Colorimetric Assay for 4-Phenylthiosemicarbazide Detection in Environmental Samples Based on Prussian Blue Nanoparticles Formation Ion

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ABSTRACT: *In this research, a fast colorimetric method for the detection of 4-phenylthiosemicarbazid (4-PTSC) in environmental samples, is reported for the first time. Semicarbazide compounds have been used as pesticides or fungicides in agriculture and for chemical synthesis in industrial processes. With this method, one or the total amount of Semicarbazide in real samples can be detected within 6-7 min. For this purpose, 4-PTSC was determined and can be used as a representative of the Semicarbazide family. The assay principle is based on the oxidation of 4-phenylthiosemicarbazid (as reducing agent) with Ferric ions in the presence of ferricyanide ion and triton X-100 as a stabilizer, as well as the formation of Prussian Blue Nanoparticles (PBNPs). These nanoparticles exhibit a strong UV-Vis extinction band at 700 nm with high absorption coefficient (3.0×10^4 M^{-1} cm^{-1} at 700 nm). A UV-Vis spectrophotometer is used to monitor changes in the absorption intensity of PBNPs. A change in the color of the solution can be easily observed by naked eyes, in the presence of sub-ppm levels of 4-PTSC, which is directly related to the 4-PTSC concentration. TEM images showed an average diameter of 30 nm. The effect of several reaction variables on the formation rate of PBNPs was studied. Beer's law was obeyed in the concentration range of 0.20-3.20 µg/mL. The detection limit was found to be 0.10 µg/mL. This method was successfully applied for the determination of 4-PTSC in different environmental samples. Interfering species with reducing properties are not commonly present in environmental samples. Hence, this optical assay is simple and has acceptable selectivity.*

KEYWORDS: *Spectrophotometric probe. Pesticide; Prussian blue nanoparticles; Environmental samples.*

INTRODUCTION

Pesticides, fungicides and related hazardous compounds have played a major role in the improvement of agricultural productions and in the control of many disease vectors in the area of public health. However, their harmful effects on environmental quality and human health have been observed and investigated and have become a prominent issue at international levels [1-2]. The concentration of these hazardous compounds have been regulated in many samples such as drinking waters, fruits, vegetables, etc. by the European Commission and Food and Drug Administration among other agencies. The residues of hazardous compounds such as pesticides retained in crops through soil and water enter the food chain and are consumed by humans through foodstuffs and drinking water. Therefore, the determination of these is very important environmentally especially to the food quality parameter that has attracted a great amount of human labor and resources worldwide [2-5]. Therefore, many studies relating to the detection and determination of pesticides related compounds in different samples such as soil, sediment, plant, grain, and water samples have been conducted.

The development of sensitive and selective colorimetric sensors has become widely popular. This is partly due to their simplicity, rapidity, precision, and common availability of the basic equipment for laboratory and field uses [1, 6-7]. Nanotechnology and nanoscience, being an interdisciplinary subject of physics, chemistry, biology, and engineering, has advanced contemporary fundamental and application research in the past two decades. Nanomaterials possess interesting properties such as large surface area, high surface reactivity, and strong adsorption capacity. In the field of environmental monitoring, nanomaterials-based sensors showed great potential in the detection of trace contaminants [6, 8-13]. Nanomaterials play different roles in the design of sensors. For example, colorimetric sensors utilize the color changes of nanomaterials for environmental monitoring, such as silver nanoparticles [14-15], gold nanoparticles [16-18], and copper nanoparticles [19] etc. Recently, Prussian Blue Nanoparticles (PBNPs) as a new colorimetric Nano probe have been developed for the detection of chemical species [20-22]. Prussian blue is a well-known complex because it is considered to be the first synthetic coordination polymer compound reported in scientific literature. Prussian blue-type metal complexes, collectively called metal hexacyanoferrates, have been considerably investigated for practical applications. It has been widely used for the fabrication of electrochemical, optical and bio-sensors. PBs are promising organic–inorganic hybrid materials that exhibit interesting characteristics, such as photo-induced magnetization, electrochromism, excellent electron transfer mediators, and sensing [20-24]. The representatives of different oxidation states of PB are as follows: Prussian white ($[Fe^{II}Fe^{II}(CN)_6]_2^-$), and Prussian brown ($[Fe^{III}Fe^{III}(CN)_6]$). Some of them can only be obtained by electrochemical methods. These iron hexacyanoferrate exhibit multicolor electrochromic, depending on its redox state. Among them, PB can be easily obtained by the wet chemical method. Now, the preparation of PBs in nano size would enable their application in growing new nano devices. These NPs can be synthesized easily and show interesting optical properties. PBNPs have an intense absorption band near 700 nm due to transition from the ground to excited states, upon which an electron is transferred from a ground state $Fe_A(III)Fe_B(II)$ to an excited state $Fe_A(II)Fe_B(III)$ form. The molar absorption coefficient of the soluble form is 3.0×10^4 M^{-1} cm^{-1} at 700 nm [23-25].

