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In the present study, a highly selective optical sensor for the measurement of Pd^{2+} was created by immobilizing 4-(2-amino-3-hydroxypyridine-4-ylazo) 1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one (AHDDO) on an agarose membrane. The proposed sensor has excellent optical properties that make it suitable for use as an optical sensor, including good selectivity, low cost, appropriate lifetime, rapid and reproducible regeneration, and ease of manufacture and handling. The sensor also demonstrated a rapid response time, a suitable linear calibration curve, and low detection and quantification limits. By the means of an easy and low-cost methodology, satisfactory experimental results were achieved for the determination of Pd^{2+} ion by the prepared sensor. Without any significant interference from other metal ions, the suggested sensor can be used for the quantitative and qualitative measurement of Pd^{2+} ions in various real samples.

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Fabrication of a novel palladium membrane sensor to its determination in environmental, and biological samples

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A novel sensitive, specific, and reversible optical sensor for the palladium(II) ion was created by impregnating an agarose membrane with 4-(2-amino-3-hydroxypyridine-4-ylazo)1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one (AHDDO). Spectrophotometric studies of complex formation between AHDDO base ligand and Mn^{2+}, Cd^{2+}, Co^{2+} Hg^{2+}, Zn^{2+}, Cu^{2+}, Pd^{2+}, Sr^{2+}, Al^{3+}, Fe^{3+}, Au^{3+}, and Ag^{+} metal ions in ethanolic solution indicated a substantially larger stability for the palladium ion complex. Therefore, the AHDDO was immobilized on a clear agarose film and used as a suitable ionophore for the building of a selective Pd^{2+} optical sensor. By combining the sensing membrane with Pd^{2+} ions at pH 5.75, a transparent color change from orange to violet was observed. On the immobilization of AHDDO, the effects of ionophore concentration, pH, temperature, stirring, and reaction time were investigated. A linear relationship was observed between the membrane absorbance at 633 nm and Pd^{2+} concentrations in a range from 15–225 ng mL^{-1} with a detection (3σ) and quatification (10σ) limits of 4.25 and 14.25 ng mL^{-1}, respectively. For the determination of Pd^{2+} ions, no significant interference from at least 400-fold excess concentrations of a number of possibly interfering ions was found. The sensor exhibits remarkable selectivity for Pd^{2+} ions and can be regenerated through exposure to 0.15 M HNO_3. The sensor has been successfully used to find palladium in biological, soil, road, and water samples.

Keywords: Optical sensor; Azo dyes; palladium determination; Agarose membrane; Colorimetry; Environmental analysis.

1 Introduction

Noble metals, particularly palladium (Pd), are widely used in the electrical industry.[1] Palladium's significance has expanded in recent years as new applications for dentistry, medical equipment, jewelry, and vehicle catalytic converters have emerged.[2] Despite the evident benefits of automobile catalysts, palladium emissions into the environment are linked to the production and recovery of emissions controls in the manufacturing industries, as well as the functioning of car catalysts. Precious metals with unique physical and chemical properties are significant materials that have recently seen widespread application in industry and technology.[3,4]

Palladium is widely known for its capacity to treat viral infections (leukemia and AIDS) as well as its anti-cancer activity.[5] Certain palladium compounds have been described as a potential threat to people, causing asthma, allergies, rhino conjunctivitis, and other major health problems, and are easily transmitted to biological material and

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eventually amplified along the food chain.[6,7] Palladium salts have been proven to be highly toxic to aquatic plants even at low concentrations.[8] According to a World Health Organization report,[9] data on Pd^{2+} losses from automobile exhaust emission control catalysts is currently sparse.

Palladium monitoring in environmental samples is a crucial issue for assessing the dangers to the ecosystem and human health that may arise in the future due to its broad spectrum of applications.[10] Concentrations of palladium in surface fresh waters and surface salt waters were found to be in the range of 0.4 to 22 ng L^{-1} and 19 to 70 ng L^{-1}, respectively whereas in the dense traffic road soil samples, concentration of palladium was found to be in the range of less than 0.7 to 47 μg kg^{-1}. Palladium exposures are thought to pose a number of potential dangers to both human health and the environment, according to the World Health Organization. Palladium appears to be consumed by humans in diets up to 2.0 μg per day on average.[11] A significant field of research now involves quantitative techniques for detecting Pd(II) and other contaminants in industrial, environmental, geophysical, and biological samples.[10–13] Even while modern technology makes it feasible to detect analytes at extremely low concentrations, most samples contain far less palladium than would be necessary to make a direct determination. Consequently, before making the actual determination, proper enrichment procedures are necessary.[14]

