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Research Article

Preparation of silica nanoparticles coated with fluorescent nanomaterials (imidazole) for pesticide detection in aqueous solutions

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Abstract- Silica quantum dots are a preferred type of fluorescent materials and are highly appreciated due to their exceptional properties and size. The study is summarized in several parts In the preparation of fluorescent quantum dots by the reaction of ascorbic acid with Aptes (3-aminopropyl) triethoxy silane (SIQDs). Then, the surface modification of SIQDs with a fluorescence-enhancing substance (amidazole) becomes SIQDs-M. A simple alkaline hydrothermal process was used to synthesize and modify the surface of silica quantum dots using imidazole to enhance the fluorescence emission and thus improve the detection limit ratio. The structural information of the prepared silica for the two compounds SIQDs) 3 and (SIQDs-M) was obtained by XRD and then characterized by (FE-SEM), as well as TEM) and (FT-IR). The results also showed that the prepared silica quantum dots have a consistent size distribution ranging from (12-20) nm, in addition to the optical properties, including a tenfold increase in fluorescence intensity. The limit of quantitation (LOQ) and limit of detection (LOD) of the identified compounds were determined using fluorescence spectroscopy at room temperature, and the results confirm that these values are important in the use of fluorescence spectroscopy and have the necessary selectivity for environmental applications and can effectively detect the pesticide (boric acid) in aqueous samples. The optimum factors for the pesticide detection process (mixing time of solutions, concentration, pH effect and ions) were studied, which proved the effectiveness of the prepared quantum dots in detecting the pesticide.

Keyword ; Fluorescent Nanomaterials, Quenching, Imidazole, Pesticides.

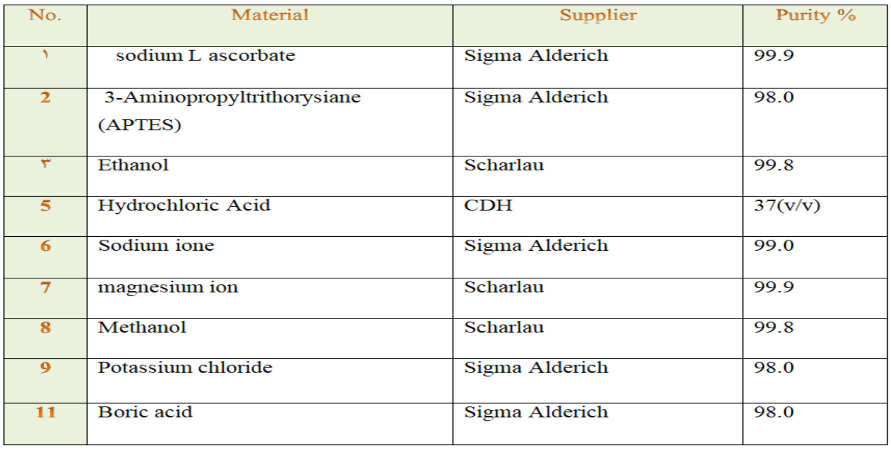
I. INTRODUCTION

The silica quantum dot nanosensing approach is a novel technique used for the quantitative detection of pesticides in aqueous solution [1]. This technique relies on the use of silica nanoparticles coated with fluorescent nanomaterials called "quantum dots", which can be activated by light [2]. When the silica quantum dots are exposed to an insecticide in an aqueous solution, an interaction occurs between the insecticide and the surface of the quantum dot. This interaction changes the polarization properties of the light signal emitted by the quantum dots, such as changing its color and intensity [3]. Using appropriate sensing techniques, these changes in light can be measured and converted into quantitative signals that reflect the concentration of pesticides in the aqueous solution. One of the main advantages of the silica quantum dot nanosensing approach is its ability to accurately and quantitatively detect pesticides in aqueous solutions at low concentrations [4]. They have high sensitivity and fast response and can be used for applications such as water quality monitoring and crop testing, for example SiQDs are short for “semiconductor quantum dots”, a type of nanostructured semiconductors with a quantum structure [5] and were first developed as a promising alternative to conventional materials used in solar cell technology and thin-film electronics [6]. They consist of small silicon particles ranging in size from 1 to 10 nanometers. A key property of SiQDs [7] is that, due to their nanoscale size, they exhibit unique properties that differ from those of ordinary silicon. These unique properties result in quantum effects and can be used in areas such as solar energy, thin-film electronics, and photovoltaics. [8] SiQDs efficiently absorb light and convert it into electrical energy, which can be used to produce energy-efficient solar cells. They can also be used in thin-film displays and high-efficiency lighting devices. Furthermore, SiQDs can be used in photonics to achieve highly specific colors in display and lighting applications. Despite the early discoveries in the field of quantum dots and the growing interest in quantum dots[9],[10] their applications are still in the research and development stage; for these dots to be widely used in industry, their fabrication techniques must be improved to improve their efficiency and stability. In the case of SiQDs, silicon,[11] depending on the semiconductor material used in their fabrication, include conventional processes for manufacturing SiQDs [12][13].

II. METHODOLOGY

2.1. Chemicals

These materials are characterized by high purity and can be used without the need for additional purification.



No.	Material	Supplier	Purity %
١	sodium L ascorbate	Sigma Alderich	99.9
2	3-Aminopropyltrithorysiane (APTES)	Sigma Alderich	98.0
٣	Ethanol	Scharlau	99.8
5	Hydrochloric Acid	CDH	37(v/v)
6	Sodium ione	Sigma Alderich	99.0
7	magnesium ion	Scharlau	99.9
8	Methanol	Scharlau	99.8
9	Potassium chloride	Sigma Alderich	98.0
11	Boric acid	Sigma Alderich	98.0

2.2.Instrumentation

Required instruments

(UV-visible spectrophotometer. FluorescenceSpectrometer,Scanning electron microscope ,Transmission electron microscope ,Fourier transform infrared spectroscopy ,X-ray diffraction spectroscopy ,pH meter ,Sonicator ,Centrifuge)