In practical experiments, a colorimetric probes used for detection of 4-Phenylthiosemicarbazide (4-PTSC) (Fig. 1) which is used as pesticide and fungicide. It also possesses antibacterial properties attributed to electron delocalization in the semicarbazide moiety. In general, the semicarbazides are poisons and may be fatal if swallowed [26].

In this work, a new simple and fast colorimetric method were proposed for determination of 4-PTSC. To the authors best knowledge, no colorimetric or electroanalytical methods are available for the determination of 4-PTSC. PBNPs were synthesized by the reaction of $FeCl_3$ and $K_3Fe(CN)_6$ in the presence of a trace amount of 4-PTSC (as a representative of semicarbazide compounds) and one stabilizing agent. The semicarbazide family has hydrazine groups in their structures. Therefore, they can act as a strong reducing agent. When the concentration of 4-PTSC was increased, the absorption intensity of the formed PBNPs was increased and the enhanced intensity was linearly proportional to the 4-PTSC concentration. The intensity

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Fig. 1: (A)Schematic mechanism of 4-PTSC colorimetric detection and UV–vis absorption spectrum of PBNPs in the presence of 4-PTSC (2.0 μg/mL in optimum conditions),(B) A picture of the face-centered cubic structure of PB, (C) Transmission electron microscopy image of PBNPs.

of absorption of PBNPs was monitored at the maximum wavelength of 700 nm. A change in the color of the solution can be easily observed by naked eyes, in the presence of sub-ppm levels of 4-PTSC in environmental samples and was directly related to the 4-PTSC concentration such as a sensor. Most times, interfering species with reducing properties like the hydrazine family are not present in environmental samples. Hence, this optical assay is simple and has good selectivity.

EXPERIMENTAL SECTION
Materials

All the chemicals were of analytical reagent grade purity. 4-Phenylthiosemicarbazide was purchased from Sigma and potassium hexacyanoferrate(III)), Acetic acid, NaOH, HCl, ferric chloride, nonionic surfactant Triton X-100, and acetic acid were purchased from Merck (Darmstadt, Germany) and used without any further purification. Phosphoric acid (84–85%) was purchased from Fluka (Fluka, Buchs, Switzerland). All the experiments were performed at ambient temperature (25±2°C).

Instruments

UV–Vis absorbance spectra were recorded by utilizing a Cintra 101 spectrophotometer (GBC Scientific Equipment, Australia). Images of the nanoparticles were obtained by a Transmission Electron Microscope (TEM) (Zeiss EM 10C, Carl Zeiss Inc., Oberkochen, Germany), working at 80 kV.

Detecting 4-PTSC

Typically, to detect 4-PTSC appropriate amounts of the target solution were added to a 10 mL calibrated flask. Subsequently, 1.0 mL of 0.01 mol L^{-1} acetic acid, 1.0 mL of 100 μg/mL $K_3[Fe(CN)_6]$ solution, 0.1 mL Triton X-100 1% W/V, and 1.5 mL of 100 μg/mL ferric ion solution were added in succession. The mixture was then diluted to the mark with distilled water and mixed. Afterward, within 6–7 min, a portion of the mixture was transferred to a 1 cm spectrophotometric cell to record absorbance at 700 nm against a blank prepared with the same reagents, except 4-PTSC. The mechanism of formation of PBNPs is shown in Fig. 1. Also, Fig. 1 shows the UV–Vis spectrum that resulted from changes in the color of the mixture in the presence of 4-PTSC.