To date, different kinds of conventional analytical techniques like atomic absorption spectroscopy (AAS)[15] flame atomic absorption spectroscopy,[16] electro-thermal atomic absorption spectroscopy,[17] inductively coupled plasma mass spectrometry (ICP-MS),[18,19] inductively coupled plasma atomic emission spectroscopy (ICP-AES),[20] [30], X-ray fluorescence (XRF),[21] high performance liquid chromatography (HPLC),[22] electrochemical[23] and voltammetry,[24] have been widely adopted for quantitative and qualitative analysis of palladium. However, their affordability and effectiveness in detecting palladium are limited by high equipment costs and time-consuming sample pre-treatments. When Pd(II) is present in environmental samples, its low concentration (at μg L^{-1}) combined with the high concentration of interfering matrix components frequently necessitates a matrix separation step accompanied by an enrichment step. This allows for an accurate and precise determination of Pd(II) in samples with very low analyte contents.[25] As a result, there is a great need for designing and building novel instruments for the detection and identification of diverse contaminants in the environment.[26–34]

Optical chemical sensors (optodes), which are cost-effective and selective tools for determining the presence of heavy metal ions, have undergone significant development in recent years.[32–36] To provide straightforward and quick measurement methods with improved selectivity and low detection limits, optodes are typically employed in conjunction with low-cost spectrophotometric techniques.[37,38] One of the critical steps for building optical sensors is immobilization ionophores on transparent membranes. The ionophore immobilized is accomplished by either physical entrapment,[39] sol–gel,[40] multilayered films[41] or chemical (covalent) bonding methods.[42] On the other hand, covalently bonded sensors have reproducible responses and lengthy lifetimes.[43] Different approaches to covalent immobilization can be found in the literature.[44] Ionophores are essential components in the fabrication of optical sensors. Because azo dye ligands can create stable complexes with transition metal ions, they are commonly utilized as ionophores in the development of membrane sensors. For a particular ion, they exhibit extraordinary selectivity, sensitivity, and stability.[45]

The most widely used techniques are spectrophotometric ones, which are still very popular. Spectrophotometric techniques are appealing due to the instrumentations widespread availability, the procedures' simplicity, and the

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technique's speed, precision, and accuracy. Optical sensors, which are crucial for biological imaging, provide relatively straightforward, sensitive, and affordable detection techniques for interested analytes. As a result, numerous optical sensors for the colorimetric and fluorometric detection of palladium have been developed.[46–50]

Agarose is a strongly hydrophilic, chemically inert and microbiologically resistant material.[51] It is quite stable in gel form and is the most widely used support in affinity chromatography.[52] Chemical compounds containing primary aliphatic or aromatic amines can be covalently bonded to activated agarose beads. Agarose has been used for manufacturing of an optical fiber humidity sensor.[53] compared to PVC use of hydrophilic agarose as a support for the fabrication of covalently immobilized optical sensors has the advantage of being easily manufactured and handled. According to our review of the literature, no species has yet used 4-(2-amino-3-hydroxypyridine-4-ylazo)1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one (AHDDO) as a sensing agent. In order to build a selective optical sensor for the spectrophotometric detection of Pd^{2+} in aqueous real sample solutions, AHDDO is covalently immobilized on an agarose membrane and used as an efficient ionophore with N and O donor atoms.

2 Materials and methods

2.1. Instrumentation

An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. A Shimadzu model 670 atomic absorption spectrometer with flame atomization was used. The operating parameters were set as described by the manufacturer. A Perkin Elmer (USA) graphite furnace atomic absorption spectrometry model A Analyst 300 was used in a nitrous oxide–acetylene flame for all GFAAS measurements. UV–vis spectrophotometer model V 53 from JASCO (Tokyo, Japan) was achieved for recording the spectra and the absorbance measurements. The absorbance measurements were given by mounting the optical membrane sensors samples ($1\times9\times50$ mm^3) inside a quartz cuvette. The absorbance measurements of the optical membrane sensors samples were obtained with respect to air as well as blank sensor sample. A Hamilton syringe (10 µL) was performed to transport minor Pd^{2+} ion volumes into the cell. The film thicknesses of the sensing slides were measured by using digital microscope (Ray Vision Y 103) that was coupled with video camera (JVC TK-C 751 EG) and a digital micrometer (Mitutoy, Japan) with an accuracy of ± 0.001 mm.