2.3. Methods for preparing nanomaterials Quantum dots

2.4. Preparation of SiQDs

(Bottom-up approach) The bottom-up synthetic approach involves converting smaller organic molecules such as ascorbic acid into SiQDs via stepwise chemical reactions. To obtain SiQDs, simple techniques such as direct pyrolysis (carbonization) or hydrothermal treatment using autoclave reactors are then used. In contrast to the top-down approach, this method is cost-effective, scalable, provides control over morphology, shape, surface state, and size, and results in fewer defects. Pyrolysis is the simplest synthetic method used to prepare SiQDs, and SiQDs can be synthesized by direct pyrolysis. This is done by taking a weight of (0.2) mg of sodium ascorbate, then adding 10 ml of deionized water, then placing a stirrer in it and stirring for 10 minutes. We take 4 ml of deionized water, then adding 1.5 ml of (APTES) to the water, then stirring by a stirrer for 10 minutes without heat. We take (1.25) ml of the sodium solution prepared in the first step, then adding it to the (APTES) solution, then stirring for 30 minutes with heating at a temperature of 40 °C.

3.1-Surface synthesis

A wide range of inorganic and organic molecules (PEI) have been used to modify/functionalize the surface of SIQDs to give them tunable photoluminescence properties. The use of imidazole in surface modification is an important factor in increasing the fluorescence intensity. The surface is modified by adjusting the pH of the SiQDs solution to 7 by adding hydrochloric acid solution (0.1M). Then, an amount of the compound to be modified with the surface is added to the SiQDs solution.

3. 2. Synthesis of the surface using imidazole

This is done by taking a weight of (0.1) mg of SIQDs previously prepared, then adding it to 10 ml of non-ionic water and stirring for 10 minutes using a magnetic stirrer at a temperature of 50 °C. Then we take a weight of (0.1) mg of imidazole in a glass beaker containing 10 ml of non-ionic water, then stirring for 10 minutes with heating at a temperature of 40 °C. Then, the tannic acid solution is added to the SIQDs solution gradually with heating at a temperature of 50 °C for three hours. After that, the resulting solution is dried in a drying oven at a temperature of 50 °C, then the product is washed.

3.3. Sensing Process

The recognition properties of the modified SiQDs were studied by recording the fluorescence spectra in the presence of different concentrations of organic fertilizers at a selected wavelength. The selected excitation wavelength was used in the fluorescence spectroscopic measurements. 1 mg of the modified SiQDs was dissolved in 3 mL of phosphate buffer (pH 7.5) in a quartz cuvette. Then, different concentrations of organic fertilizers were sequentially injected into the cuvette and the fluorescence spectra were recorded after each addition.

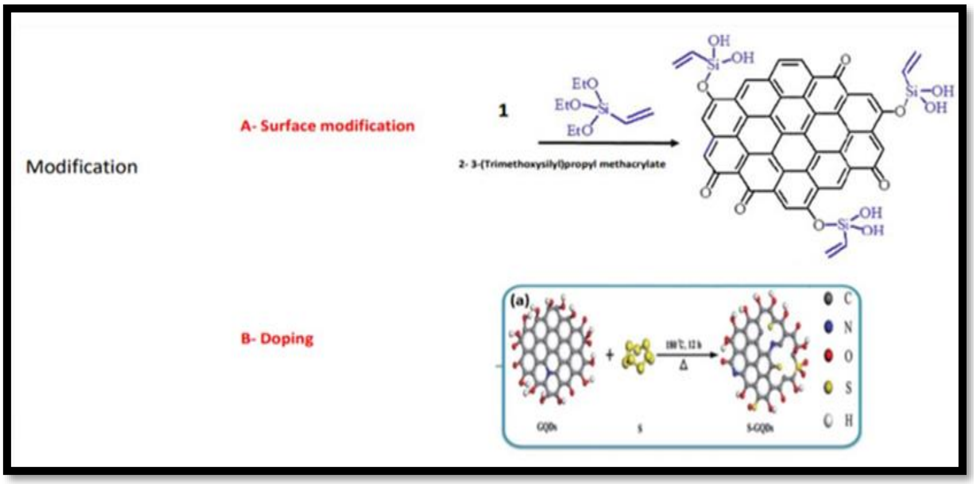


Figure (1) shows the steps for modifying the surface of SIQDs.

4.Fluorescence Spectroscopy

Fluorescence spectroscopy is a type of electromagnetic spectroscopy where a beam of light, usually in the ultraviolet range, is used. This beam passes over the sample, where the substance to be studied absorbs photons of light at a specific wavelength, causing it to be excited from the stable electronic state to one of the different vibrational states in the excited electronic state. Collisions between the excited molecules and other molecules cause a loss of vibrational energy until the electronically excited molecules reach their lowest vibrational level in the excited electronic state, then drop back to lower vibrational levels in the stable electronic state, resulting in the emission of photons. These electrons then return to the stable state again by re-emitting the absorbed energy again in the form of fluorescence, but the emitted energy is less than the absorbed energy, and the wavelength of the emitted spectrum is also larger than the wavelength of the absorbed spectrum.

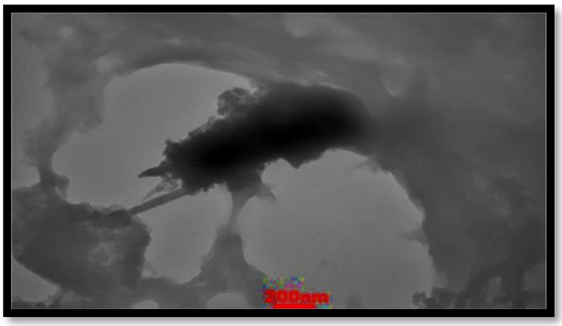
5. The process of detecting the pesticide used

Standard solutions of the pesticide used were prepared precisely at a concentration of 180 ppm. The total volume was exactly 200 ml and then diluted to several concentrations by using stepwise preparation under the same conditions. We put the SIQDs-M solution in a cuvette and then recorded the fluorescence intensity in the solution with a resolution of (220-650) nm, with the excitation wavelength fixed at the wavelength chosen to show the highest measurable intensity in nanometers. Then after adding a specific amount of boric acid (the pesticide), we then measured the fluorescence intensity in the solution. We repeated the measurement at different pre-determined concentrations of the pesticide as well as in the presence of metal ions in the solution, which confirms the reliability of the results for comparison. The volume of the SIQDs solution was fixed at (1.5) ml before adding boric acid, then (1.5) ml of boric acid was added, then the fluorescence intensity was measured and the results were compared before and after adding boric acid. The fluorescence spectra were recorded after the addition and we noticed a significant decrease in the fluorescence intensity, indicating the occurrence of quenching due to the presence of the pesticide when the silica-coated quantum dots were exposed to the pesticides present in the aqueous solution. All these measurements and preparations were carried out at room temperature.

