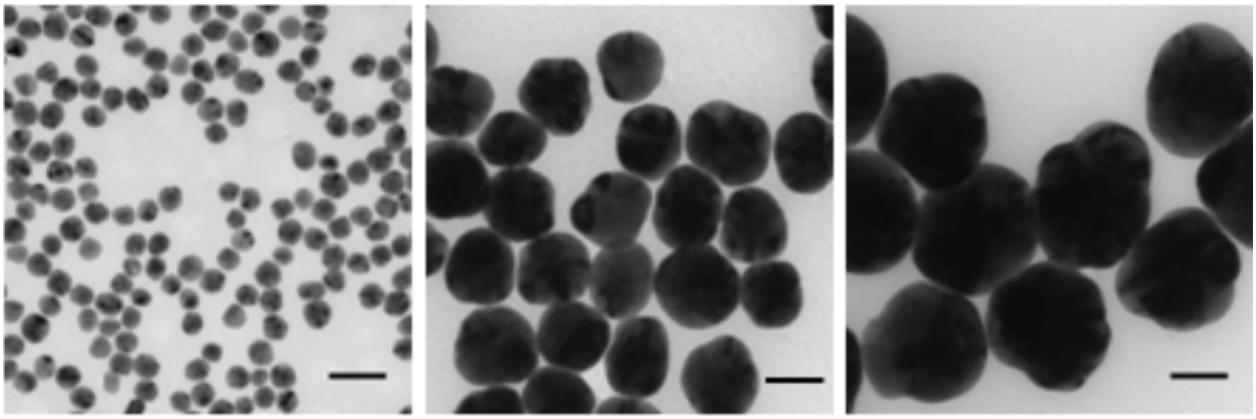

Fig.2 TEM image of the AgNPs.

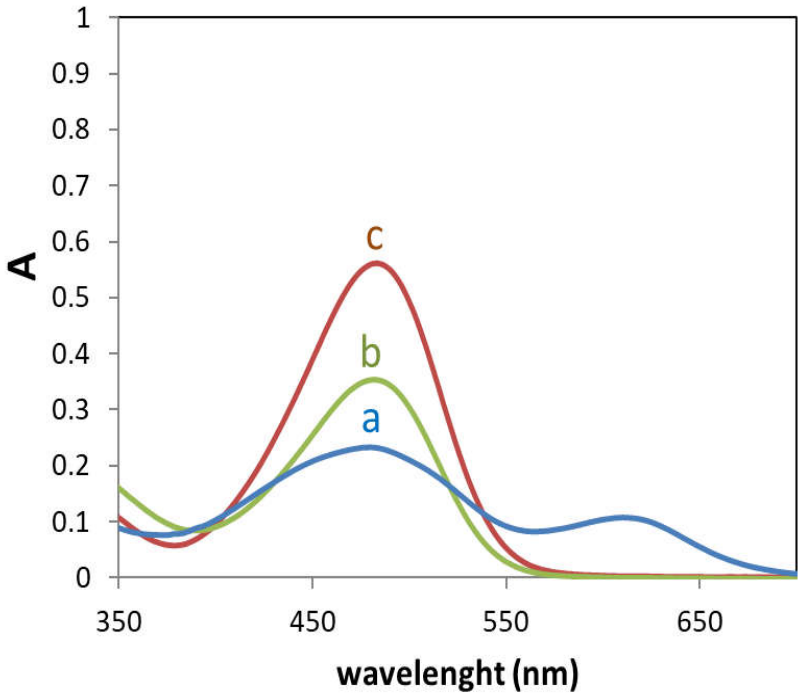

Fig. 3 AgNPs UV–visible absorbance in 0.00, 0.02µM and 0.05 µM of Paraquat, respectively. Conditions: AgNO3 concentration: 0.5mM, pH=7.

3.1 Optimization of parameters

The effect of important variables (pH, kind of buffer, volume of buffer, the amount of AgNPs and incubation time) on the measurement parameter was studied by one-at-a-time method. The initial pH values were adjusted from 4 to11, using Britton–Robinson (BR) buffer. As can be seen from Fig 4a, the maximum value of ΔA appeared at pH 7.0 and at higher or lower pH a significant decrease in the ΔA values is observed. Therefore, pH 7.0 was selected for Paraquat determinations. Among three buffer solutions (i.e. acetate, phosphate and BR buffer solutions), BR buffer gave the best results in terms of sensitivity and repeatability. Then, the concentration of BR buffer by adding different volumes of buffer (0.1 M) was optimized. The results indicated that by using 1 mL buffer maximum ΔA obtained (Fig 4b).