RESULTS AND DISCUSSION

Prussian blue-type metal complexes, collectively called metal hexacyanoferrates, have considerably been researched and studied for practical applications. The structure of transition metal hexacyanoferrate is three-dimensionally cross-linked with the cyano groups and contain two metal atoms or one metal atom (such as Co, Fe, etc) in two different oxidation states. The Prussian blue-type metal complex has a face-centered cubic structure in which two different iron centers Fe^{3+} and Fe^{2+} are joined by the cyanide groups (Fig. 1). In each network unit of PB, Iron (II) ions are linked by carbon atoms of cyanide ions, and Iron (III) ions are surrounded by the nitrogen ends of cyanides. Fig. 1 shows the mechanism of PBNPs formation. The reaction between 4-PTSC and Fe^{3+} ions is a simple redox reaction.

This method utilizes the detection system of potassium ferricyanide–Fe(III) for the determination of 4-PTSC. The experiment shows that Fe (III) is reduced to Fe(II) by semicarbazides at pH 4.0 in the presence of potassium ferricyanide. The in situ formed Fe (II) can react with potassium ferricyanide to form soluble Prussian blue ($KFeIII[FeII(CN)_6]$). While the amount of semicarbazide can be calculated based on the absorbance of the product. It is well known that the hydrazine group in the 4-PTSC and semicarbazide compounds has a reducing ability [27-28]; absorption peak appeared at about 700 nm, indicating the formation of PBNPs [28-29]. The TEM image of the PBNPs is shown in Fig. 1.

Effect of reaction time

Chemical oxidation is a well-known reaction that has been extensively exploited for the determination of some chemical species. In this study, 4-PTSC exhibited a kinetic behavior and the absorbance at 700 nm changed with time during the first few minutes from initiation of the reaction. The results showed that absorbance intensity increased with increasing reaction time. In the first few minutes from the initiation of the reaction, the color of the solution changed to blue-green, the absorbance changed slowly until reaching the maximum after about 6-7 min and remained nearly constant afterward. Fig. 2 shows the changes in absorbance at 700 nm versus time for the reaction of 4-PTSC with Fe^{3+} ions. As is obvious, the reaction of 4-PTSC with Fe^{3+} ions needed time and was almost completed within 7 min. Therefore, 7 min was chosen as the optimal reaction time.
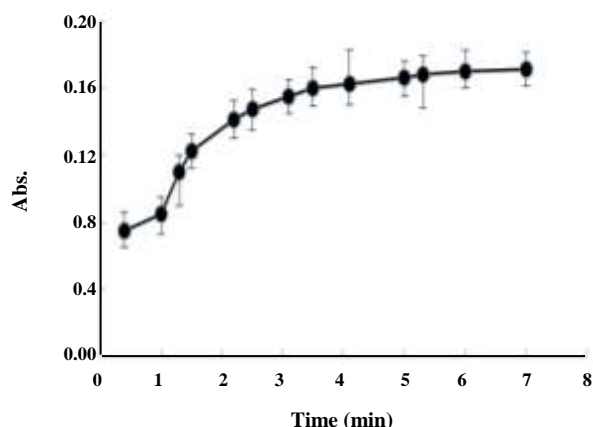
Fig. 2: Effect of reaction time from the addition of Fe^{3+} solution on absorbance [condition of 10 mL solution: 2.0 µg/mL 4-PTSC; 0.01 mol/LHCl; Triton X-100: 0.01% V/W; $K_3[Fe(CN)_6]$: 10 µg/mL; $[Fe^{+3}]$:15 µg/mL, n=3].

Fig. 3: Effect of pH variation on intensity absorbance [condition of 10 mL solution: measurement time: 7 min, 2.0 µg/mL 4-PTSC; Triton X-100: 0.01% V/W; $K_3[Fe(CN)_6]$: 10 µg/mL; $[Fe^{+3}]$:15 µg/mL].