III. RESULTS AND DISCUSSION

3.1- Characterization of the prepared particles

SIQDs-M complex also shows in Figure (1) accurate images of SIQDs particles that show that the dark-colored nanoparticles are (the core) which represents ascorbic acid with aptes and are coated with light-colored particles (the shell) which represents imidazole, which is evidence of the formation of the core-shell M -SIQDs.



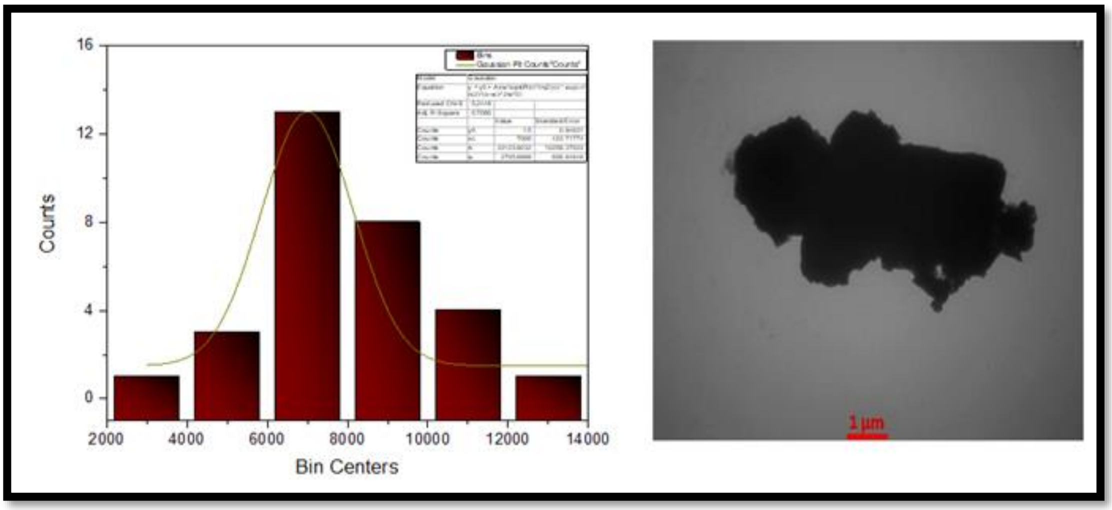


Figure (2) shows the particle size distribution of the compound.

It is shown that the dark colored nanoparticles are (the SIQDs core) which represents the APTES association with ascorbic acid and are covered by the light part (the M shell) which represents imidazole which is evidence of the formation of the SIQDs-M core-shell. Figure (3) also shows other magnifying powers SIQDs-M. The initial compositions as well as the dispersion were estimated by measuring EDX, which indicates the distribution and quantities of the elements. The chemical composition of ascorbic acid and the resulting quantum dots were determined by EDX spectroscopy in Figure (4). We also note that the results are with a high carbon content of 28% compared to an oxygen content of 18%.

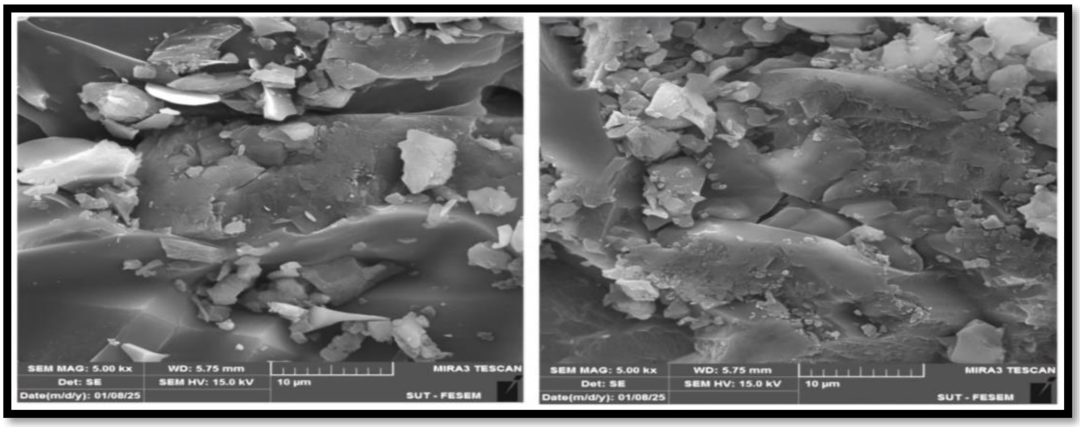


Figure (3) shows an image using FESEM on the core-shell configuration of SIQDs-M.

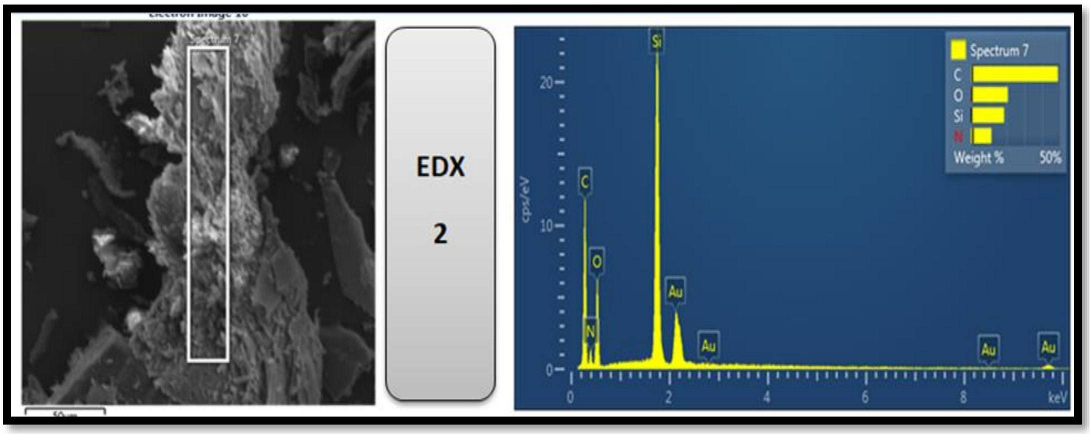


Figure (4) The chemical structure of SIQDs-M was determined by EDX spectroscopy.

