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Designed a Fluorescent Method by Using PbS with Gelatin via Quantum Dots for the Determination of Amount Insecticide toxic Fenpyroximate in Water Samples

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Abstract
In this current article, a chemical sensor was synthesized PbS functionalized with Gelatin Quantum Dots for Fenpyroximate. The measure of Fenpyroximate was performed using concentration (2.5×10^{-3} mol L^{-1}), PbS Quantum Dot-Gelatin nanocomposites sensor, pH 6, and time 40 s, wavelength 328 nm. Under the optimum conditions, the detection limit linear range were obtained (0.02 to 20.0 µg L^{-1}). The standard deviation of less than (2.0%), and detection limits (3S/m) of the method (0.02 µg L^{-1}) for determination of Fenpyroximate, was obtained. The observed outcomes confirmed the suitability recovery and a very low detection limit for measuring the Fenpyroximate. The chemical PbS Quantum Dot–Gelatin nanocomposites sensor as excellent sensor in the practical application of Fenpyroximate related to residue management is in surface water samples.

Keywords
Fenpyroximate, Insecticide, Fluorescence, Sensor, Quantum Dots.

1. INTRODUCTION

Fenpyroximate (tert-butyl (E)-a-(1,3dimethyl-5phenoxypyrazol 4 ylmethyleneamino-oxy)-p-toluate) is an acaridae belonging to the phenoxypyrazole group, with selective activity on phytophagous species one widely used pesticide is fenpyroximate, an acaridae with oxide-bearing pyrazole [1,2]. It has high efficacy against larvae by inhibition of mitochondrial electron transport [3]. Assuming that they will be applies according to the authorized agricultural waste patterns of Good Agricultural Practices. On the other hand, the misuse of pesticides may lead to extensive concentrations of residues in the agricultural products, which has forced international agencies and governments to established maximum residue limits (MRLs) as to ensure that safe, to the consumer, products enter the market [4,5].

Since toxic fenpyroximate is the widely applied an acaridae, monitoring and determination of fenpyroximate in ground and surface waters and in cultivated areas where it is used are of high significance [6]. Until now, different methods such as gas chromatography [7], liquid mass chromatography [8], liquid chromatography [9,10]. Flow injection [11]. Molecularly imprinted polymers (MIPs) [12]. Despite the selectivity and specificity of some analytical techniques, they are time-consuming and require a larger amount of samples. On the other hand, Fluorometrically techniques have many benefits in comparison to the others, for example, simplicity, low-cost, accurateness, sensitivity, ability to determine, can be the good candidate in studies on the persistence of pesticides in water samples [13,14].

Recently, attention has been directed to fluorescent sensors due to their selectivity, high sensitivity, and real-time monitoring of tracing toxiowing [15,16]. In the past few decades, numerous fluorescence probes [17] and quantum dots [18] have been announced for recognition of biomolecules (organic and inorganic). However, the necessity to develop alternative and ecologically friendly materials became apparent [19,20]. Also, methods for the detection of various analytes and their characterization have become a pivotal research area in materials science research. PbS nanocomposites can be prepared by various methods such as the application of stabilizing and reducing chemicals, e.g., glutaraldehyde [21]. The gelatin as a natural, completely non-toxic, and biocompatible polymer derived from collagen is suitable for coating nanoparticles of lead sulfide quantum dots since it results in obtaining fine and stable particles; at the same time, it can be used as a transfer agent which creates significant stability owing to cross-linking in these materials, and more importantly, its by-products can be absorbed in the

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body and decomposed [22-24]. In the present article, an uncomplicated facile strategy was employed to prepare water-soluble stable PbS with gelatin by utilizing glutaraldehyde as a stabilizer, which is shown in (Fig. 1) [25,26].