Effect of acidity

Fig. 3 shows the effect of solution pH on absorbance intensity; it had a critical effect on the formation of PBNPs. The pH dependence of the process was studied in the range of 1.0–7.0. The experimental results showed that the absorbance of the PBNPs in acidic medium (about pH 2 to 4) was at the maximum level. For this purpose, different acid solutions ($HCOOH$, H_3PO_4, H_2CO_3, and CH_3COOH) with a concentration of 0.1M were prepared and used. Under the same conditions, acetic acid produced a greater signal in comparison to other acid solutions. pH values greater than 3 (pH>3) are not suitable for the reaction because of the formation of ferric hydroxide ($Fe(OH)_3$), and PBNPs which are unstable at higher pH values [20-21, 28]. Hence, the acetic acid solution was selected and different volumes of acetic acid solution were investigated and the optimum value was determined (Fig. 4).

Effect of stabilizer

Nanoparticles are generally unstable due to their high surface energy and need to be stabilized against agglomeration by using suitable stabilizers such as surfactants and polymers. It is known that the stabilization of nanoparticles in the dispersing medium can be achieved by either electrostatic or steric stabilization. Also, the shape and size of NPs can be controlled by varying the molar ratio of the stabilizer to precursor and decreasing the size of these transition metal
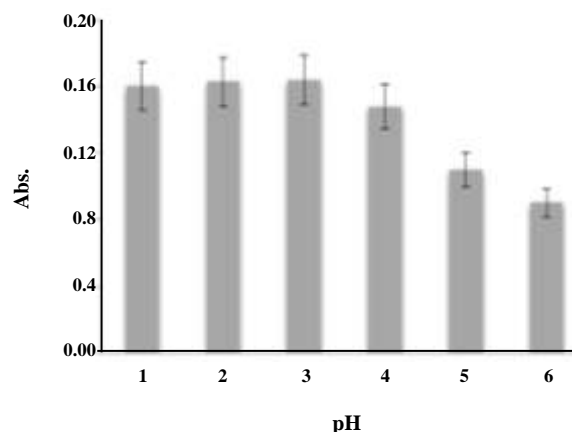
hexacyanoferrates which plays an important role in terms of application. The smaller sizes improve the activity and dispersibility of these transition metal hexacyanoferrates compound. Generally, the nanoparticles formed by colloidal methods (wet method and …) have high free energy state and therefore tend to aggregate due to Van der Waals forces and lower their energies [18, 29]. Surfactants are common stabilizers that have been used as stabilizers to prevent nanoparticle agglomeration because they provide steric stabilization [29]. In this study, nonionic surfactant Triton X-100 was selected as the stabilizer. Different amounts of surfactant stock solutions (1% (w/v)) were added to the reaction mixture. Results revealed that the addition of more than 0.1 mL of the surfactant solution had a significant effect on absorption intensity. Hence, 0.1 mL of 1% solution of the surfactant was chosen and used.

Effect of Fe^{3+} and $K_3[Fe^{3+}(CN)_6]$ concentration

The influence of potassium ferricyanide concentration was also investigated in this research. It was found that the effective intensity was a maximum value when the concentration of potassium ferricyanide was 10.0 µg/mL, which indicated that the amount of formed PBNPs reached its maximum value. Therefore, 10.0 µg/mL of potassium ferricyanide was selected as the optimum concentration. Also, the effect of Fe^{3+} concentration on the absorption intensity of the reaction was investigated. When Fe^{3+} concentration was in the range of 10.0–20.0 µg/mL in the presence of about 2 µg/mL of 4-PTSC,

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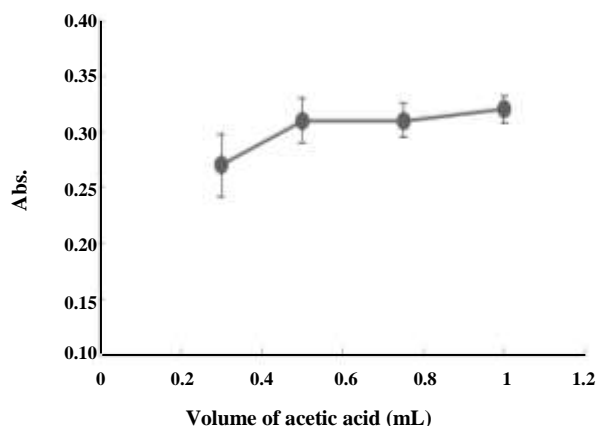*Iran. J. Chem. Chem. Eng.*   *Hatamie A. et. al.*   *Vol. 36, No. 1, 2017*