The shape. (5) XRD patterns of ((SIQDs-M) show distinct and broad diffraction peaks at 2θ = 18.26,19.29,22.4- 26.8o)), corresponding to the (S1,S2,S3) plane of SIQDs, proving that the prepared SIQDs have good crystallinity. We also notice an increase in the intensity of the broad peak with an increase in the values of the full width of the mid-height of the peaks, a clear indication of the presence of the M group. The average particle size value of the (SIQDs-M) complex calculated from the Scherrer equation reaches 26.3 nm. The average particle size of the compound in the prepared samples was estimated according to the Scherrer equation ($D = K\lambda/\beta\cos\theta$), where the constant $K = 0.943$, $\lambda = 0.15405$ nm, diffraction angle $\theta = 13.4°$, and the half-height width of the diffraction peak $\beta = 0.257$, The grain size D is 35.4 nm. According to the calculations, the grain size inferred from XRD is larger than the actual size. When the size of the prepared particles is <10 nm, the surface has multiple grain boundaries. XRD measurement cannot distinguish between these two boundaries, so the size of some samples may be smaller than the value calculated by this equation. The structure and crystallinity of the modified SIQDs were.

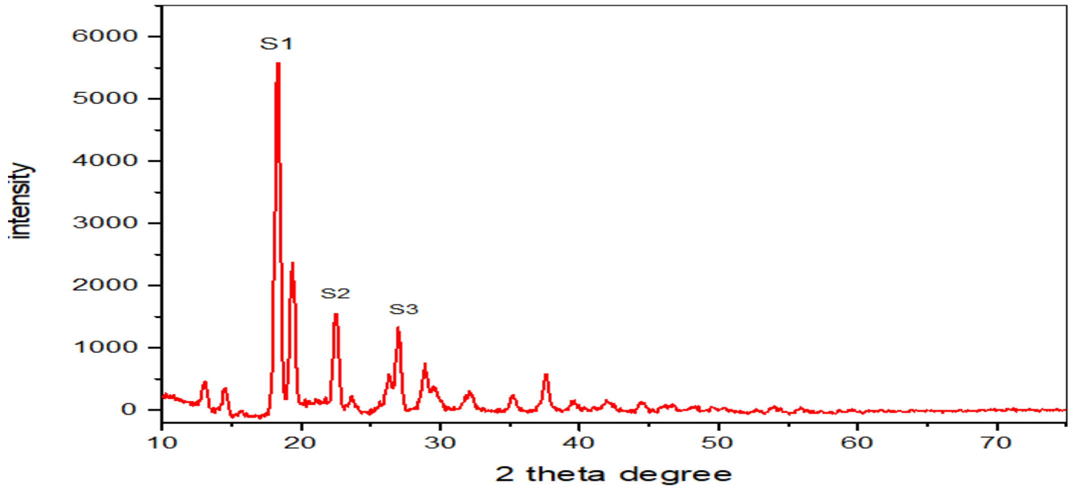
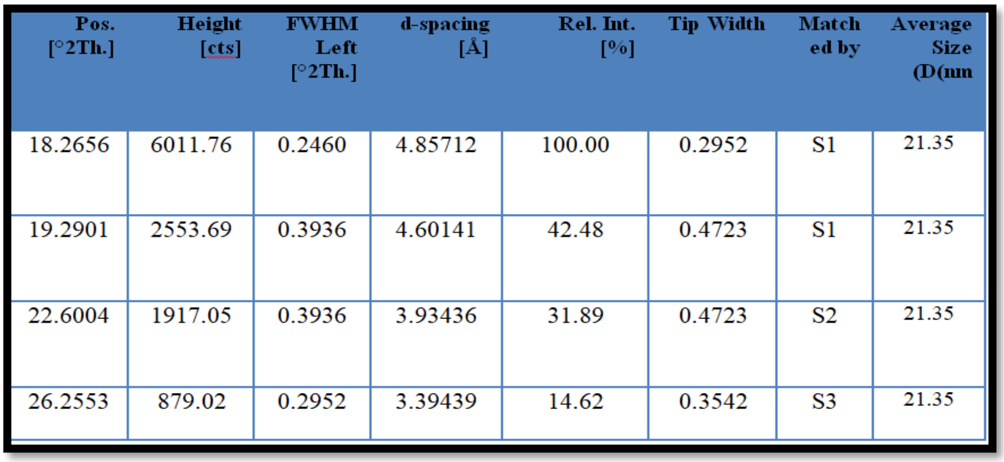


Figure 5 XRD pattern of SIQDs after surface modification with imidazole.

Table 2 Data of the sample of SIQDs-M nanocomposite after surface modification with imidazole.



Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip Width	Matched by	Average Size (D(nm
18.2656	6011.76	0.2460	4.85712	100.00	0.2952	S1	21.35
19.2901	2553.69	0.3936	4.60141	42.48	0.4723	S1	21.35
22.6004	1917.05	0.3936	3.93436	31.89	0.4723	S2	21.35
26.2553	879.02	0.2952	3.39439	14.62	0.3542	S3	21.35

The FTIR spectra of the prepared SIQDs and their infrared spectral properties are shown. The infrared spectrum in Fig. (6) showed the appearance of broad absorption bands in the range (2877, 33241) cm-1, indicating the presence of amino group (NH2), in addition to the appearance of an absorption band in the region (1466) cm-1, indicating the presence of methyl group and C-H bond. The IR spectra also showed another absorption band in the region of 1059 cm-1, indicating the presence of Si-O. The modification with imidazole can assign a broad peak at 1130 cm-1 to the Si-O-C asymmetric stretching vibration, which predicts the successful synthesis of SIQDs. The imidazole modification also shows the presence of C=O bonds and asymmetric carboxyl group around 1610 and 1535 cm-1, respectively. The outer peak at around 3440 cm-1 corresponds to the N-H and O-H bond stretching vibration in SIQDs. The band obtained at 1422 cm-1 is the C-N absorption and the appearance At 3095 cm-1 it was associated with the N-H stretching vibration of amine groups, indicating the successful incorporation of nitrogen atoms (from imidazole) into SIQDs.