In this current article, a fluorometric method was designed for determining toxic fenpyroximate. In addition, the successful application of nano-probes in detecting toxic fenpyroximate in different real samples along with their significant efficiency and perfect recovery prove their great potentialities in practical application. The chemical PbS quantum dot–gelatin nanocomposite sensor made it possible as an excellent sensor with reproducibility, good recovery and a very low detection limit for measuring toxic fenpyroximate. The method by fluorescence emission intensity introduced to measure toxic fenpyroximate in water samples and can be used for other samples.

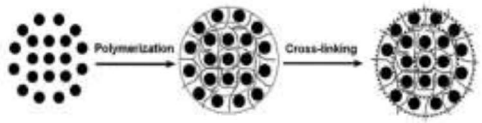

Fig. 1. Schematic illustration of the PbS quantum dots sensor functionalized with gelatin synthesis.

2. EXPERIMENTAL

2.1. Materials and Instrumentation

All chemicals of lead nitrate $Pb(NO_3)_2$ (99%), sodium sulfide (Na_2S) (99.0 %), gelatin, and glutaraldehyde were bought from Merck Company. A stock solution of 1000 mg/L of analytical grade toxic fenpyroximate (97%) from Sigma-Aldrich, was prepared by dissolving 0.1 g of the toxic fenpyroximate in solution and diluting it to 100 mL in a volumetric flask.

2.2. Apparatus

All the recordings were done at room temperature, measurements toxic fenpyroximate were done using a Horiba JY Fluorolog-3 molecule fluorometer (Paris Company, France). X-ray diffraction from the device Rigaku-Dmax 2000 used. X-ray diffraction test pattern analysis by JCPDS (No. 5-592), software was performed. Fourier transform infrared (FT-IR) spectra were registered on a PerkinElmer (FT-IR spectrum BX, Germany). Differential thermal analysis (DTA) and Thermal gravimetric analysis (TGA) were registered on a barer 10ºC/m (Shimadzu DSC-50 Company, Japan).

2.3. Pretreatment of water samples

In a 50 mL beaker, Water samples were collected from Karkheh River water, Maron River water, and Karon River water, Iran. All the water samples were filtered using 0.45 µm micropore membranes to remove suspended particles filtered if necessary, (or a spiked samples) and diluted in a volumetric flask. An aliquot of the above sample solutions was treated under the general procedure for subsequent determination of toxic fenpyroximate [5,12].

2.4. Synthesis of PbS Quantum Dot–Gelatin Nanocomposites Sensor

The nanoparticle PbS was synthesized in reactive solution prepared using lead nitrate $Pb(NO_3)_2$ and sulfide sodium (Na_2S) with concentration of (0.1 M and 0.1 M). The Gelatin pellets were used as a base medium and its concentration was set to (0.1 M). 20 mL of all the above solutions were prepared separately, using distilled water as a solvent and mixed together in a beaker. 2 ml of glutaraldehyde (25%) was added into the solution as a complexing agent, which can easily bind the metal ions. The reactive vessel with solution was immersed into 20 ml acetone maintained at 40ºC and pressure of 10-5 mbar. The prepared solution was colorless and turned yellowish after (30 min) and suddenly changed into gray color, these indicate the chemical reactions and also confirm the formation of PbS. The powder was collected and dried in a hot air oven at (57ºC) [26,27].

2.5. Mechanism of fluorescence quenching toxic fenpyroximate

The sensitivity of the PbS quantum dot–gelatin nanocomposite platform was significantly high to toxic fenpyroximate. Meanwhile, with the combination of the toxic fenpyroximate with PbS as well as the huge specific area of the fabricated PbS quantum dot–gelatin nanocomposite can probably reversibly absorbing ~95.0% of toxic fenpyroximate in samples. It should be noted that due to the large surface area and high electron transfer ability the affectivity of fluorescence quenching is high. The mechanism of toxic diazinon can be defined as the schematic process shown in (Fig. 2) [14, 26].

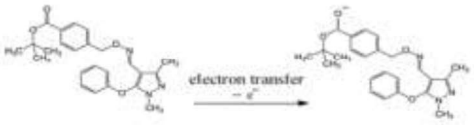

Fig. 2. The mechanism of toxic fenpyroximate.