Fig. 4: Influence different amounts of acetic acid solution on absorbance intensity: [condition of 10 mL solution: measurement time: 7 min, n=3, 2.0 μg/mL 4-PTSC; Triton X-100: 0.01% V/W; $K_3[Fe(CN)_6]$: 10 μg/mL; $[Fe^{+3}]$:15 μg/mL].
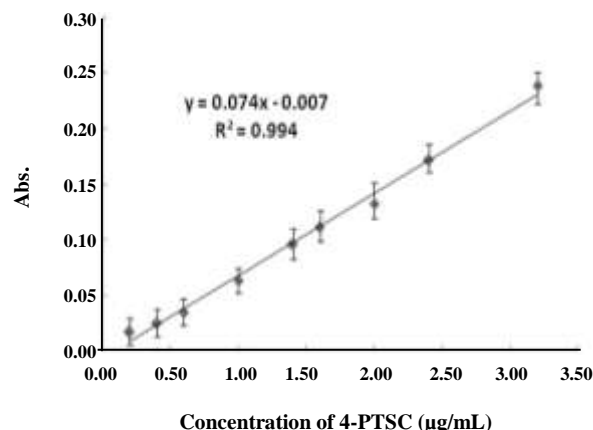

Fig. 5: Calibration curve of the relationship between absorption intensities and 4-PTSC concentrations [Condition of 10 mL solution: 0.2, 0.4, 0.6, 1.0,1.2, 1.6, 2.0, 2.4 and 3.2 μg/mL 4-PTSC (n=9); 0.001 mol/L acetic acid; Triton X-100: 0.01% V/W; $K_3[Fe(CN)_6]$: 10 μg/mL; $[Fe^{+3}]$:15 μg/mL, measurement time: 7 min, n=3] .

the absorption intensity of the system reached its maximum value. Therefore, the Fe^{3+} concentration of 15.0 μg/mL was selected and used in further studies (data not shown).When the Fe^{3+} concentration was low, the absorption intensity decreased as a result of the incomplete reaction.

Calibration graph, limit of detection, precision, and tolerance of foreign substances

The calibration graph for the determination of semicarbazide was described under the optimum conditions. The method showed good linearity over the calibration range of 0.2-3.2 μg/mL and the linear regression equation was y = 0.074x - 0.007 with the correlation coefficient (R^2) of 0.9940, the curve is shown in Fig. 5.

According to the IUPAC definition, the limit of detection (LOD) is 0.10 μg/mL (calculated by $3S_b/m$, here $3S_b/m$ [30] refers to the quotient between triple of the blank reagent's standard deviation and slope of the working curve and S_b shows the standard deviation of parallel analysis of the blank samples) and m is the slope of the calibration graph. The Limit Of Quantitation (LOQ) is 0.27 μg/mL, obtained by the formula $LOQ=10S_b/m$. The relative standard deviation (R.S.D.) for the determination of 0.30 and 2.00 μg/mL of 4-PTSC was 7.5 and 6.3% (n = 5), respectively. In order to study the effect of various species on the determination of 4-PTSC,

the influence of some possible coexisting foreign substances including inorganic ions (Al^{3+}, Ca^{2+}, Zn^{2+}, Ba^{2+}, K^+, Na^+, NO_3^-, CO_3^{2-} ,PO_4^{3-}, NH_4^+, and Cl^-) was tested for the analysis of real samples. For this purpose, the fixed amount of 4-PTSC (1 μg/mL) was taken with different amounts of foreign species and the recommended procedure was followed. As can be seen in Fig. 6, no color change intensity was observed in less than 6 min for the common ions, even at 100-fold higher concentrations than those of 4-PTSC. This selectivity can be visualized by naked eyes (Fig. 6).