The effect of concentration of AgNPs solution on ΔA values was also investigated. The results (Fig 4c) indicated that 0.5×10^{-3}M of synthesized AgNPs was suitable for Paraquat. At higher or lower concentration, decrease in the ΔA values is observed. Finally, the influence of incubation time on intensity of SPR at 437 nm was studied. According to the obtained results, for Paraquat the absorbance deference intensity is enhanced rapidly following the addition of the Paraquat and reaches a plateau in about 6 min (Fig 4d).Thus an incubation time of 6 min was used throughout, as it combines good sensitivity and short analysis time. However, we selected 6 min as an optimum incubation time for experiments.

3.4- Statistical and Calibration Parameters

According to the above procedure, different concentrations of Paraquat were used to construct the calibration curves. The absorbance was obtained at 43 nm for all measurements of Paraquat. There was a linear relationship between the ΔA and the analytes concentrations ($Y = 1.2631X + 0.0037$, $R^2 = 0.9991$) over the range of 0.02-0.09µM, with the corresponding detection limit (3σ) of 0.0169µMrespectively. Five successive measurements of 0.05 and 0.10 Paraquat showed relative standard deviations of 1.19%, 2.28% respectively.

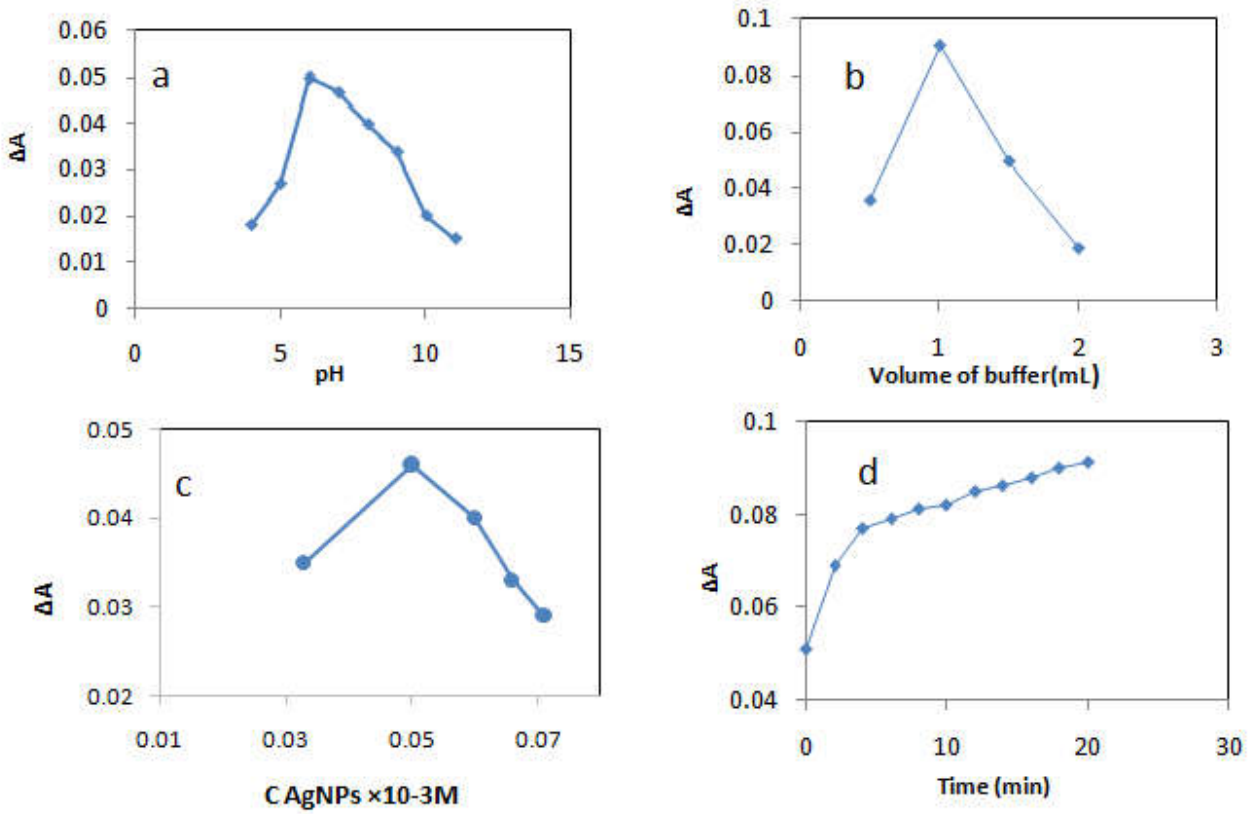

Fig.4 Effects of (a) pH, (b) concentration of buffer, (c) concentration of AgNPs and (d) incubation time at 437 nm.