2.6. Procedure Fluorescent Detection measurements

In this procedure, PbS Quantum Dot–Gelatin nanocomposites (2.5×10^{-3} M), then 2 ml of glutaraldehyde (25%), 1 mL of acetate buffer (pH 6.0), and different concentrations of toxic fenpyroximate (10.0 µg L^{-1}) were added to 10 mL volumetric flasks and diluted with double distilled

water. The difference between the quantities of the increasing fluorescence emission in a wavelength equal to (328 nm) in a time interval equal to (30-50 s), was estimated can be seen in (Fig. 3) [14,28].

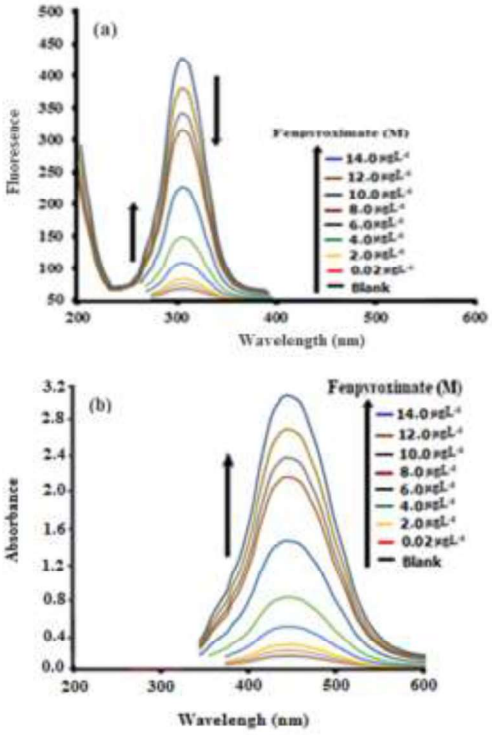

Fig. 3. (a) The Fluorescent Detection of toxic fenpyroximate by PbS Quantum Dot–Gelatin nano composites in 328 nm; and added solution increasing of the toxic fenpyroximate (2.0 μgL^{-1}) in time 10 s. (b) The absorption spectra of toxic fenpyroximate by PbS Quantum Dot–Gelatin nano composites added solution increasing of the toxic fenpyroximate solution (10.0 μgL^{-1}) in time 10 s. [2.5×10^{-3} M of PbS Quantum Dot–Gelatin nano composites, pH 6.0, time 40 s, and phosphate buffer solution].

By adding toxic fenpyroximate to the solution, it was observed that fluorescence emission intensity of acetonitrile solution of PbS quantum dot–gelatin nanocomposite decreased at the wavelength of 328 nm. At the same time, with the help of fluorometric and UV-visible spectra (ΔI), the apparent spectral evolution including the formation of a well-defined isosbestic point at around 328 nm was estimated. All reaction steps were repeated by increasing toxic fenpyroximate concentration by 0.2 µg/L every 10 s. During the fluorometric detection of toxic fenpyroximate (ΔI), a blank sample (I_0) was also analyzed. There was a sharp change in the fluorescence emission of the sensor in the 328 nm region, a continuous increase in toxic fenpyroximate intensity at intervals of 10 s in solution, and changes in the fluorescence emission intensity of the sensor. Peak fluorescence emission at 328 nm with an increase in fluorescence emission intensity can be seen in the UV-visible spectrum given in (Fig. 3a). All these steps were repeated for a reaction in the absence of toxic fenpyroximate; finally, the fluorescence emission intensity obtained for toxic fenpyroximate sample was subtracted from the intensity of the blank sample. The spectrum changes occurred due to the addition of toxic fenpyroximate in the range of 0.02 to 1.4 µg/L and the formation of a complex. As can be seen, the complex (toxic fenpyroximate–sensor) has two absorption peaks at the wavelengths of 328 and 460 nm (Fig. 3b) [13, 29].