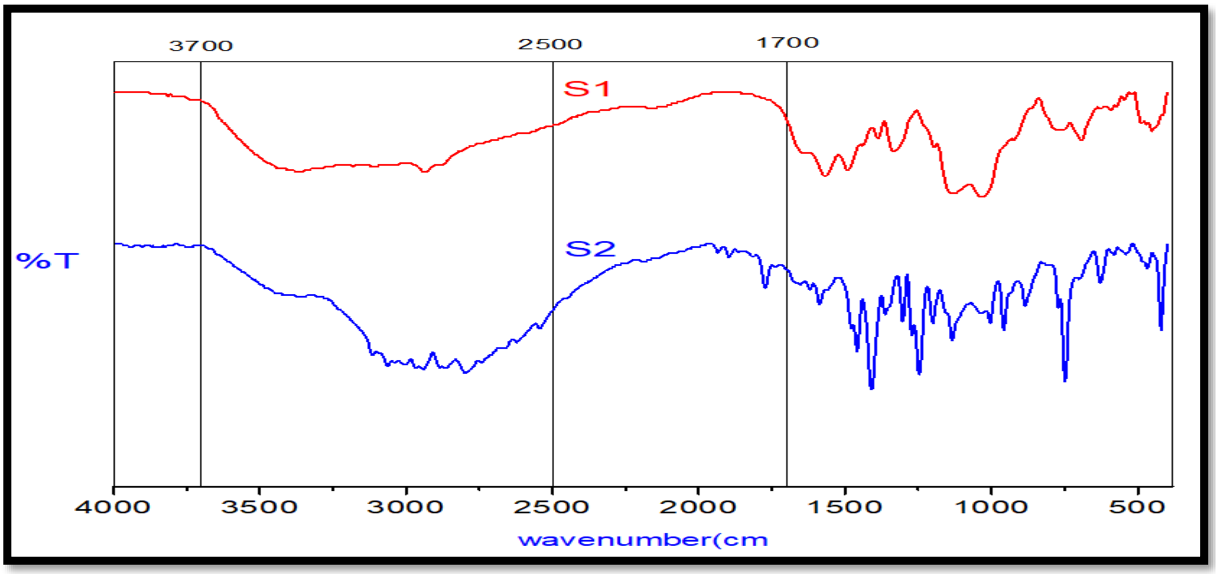


Figure (7) S1 shows the FT-IR spectrum of SIQDs before surface modification. S2 represents SIQDs-M after surface modification with imidazole.

3.2 Fluorescence spectroscopy of SIQDs-M

A concentration of 100 ppm was prepared by dissolving the compound in a certain amount of deionized water, for the compound before and after surface modification and then finding the excitation-emission spectrum of the compound shown in Figure (8), the spectrum of SIQDs-M represents the fluorescence emission peak at 585 nm when excited at a wavelength of 297 nm while after surface modification using imidazole, no change in the peak position is observed, but only an increase in the intensity of the fluorescence emission at the mentioned wavelength. This indicates that surface modification has a significant effect in increasing the intensity of fluorescence.

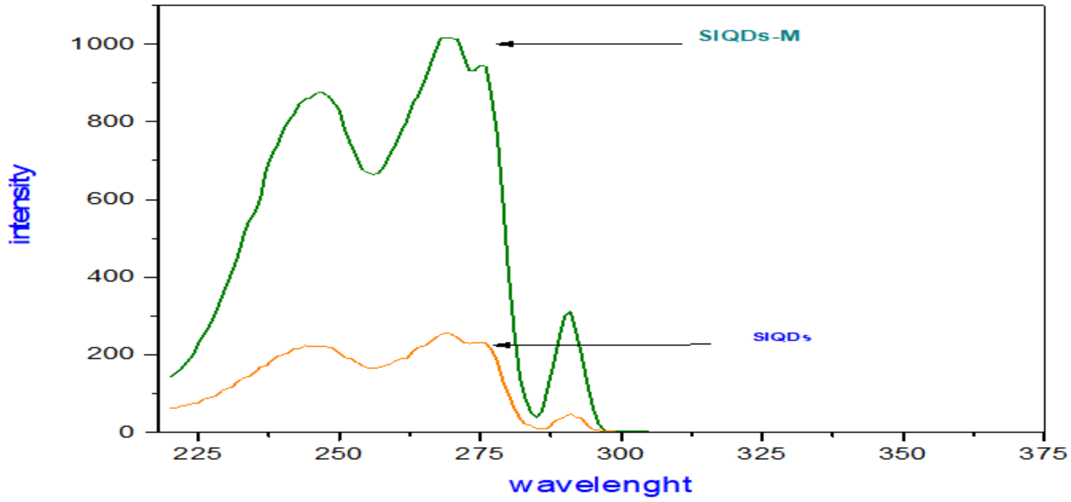


Figure (8) represents the fluorescence spectra of SIQDs before and after surface modification using imidazole.

3.3 Selective detection of pestesid

A second test was performed for selective sensing of boric acid using ex/em = 585/297 nm at pH = 7.1. The recognition properties of the modified SiQDs were studied by recording the fluorescence spectra in the presence of different concentrations of organic pesticides at the selected wavelength. The fluorescence was measured in the same way as the previous one only for SIQDs, and the fluorescence spectra were recorded after addition. We notice a significant decrease in the fluorescence intensity indicating the occurrence of quenching due to the presence of the pesticide, when excited at a wavelength of 585 nm. As a result, the presence of the pesticide was detected at a specific wavelength. Then, the fluorescence intensity levels of SIQDs were analyzed after adding a certain concentration of the pesticide. Scheme (9) shows that the fluorescence signal of SIQDs decreased significantly with the addition of the pesticide.