2.2. Preparation of reagent

The AHDDO azo dye under investigation is prepared by the common way used for preparing azo dye derivatives of aromatic amines. The aromatic amine involve aminoantipyrane, 0.01 mole of the aminoantipyrane was converted to the hydrochloric form by adding the least amount of 1:1 HCl then diluting with water and cooling at –2.0 °C. A cooled solution of $NaNO_2$ (0.01 mole) is added gradually with continuous stirring to the amine salt. The resulting diazonium salt solution is allowed to stand in ice bath for 15 min with stirring at –2.0 °C and added gradually to a solution of 0.01 mole of 2-amino-3-hydroxy pyridine dissolved in 10% NaOH which cooled at –2.0 °C. The resulting solution is allowed to stand for 15 min with constant stirring until the azo dye completely formed. The obtained azo is filtered off, dried and recrystallized in ethanol. The purity of the resulting azo compounds is checked by measuring the melting point constancy. The chemical structure of AHDDO is detected by elemental analysis (C, H, N), IR and ^{1}H-NMR spectra. The separated azo have the following structural formula:

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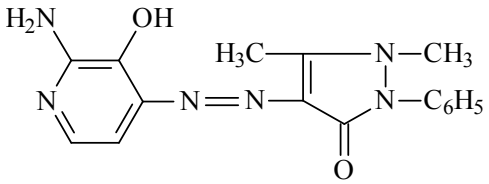

4-(2-amino-3-hydroxypyridine-4-ylazo)1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one (AHDDO)

2.3. Chemicals

All chemicals are of analytical-reagent quality and freshly deionized water was used throughout. For fabrication and preparation of membrane, agarose and epichlorohydrine supplied by Merck Chemical Company. The solutions of pH 2.75–10.63 universal buffer were prepared as described earlier.[54]

2.4. Procedures for spectrophotometric titrations

2.0 mL of the AHDDO ionophore solution (1×10^{-4} M) in ethanol was transferred into a quartz cell of the spectrometer. Microliter amounts of 1×10^{-3} M solution of each metal ion were transferred to the ionophore solution by a 50 µL microsyringe. Each spectrum was recorded immediately after vigorous mixing of the solution. All the absorbances data were corrected for the dilution.

A method described elsewhere[55,56] was used for preparation and epoxy activation of agarose membranes with a thickness of 0.25 mm from 4.0% agarose aqueous solution. The transparent-viscose solution was dispersed between two 20 cm × 20 cm dust-free glass plates, applying a gentle pressure. Borders of one of the glass plates were already lined with a 0.20 mm thickness tape to adjust the thickness of the membrane. For the epoxy activation, an epichlorohydrine method was used.[57] The membranes were cut into 1 cm × 3 cm pieces and stored at 4 °C under 50% ethanol solution before the use. For immobilization of the AHDDO, the agarose membranes were treated with a 1×10^{-2} M AHDDO solution, in an alkaline medium, with a method described elsewhere.[55] The resulting orange color membranes were thoroughly washed with 50% ethanol on a glass filter, soaked in 50% ethanol overnight, and washed vigorously by water to displace any non-bond dye. A 1 cm × 3 cm piece of the fabricated membrane sensor was cut and mounted in a polyacrylamide holder and placed inside the quartz cell of the spectrophotometer. The cell was then used as usual for the absorbance determinations. All the measurements on the agarose membranes were performed in aqueous medium.

2.5. Procedure

The membrane was carefully placed into the spectrophotometer cell, which had been previously filled with 2.5 mL of buffer solution adjusted to pH 5.75. Subsequently, a solution containing Pd^{2+} ions at a specific concentration was introduced, and the absorption spectrum was recorded over the wavelength range of 350–750 nm at 10 mm intervals, using a reference membrane. All measurements were carried out at 35 °C. The calibration curve was generated by plotting the absorbance values obtained from a series of standard solutions with varying concentrations of Pd^{2+} ions. To determine the Pd^{2+} ion content in the sample, the calibration curve was employed. For membrane regeneration, a 2.0-min treatment in a 0.15 M HNO_3 solution was conducted, preparing the sensor membrane for subsequent use.