3. RESULT AND DISCUSSION

3.1. Characterization

The results of IR for the samples of uncoated PbS Quantum Dots and the sample coated with gelatin can be seen in (Fig. 4a). In the figure for the uncoated sample, two very weak bands are seen in 835 cm^{-1} and 1110 cm^{-1}, which are characteristic of the presence of the Pb-S bond, and the reason for the severity of the weakness of these bands is only due to covalent bonding and very weak vibrations. Also, the indicator bands in 1350 cm^{-1} and 1380 cm^{-1} indicate the presence of nitro compounds, and the presence of a band at 3445 cm^{-1} indicates the O-H groups in the sample. The IR spectrum of the gelatin-coated specimen indicates the bands associated with the coating at 3416 cm^{-1} and 1733 cm^{-1} belonging to the N-H bond and the vibrations associated with the C=O bond in the 1633 cm^{-1} region. Pb-S covalent bond bands have also been observed, except that they have appeared in regions 985 cm^{-1} and 1110 cm^{-1} [30,31]. In Fig. 4b, the XRD pattern of the PbS Quantum Dot–Gelatin nanocomposites is displayed. the great intensity of signal at 25.8 (111) and 30.5 (200) confirmed that there has been a slight amount of material in amorphous state. XRD pattern of crystal, JCPDS (No. 5-592) [31,32]. As shown in (Fig. 5a), which relates to differential thermal analysis (DTA) of PbS quantum dot–gelatin nanocomposites, at 250 and 350°C, bands related to the decomposition of gelatin chains by weight are seen. Molecular is low. Also, at 570°C, a large calorific band is observed due to the large amount of gelatin and organic compounds remaining in the sample, which are destroyed at temperatures above 600°C. The results indicate that lead sulfide particles have a suitable coating of the desired polymer [32]. As shown in (Fig. 5b), which deals with the (TGA) of PbS quantum dot–gelatin nanocomposites, at temperatures below 650°C for gelatin we see a 98% weight reduction. While under the same conditions for PbS quantum dot with a high molecular weight polymer, we see only 28% weight loss [15, 32].

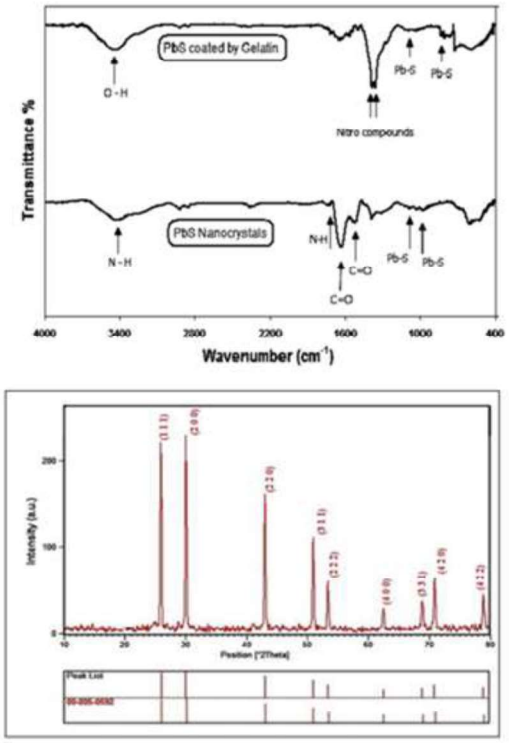

Fig. 4: The (a) FT-IR transmittance spectrum image and (b) XRD of the preparation of synthesized PbS Quantum Dot–Gelatin Nano composites.