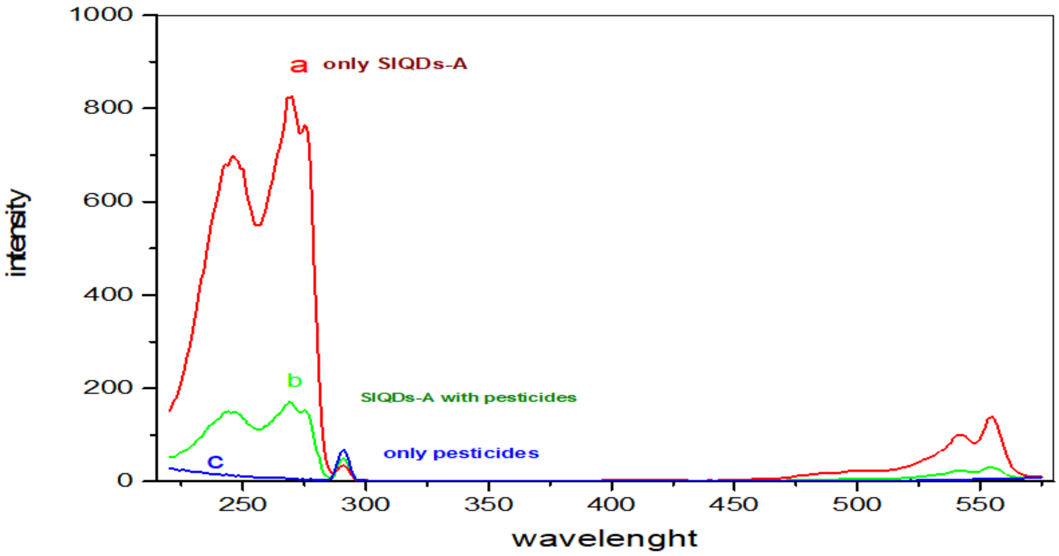


Figure (9) -a represents the fluorescence intensity only for the modified M-SIQDs -b represents the fluorescence intensity after adding the pesticide -c represents the pesticide intensity only

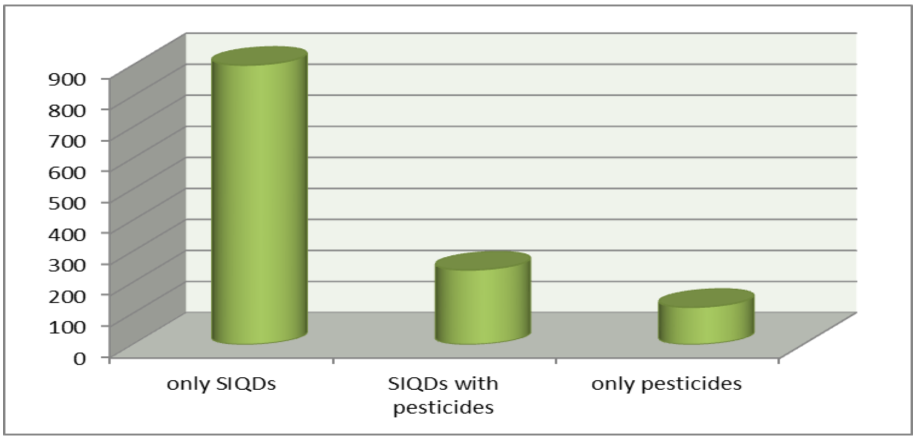


Figure (10) A graph showing the intensity ratio of the fluorescence signal of SIQDs and its decrease in

When the detection process was carried out using SIQDs-M for the pesticide in aqueous solutions in the presence of other ions such as sodium ions, potassium ions, and chlorine ions, all together, the fluorescence intensity levels of SIQDs were analyzed after adding the ions (Na+, Mg+, Cl+, K+) to the aqueous solutions. We noticed that the pesticide was well suppressed without any significant effect from the ions present in the solution, as shown in the following figures (11).