Determining 4-PTSC in real sample

In order to test the practicality and verify the accuracy of this sensor in a real matrix, the content of 4-PTSC was determined in real samples matrix (water and soil samples) according to the experimental method. For this purpose, the spiking method was used and applied for the determination of 4-PTSC in river water sample (Karun River, Ahwaz, Iran) and a local spring water sample. To evaluate the sensing system, 5 mL of each water sample, without any pretreatment, was spiked with the known amount of 4-PTSC and then analyzed with the purposed method; the experimental results are listed in Table 1. Based on the obtained results, 4-PTSC was rapidly detected in real matrix samples and acceptable results (Recovery percent) were found.

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Table 1: Results of determining 4-PTSC in real samples matrix.

Sample	Add (µg/mL)	Expect (µg/mL)	Find[2] (µg/mL) (n=3)	Recovery[3] (%) (n=3)
River water [1] sample	-	ND	-	-
	0.60	0.60	0.640±0.001	106.6
Spring water sample	-	ND	-	-
	0.60	0.60	0.620±0.002	103.3
Soil sample	-	ND	-	-
	0.60	0.60	0.560±0.002	93.3
	0.80	0.80	0.770±0.001	96.3

1) Water sample of Karoon river in the south of Iran. 2) Average value of three determinations ± standard deviation.
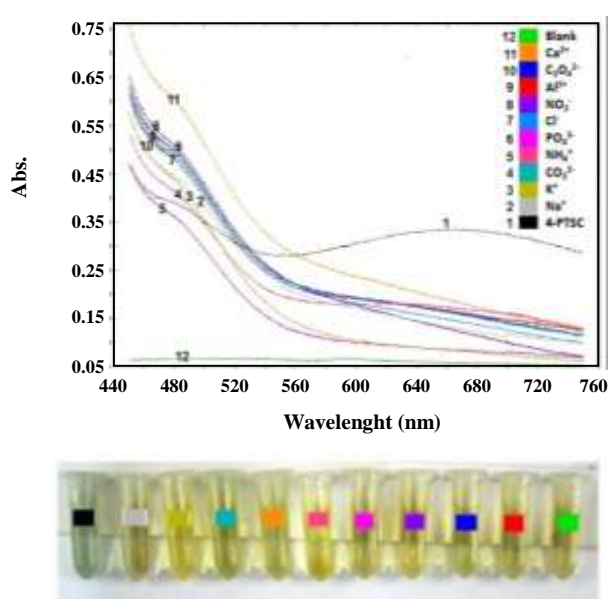3) Average value of three determinations. ND: not detected.

Fig. 6: Photographic images of the colorimetric response of the proposed optical sensor to various ions in optimum conditions and absorption spectrums of the solution of 4-PTSC and 100 ppm of different ions in the same conditions (1 µg/mL 4-PTSC and 100 µg/mL of different ions in the optimum conditions).

Also, the soil samples (4 samples, 2 g each) used in this study were accurately collected and weighed from a garden in different places and mixed, no pesticides had been used in this place. The samples were kept in airtight chamber glass containers at 5°C and used for spiking analysis.

A 2.0 g portion of the soil sample was transferred to a screw-capped 10 mL glass vial. In the next step, the determined volume of the standard solution of 4-PTSC was added to the soil sample and mixed. Then,

the soil sample was mixed with acetone solvent (4 mL). The vial was capped and mixed. The slurry was mixed for 3 min and then the sample was centrifuged and the extraction solvent in the upper portion was poured into a clean test tube and kept at room temperature. Then, the extracted analyte was transferred to a 10 mL flask and spiked and analyzed using the proposed method in optimal conditions. The experimental results are listed in Table 1.

CONCLUSIONS

It is an inexpensive, and easy-to-use optical sensor, with a low-cost development process that makes it possible for the *in situ* detection of 4-PTSC pesticides or other semicarbazides in environmental samples. The assay was based on the formation of PBNPs induced by the analyte itself. To the best knowledge of the authors, this work presents the first colorimetric method for detecting 4-PTSC pesticide. Furthermore, 4-PTSC could be detected when the concentration is at the sub-ppm level (without any pre-concentration step) by naked eyes alone, less time-consuming, without resorting to advanced readout equipment. Also, it could be used to detect the total semicarbazide compounds in future real samples.

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