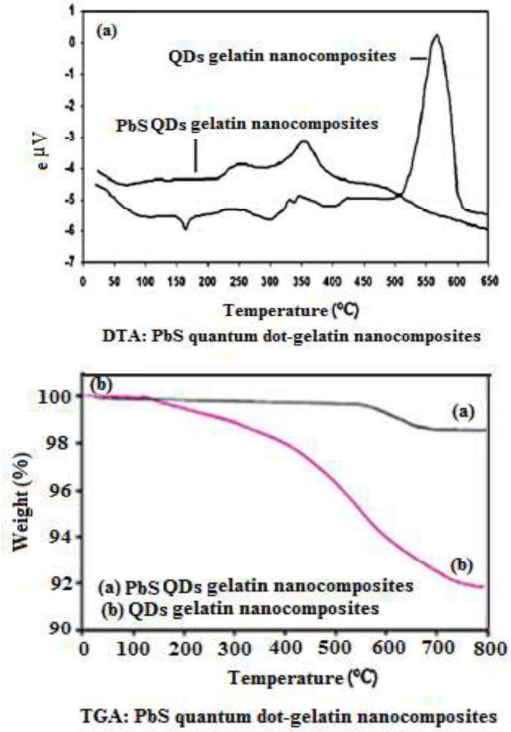

Fig. 5. (a) Differential thermal analysis (DTA) and (b) thermal gravimetric analysis (TGA) of gelatin-coated lead sulfide nanoparticles.

3.2. Optimization of Sensing Conditions

In order to reach the best result response in detecting toxic fenpyroximate rests upon the systematic optimization of buffer, pH, PbS Quantum Dot–Gelatin nanocomposites and incubation time step by step were optimizad.

3.2.1. Impact buffer

In this section, the best type of buffer and its volume for maximum absorption toxic fenpyroximate with PbS quantum dot–gelatin nano composites sensor are investigated. Based on the results, So phosphate buffer (1.0 M) to adjust the pH solution as the optimal buffer [33].

3.2.2. Impact pH

After measuring the fluorescence intensity of the solution, a thorough investigation was carried out on the fluctuating pH values in the range of 1-10 for the fenpyroximate-PbS Quantum Dot–Gelatin nano composites complex at 328 nm. As evident in Fig. 6A. The fluorescence intensity increased rapidly on changing the pH from 1.0 to 6.0, while it decreased at pH values higher than 6.0. This phenomenon might be because of the weak complexion at lower pH values (pH < 6.0). On the other hand, the reduced response of the proposed PbS Quantum Dot–Gelatin nanocomposites sensor for the determining toxic fenpyroximate at pH >6.0 could be due to a possible formation of the hydroxide of toxic fenpyroximate in solution. Accordingly, pH 6.0 was chosen as the perfect pH value for detecting toxic fenpyroximate [12,34].

3.2.3. Impact PbS Quantum Dot–Gelatin nanocomposites

Concurrently, (1 ml fenpyroximate 10.0 μgL^{-1}) solution, 2 ml glutaraldehyde (25%) and 1ml PbS Quantum Dot–Gelatin nanocomposites (0.1×10^{-3} to 4.0×10^{-3} mol L^{-1}) were mixed in a volumetric flask 10 ml using DW (distilled water) to find out about the impact of PbS Quantum Dot–Gelatin nanocomposites on the reaction rate. Again fluorescence intensity of solution was assessed. The previously mentioned operation has been replicated for blank solution (the solution in the absence of fenpyroximate).

3.2.4. Impact time

The findings are exhibited in Fig. 6B. Consequently (2.5×10^{-3} M) based on those findings was determined as the perfect concentration. Also, the impact of reaction time on the absorbance spectrum was investigated. Based on Fig. 6C, it has become apparent that the fluorescence intensity enhanced expeditiously and reached its peak at around (40 s). After 40 s, a

relative stability was spotted in the fluorescence intensity. Thus (40 s) was determined as the perfect reaction time in this experiment [14, 34].