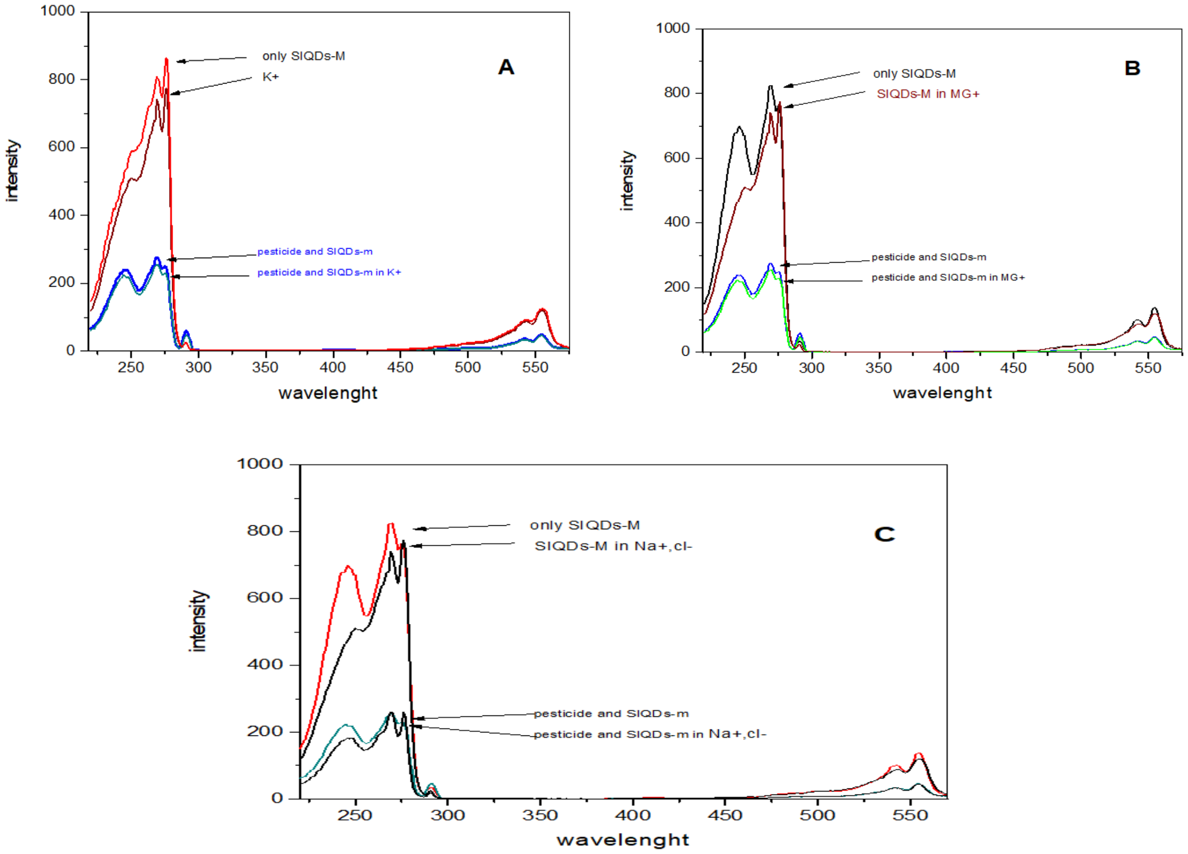


Figure (11) shows the quenching phenomenon of SIQDs-T in an aqueous solution containing (Na+, Mg+, Cl+, K+)

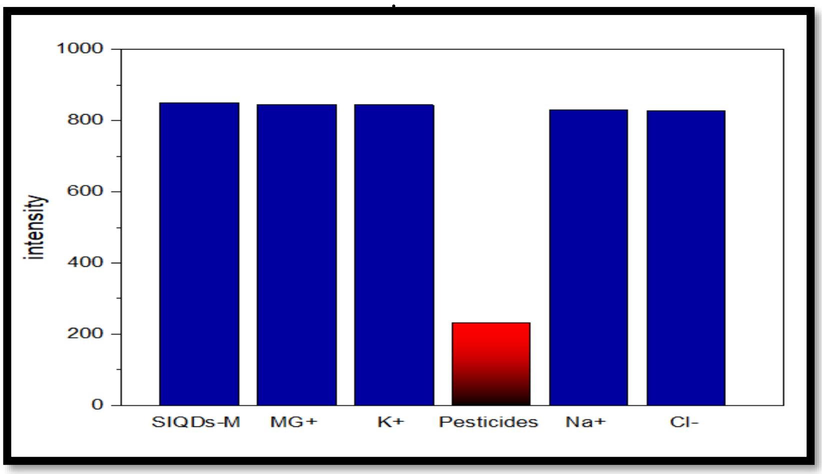


Figure (12) shows the relative fluorescence intensity of SIQDs in the presence of ions.

Figure (13) also shows the fluorescence spectra of M-SIQDs with different concentrations (200ppm, 180ppm, 160ppm, 140ppm, 120ppm, 100ppm, 80ppm) of the pesticide used. A rapid decrease in the luminescence of SIQDs was observed when the pesticide (boric acid) was introduced; and the fluorescence quenching was tested at these concentrations.

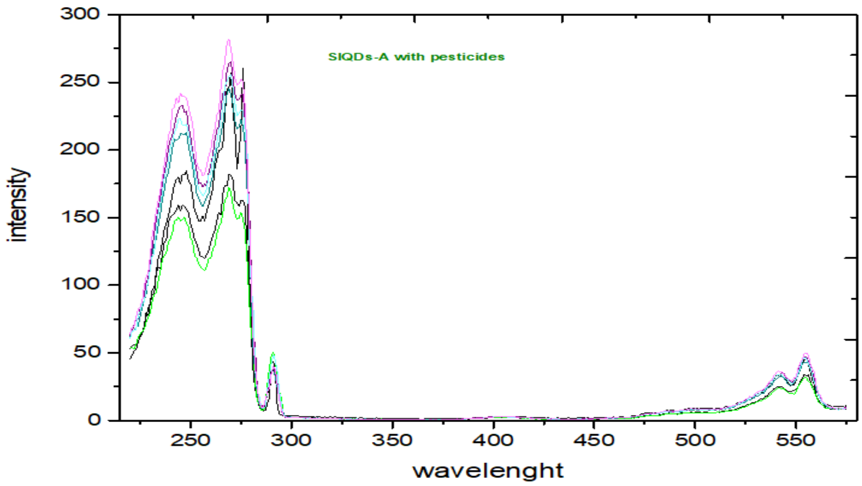


Figure (13) shows the fluorescence spectra of M-SIQDs with different concentrations of the pesticide.

An acceptable linear relationship was observed, as shown in Fig. (14), with an excellent linear regression value (R2) of 0.9966 indicating accurate detection of pesticide concentration. These results indicate that the prepared SIQDs can be a selective and sensitive sensor for the detection of pesticide (boric acid, Equation 1). The limit of detection (LOD, Equation 2) and the limit of quantification (LOQ) were determined using the following formulas:

LOD =0.041 * σ /S …… (1)

LOQ = 0.16 * σ /S. .. …… (2)

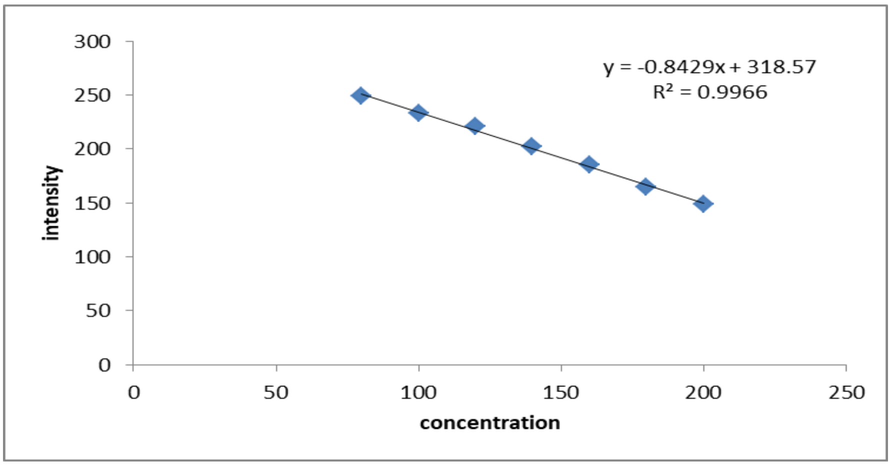


Figure 14: Linear relationship between fluorescence suppression efficiency and pesticide concentrations in the range of 80-200ppm.