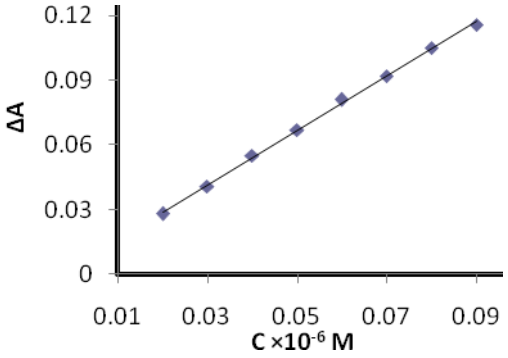

Fig.5 Calibration of Paraquat at different concentrations

3.5- Interference study

The influence of some potentially interfering substances on the determination of 0.1μM Paraquat using the developed method under the optimum working conditions was examined. The tolerance limit was defined as the maximum concentration of potentially interfering ions causing 5% error in the determination of Paraquat. As it is obvious from Table 1, most of the anions don't interfere even at high concentrations. The interference of Fe^{+3}, Na^{+}, Bi^{+3} and Mg^{+2} up to1000 times, Zn^{+2}, NO_3^- up to 100 times and Ba^{+2}, K^{+}, Ni^{+2}, Cu^{+2} up to 50 times was. The main interfering species in the determination of Paraquat were Hg^{+2} and Ca^{+2} which their interference up to 10 times was eliminated by using EDTA and Cl^-, respectively.

Table 1. Effect of interfering ions on determination of 0.1μM of Paraquat

Ions	Tolerance ratio (w/w)
Na^{+}, Fe^{3+}, Bi^{+3}, Mg^{2+}	1000
Zn^{2+}, NO_3^-	100
Ni^{2+}, Ba^{2+}, K^{+}, Cu^{2+}	50
Ca^{2+}, Hg^{+2}	10

3.6- Real sample analysis

Statistical analysis of the real sample results, showed satisfactory precision of the proposed method with no significant difference between certified and experimental results. Recovery experiments on Agricultural preparations spiked with different amounts of the analyte were also carried out. The results are given in Table 2 indicating that the proposed method has sufficient precision and accuracy (satisfactory recoveries between 91.384 and 103.419%) for the determination of Paraquat in Agricultural products[67].

4. Conclusion

In this work, a new optical method for the sensitive spectrophotometric detection of Paraquat based on surface plasmon resonance absorption peak of AgNPs was reported. The stable and dispersed AgNPs were prepared using a simple, rapid and eco-friendly procedure by applying citrate anions. The presence of Paraquat decreases surface plasmon resonance intensity of AgNPs and the absorbance changing at λmax, 527nm, was used for determination of Paraquat. The present approach can be used for the determination of Paraquat in the range of 0.02 to 0.09 μM with a limit of detection as 0.0169μM. The proposed method was successfully applied for the determination of Paraquat in plant seed samples. A comparison of the proposed method with reported techniques in the literature for determination of Paraquat is shown in Table 3. As can be seen, the limit of detection of this work is better than reported techniques is shown in Table3 [68-72]. In addition, the present work has a simple and fast procedure in comparison with the other reported methods for determination of Paraquat.

Table2. The results obtained by the proposed method on agricultural products spiked by Paraquat

Sample	Added (μg/mL)	Found (μg/mL)	Recovery (%)
Wheat	-	0.027	-
	0.050	0.070	91.384
	0.075	0.094	92.520
	0.095	0.114	93.750
Barleycorn	-	0.022	-
	0.050	0.074	102.778
	0.075	0.095	97.938
	0.095	0.121	103.419

Table 3 Comparison of the proposed method with some of the previously reported methods for the determination of Paraquat.

Method	LOD	RSD(%)	Recovery	Ref
	(µg mL-1)	(µg mL-1)		
HPLC	0.02	-	75	[68]
LC/MS	30	-	70	[69]
HPLC/MS	0.36	1.2-1.8	22-105	[72]
LC_MS/MS	10	1.5-9.2	75.8-100	[70]
HPLC-ESI-MS/MS	-	9-9.3	87.3-96	[47]
HPLC/MS	1	<25	97.2-110.6	[71]
AgNPs-SPR	0.0169	1.19-2.28	91.4– 103.4	This work

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