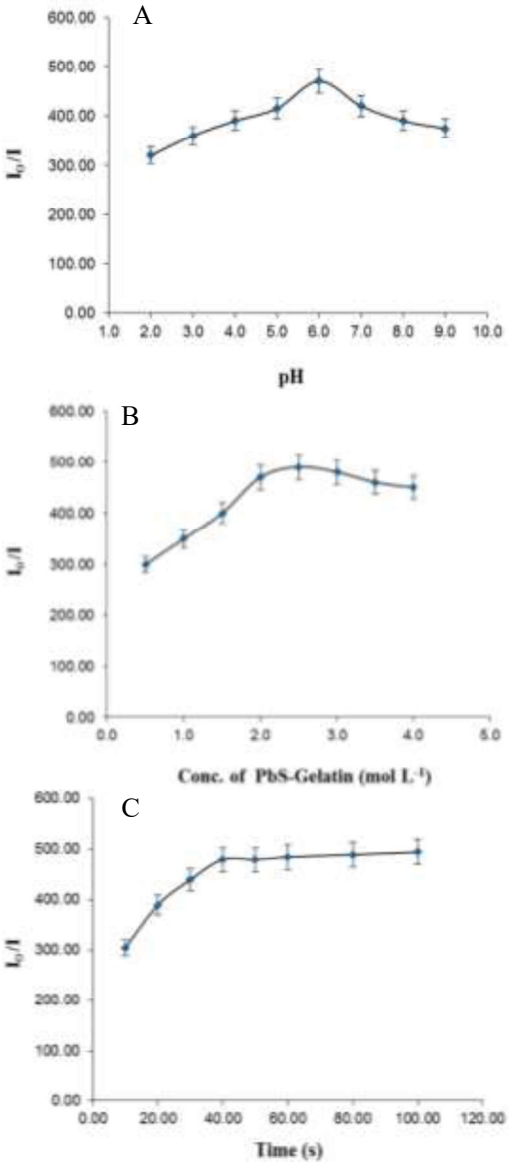

Fig.6. A) The impact of pH in the fluorescence intensity rate, PbS Quantum Dot–Gelatin nanocomposites, 2.5×10^{-3} M, glutaraldehyde (25%), time 40 s, 328 nm). B) The impact of PbS Quantum Dot–Gelatin nanocomposites in the fluorescence intensity rate. glutaraldehyde (25%), pH 6, time 40 s, 328 nm). C) The impact of time in the fluorescence intensity rate. PbS Quantum Dot–Gelatin nanocomposites, 2.5×10^{-3} M, glutaraldehyde (25%), pH 6, 328 nm).

3.3. Analytical application

Calibration graphs and detection limits: Under the optimum conditions calibration graph was constructed by plotting ΔI values as a function of the toxic fenpyroximate concentration. This in section purpose the examined and analytical performance of PbS quantum dots–gelatin nanocomposite for determination of toxic fenpyroximate. For this purpose and for the analysis of solutions, first, it is necessary to prepare a calibration curve to use to measure the concentration of unknown samples [14,35]. To prepare the calibration curve, solutions with different concentrations of toxic fenpyroximate (from 0.02 to 20.0 µg L^{-1}) were prepared and their fluorescence intensity technique, which is shown in (Fig. 7). The precision of the method was evaluated by performing (n=10) replicate measurements of toxic fenpyroximate solutions. The Relative Standard Deviations (RSD) for these determinations were (2.0 %), Limit of detection (LOD) (0.02 µgL^{-1}) and quantification (LOQ) of (0.022 µgL^{-1}) respectively [34, 35].