When performing the detection process using SIQDs-T, the effect of acidity on the pesticide and the prepared quantum dots is tested by preparing a volume of (200 ml) of a standard acidic solution with a concentration of (100 ppm), by dissolving hydrochloric acid in non-ionic water, then we take (10 ml) of the solution and put it in a tube and add (0.001) weight of the pesticide to it, then the fluorescence intensity is measured at a specific excitation wavelength of 470 and the intensity is recorded, and in the same way a solution of quantum dots is prepared with the same concentration and the fluorescence intensity is measured, and it was found that the fluorescence intensity of the pesticide and silica in non-ionic water is the same as that in the acidic solution, which indicates that acidity has no effect on the detection of the pesticide, as shown in the following figure.

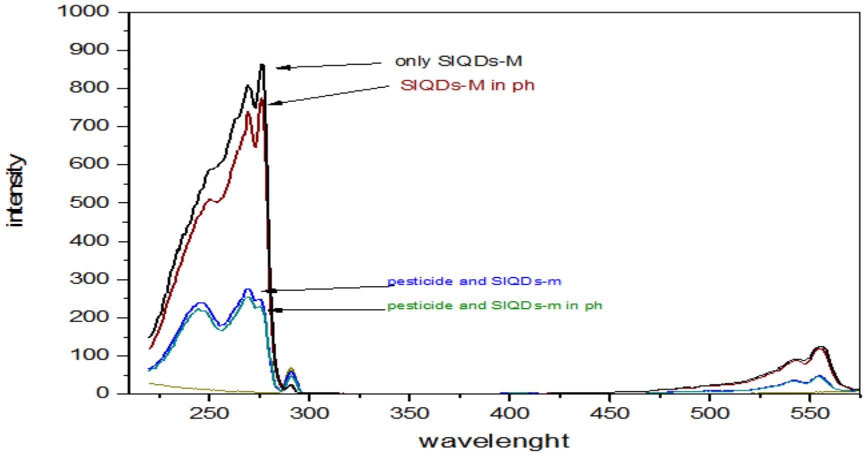


Figure (15) shows the fluorescence intensity of M-SIQDs and the pesticide without Hcl and with Hcl.

When performing the shaking effect, using SIQDs-M, we notice a difference in the intensity of suppression when shaking the mixture of quantum dots with the pesticide, as the signal intensity decreases, indicating that good suppression is achieved the longer the shaking time, as it varies from the mixing point without shaking to a time of 12 minutes, and the maximum suppression was found to be fixed at 7 minutes, as shown in the following figure.

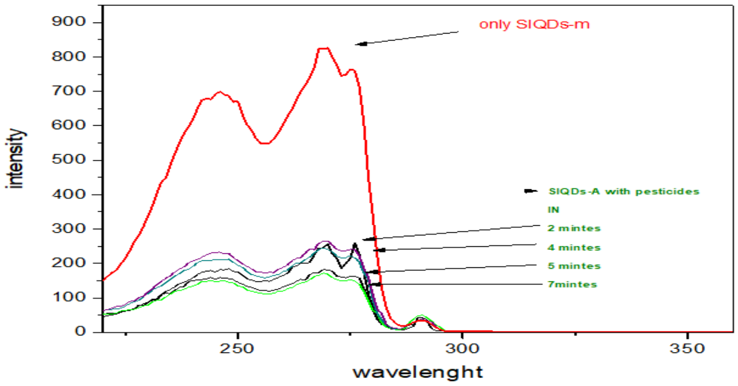


Figure (16) shows the effect of shaking time on damping when using SIQDs-M.

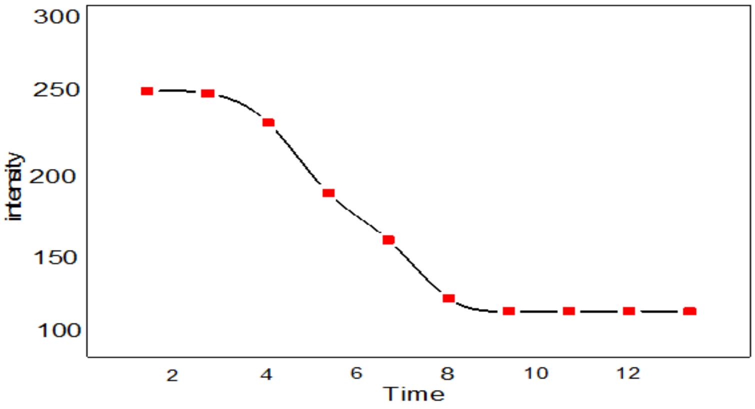


Figure (17) is a curve showing the effect of shaking time on damping using SIQDs-M.

IV. CONCLUSION

Since pesticide residues in water are a major problem and their impact on human health in particular and the environment, this method is very important, as quantum dots (QDs) are used as sensors to detect pesticides, and their detection limit was found to be 0.047 microns at a specific wavelength of 470 nm. The prepared quantum dots have reasonable prices, high sensitivity and tendency to dissolve, and detect small amounts of pesticides, making them very ideal for various sensing applications. The manufactured quantum dots achieve the required environmental properties. Based on the fluorescence data, it can be concluded that the sensing mechanism of the modified silica quantum dots is attributed to the formation of a complex between sodium ascorbate and APTES (3-aminopropyl)triethoxysilane, and then the surface is modified by adding imidazole. The average size of the resulting modified silica quantum dots is between 6 and 18 nm. The relationship between the fluorescence intensity of the modified silica quantum dots and the amount of boric acid showed a significant linear relationship in the range of 20 to 180 ppm. It showed a high degree of specificity and no interference with the existing ions, such as (K+, Mg2+, Na+, Cl-), when excited.

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