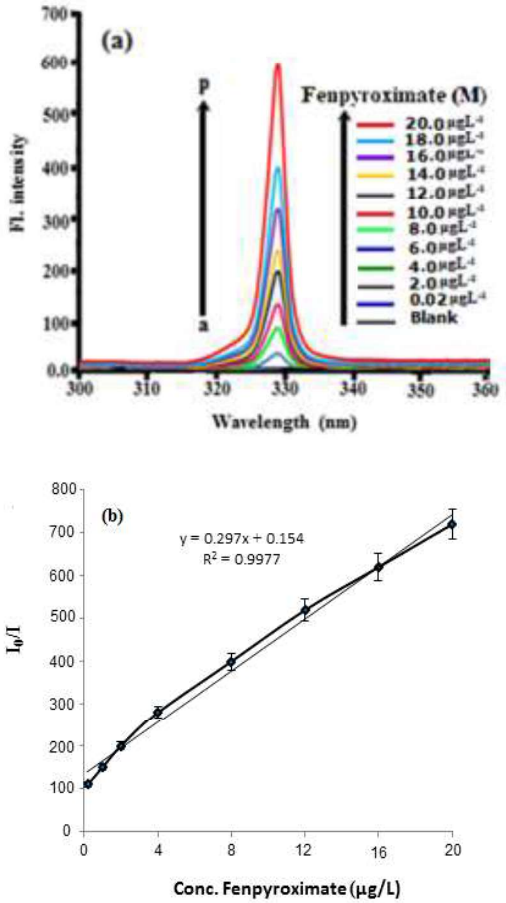

Fig.7. (a) Fluorescence emission intensity for determination toxic fenpyroximate by PbS Quantum Dots–Gelatin nanocomposite in width gap is 5 nm from (0.02 to 20.0 µg L^{-1}) of toxic fenpyroximate (b) toxic fenpyroximate Calibration curve diagram (0.02–20.0 µg L^{-1}) solution, 2.5×10^{-3} M of PbS Quantum Dot–Gelatin nanocomposites, pH 6.0, time 40 s, in phosphate buffer.

3.4. Interference Studies

To perform these studies, various pesticides and ions were introduced into the solution that

contained (10.0 μgL^{-1}) of toxic fenpyroximate and then applying the general procedure. As exhibited in (Table. 1), the tolerance limit was determined as the max concentration of the interfering substance which resulted in an error less than (±5%) for determination of toxic fenpyroximate [12, 36].

Table 1. Limit of tolerance foreign ions on determination of toxic fenpyroximate (n=5).

Foreign species	Tolerance limit (μgL^{-1})
Bentazone, Diazinon, Attrazin Abamectin, Diphenylamine	250
NH_4^+, Mg^{2+}, Na^+, K^+, Ca^{2+}, Hg^{2+}, Cr^{3+} ,Ag^+, Fe^{2+}, Fe^{3+}	500
CO_3^{2-}, SO_4^{2-}, Cl^-, I^-	500

3.5. Application to water samples

To evaluate the efficiency of the fluorescence method for the quantification of trace toxic fenpyroximate present in water samples, the results were compared with standard spectrophotometric methods, and the total amount of toxic fenpyroximate was estimated (n = 3). The results summarized in Table 2. Therefore, the recovery of toxic fenpyroximate in the samples analyzed using the standard addition method was shown to be mainly quantitative with low RSD values. The potential of the recommended method for the determination of trace quantities of this compound in distinct samples was proven [37, 38].

3.6. Comparison of presented work with different methods

The proposed chemical sensor could be renewed quickly and easily by mechanical polishing whenever needed. Comparison of the method studied with other methods is summarized in (Table. 3). The proposed sensor shows good selectivity, reproducibility, repeatability, and stability.

4. CONCLUSION

This study describes a fluorescence emission intensity method experiment for the determination of toxic fenpyroximate one of the most problematic pesticides polluting in water samples, and the extremely harmful to humans and animals even at low concentrations using PbS quantum dots–gelatin nanocomposite sensor. Applying provides a sensors based on PbS quantum dots–gelatin nanocomposite for the determination of toxic fenpyroximate in in Karon River water, Maron River water, and Karkheh River water. The calibration curve was linear in the range of (0.02–20.0 μgL^{-1}). The standard deviation method (0.02 μgL^{-1}) and quantification (LOQ) of (0.022 μgL^{-1}) for toxic fenpyroximate was obtained for the proposed electrochemical sensor by PbS quantum dots–gelatin nanocomposite sensor, respectively. The application of the sensor in the natural water sample and its validation with the standard addition method for toxic fenpyroximate detection confirms its authenticity for application in nearly every type of water. PbS quantum dots–gelatin nanocomposites sensor provides several

Table 2. Detection of toxic fenpyroximate in water samples with the proposed method (n = 3).

Samples	Added by Fluorescence Intensity (μgL^{-1})	Founded by Fluorescence Intensity (μgL^{-1})	HPLC method (μgL^{-1})	t_{exp}	Recovery %
Karon River	0.0	7.4 ± 1.1	7.2 ± 1.3	0.96	----
warerAhvaz	10.0	12.6 ± 1.2			99.0
Dez dam water	0.0	4.4± 2.3	4.3 ± 1.5	2.33	----
	10.0	9.5 ± 1.8			102.2
Karkheh dom	0.0	4.8 ± 1.1	4.6 ± 1.5	0.91	----
water	10.0	9.9 ± 1.3			103.0

Mean value ± standard deviation, (n = 3).

The recovery was calculated on the basis of the obtained results from Fluorescence intensity method.

Table 3. Comparisons of determination toxic fenpyroximate by PbS quantum dots–gelatin nanocomposites with other methods.

Model	LOD ($\mu g\ L^{-1}$)	LDR ($\mu g\ L^{-1}$)	RSD (%)	References
Liquid mass chromatography	0.2	0.01-50.0	5.0	[8]
Micro liquid chromatography	0.2	0.01-10.0	5.0	[9]
Liquid chromatography	0.3	0.5-10.0	3.78	[10]
Molecularly imprinted polymers (MIPs)	0.2	0.1-10.0	2.9	[12]
Fluorescences (toxic Bentazon)	0.5	0.05-20.0	3.0	[14]
Fluorescences (toxic fenpyroximate).	0.2	0.02-20.0	2.0	This work

LDR, linear dynamic range is the minimum detectable concentration and the largest concentration that the response factor falls outside

advantages such as simple, mild condition, easy workup, and excellent yield in a short time. All these characteristics make PbS quantum dots–gelatin nanocomposites sensor a potential biosensor for drug measurement when juxtaposed against other commercial materials.

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طراحی یک روش فلورسنت با استفاده از سولفید سرب با ژلاتین از طریق نقاط کوانتومی برای تعیین مقدار حشره‌کش فنی پیروکسی میت در نمونه‌های آب

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چکیده

در این مقاله، یک حسگر شیمیایی سولفید سرب سنتز شد که با نقاط کوانتومی ژلاتین برای فنی پیروکسی میت عامل‌دار شده است. اندازه گیری فنی پیروکسی میت با استفاده از غلظت ($۲/۵\times۱۰^{-۳}$ مولار)، سنسور نانوکامپوزیت نقطه کوانتومی سولفید سرب-ژلاتین، pH =۶ و زمان ۴۰ ثانیه، طول موج ۳۲۸ نانومتر انجام شد. در شرایط بهینه، محدوده خطی حد تشخیص (۰/۰۲ تا ۲۰/۰ میکروگرم در لیتر) به دست آمد. انحراف استاندارد (LOD) کمتر از (۲/۰ درصد)، و محدودیت های تشخیص روش (۰/۰۲ میکروگرم در لیتر) برای تعیین فنی پیروکسی میت، بدست آمد. نتایج مشاهده‌شده بازیابی مناسب و حد تشخیص بسیار پایین برای اندازه‌گیری فنی پیروکسی میت را تأیید کرد. حسگر نانوکامپوزیت نقطه کوانتومی سولفید سرب-ژلاتین به عنوان حسگر عالی در کاربرد عملی فنی پیروکسی میت مربوط به مدیریت پسماند در نمونه‌های آب سطحی است.

واژه‌های کلیدی

فنی پیروکسی میت، حشره‌کش، فلوئورسانس، حسگر، اتصالات کوانتومی عرضی.