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2.6. Analysis of water samples

In Egypt's Benha during the month of November 2024, several water samples were taken. A one-liter polyethylene bottles with stopper are used to store the samples. The samples (1.0 L) were kept at 4.0 °C to collect particles in a refrigerator after being filtered using a membrane filter with a 0.45 m pore size and acidified with 1.0% v/v HNO_3. The organic interferences in the samples oxidize when 1.0% H_2O_2 and strong nitric acid are present. In order to bring the pH to 5.75, a universal buffer solution is needed. The suggested and FAAS were used to calculate the analyte concentrations in the samples. The membranes is stored for two week in 50% ethanol/water (v/v) solution to be used without any effect on the water quality.

2.7. Road dust sample

Using a small brush and a plastic pan, road dust samples that may be containing ultra-trace amount of Pd^{2+} were collected from the free Benha-Cairo and Benha-Zagazig roads in Egypt. The samples were dried in a 100 °C oven for 24 hours without the need to sieve the substance first. In a PTFE vial, 0.2 g of the dust (road dust) sample was weighed. Aqua regia 3.0 mL was added. The mixture was nearly dried out through heating. The mixture was heated once again for two hours after 3.0 mL of aqua regia and 1.0 mL of 40% HF were added. Following the addition of 2.0 mL of 65% HNO_3, the mixture was heated until it was dry. To ensure the complete elimination of HF, the final procedure was repeated twice. The residue was diluted to 50 mL with deionized water. The digest was centrifuged for 20 min at 3000 rpm in order to separate the solid residue. The sample acidity was adjusted to pH 5.75 with universal buffer. A blank solution characterizing the procedure was prepared in the same way.

2.8. Determination of palladium in soil samples

In Benha, Egypt, a soil sample was taken from the area surrounding Farid Nada Street. The material was ground after drying at 100 °C for two hours. A beaker was filled with 5.0 g of the soil sample or the certified reference material GPP-10 (generator: GEOSTATS PTY LTD, Australia; sample type: reference ore). Following the addition of 15 mL of aqua regia, the mixture was boiled almost to dryness. Once more, 15 mL of aqua regia was added to the leftover to finish the digestion, and the mixture was boiled almost to dryness. The sample combination was cooled, added 20 mL of distilled water, and then filtered through Wattman filter paper. The pH of the solution under the filter was adjusted to 2.0-3.0, and then it was transferred into a 100-mL volumetric flask, and diluted with water. A fresh garlic sample was dried for some days and in an oven at 45 °C to a constant weight. 2.5 g of the dried sample was transferred into a beaker, to which 10.0 mL of concentrated nitric acid was added. It was placed on a hot plate to get semi-dried. Again, 10 mL of conc. HNO_3 and 2.0 mL of H_2O_2 were added, and the solution was kept on the hot plate in order to complete the digestion. Following drying, it was cooled, 20 mL of water was added, and a Wattman filter paper was used to filter the mixture. The sample solution was brought to a pH of 5.75, transferred to a volumetric flask of 100 mL, and then diluted with water.

2.9. Determination of palladium in biological samples

A 100 mL volumetric flask was filled with approximately 2.0 mL of whole blood samples, 3.0 mL of HNO_3 2.0 M solution, and then 1.0 mL of hydrogen peroxide. The flask was manually shaken to promote sample oxidation before deionized water was added to bring it up to volume.

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For the decomposition of urine sample, 20 mL of urine and 1.0 mL of concentrated nitric acid, are mixed in a 70 mL quartz vessel and slowly heated up in order to concentrate the volume to about 2.0 mL. Afterwards, a further 4.0 mL of concentrated nitric acid and 0.5 mL of 12 M hydrochloric acid are added and this sample is digested in a high pressure asher (HPA®) for 50 min at a temperature of 320 °C and a pressure up to 130 Pa. The volume is eventually lowered to roughly 0.5 mL in order to eliminate any additional acids from the resultant solution. Losses of the analytes could happen if evaporation to dryness is not prevented. The blank was created by substituting high-purity water for the human serum or urine sample, and it was then put through the same process as stated above.

2.10. Determination of palladium in tea samples

Samples of tea grown on agricultural land may contain small amounts of Pd^{2+} ions were tested. A 50 mL beaker containing 10 mg of dry tea that had been dried at 110 °C was then filled with 7.0 mL of concentrated nitric acid. The beaker was then covered with glass, and the contents were heated at 150 °C for 15 minutes. After cooling the sample, 3.0 mL of H_2O_2 was added, and the mixer was once more heated to 200 °C for roughly an hour, or until the solution was clear. After removing the glass watch, the acid was heated to 150 °C and evaporated to dryness. 5.0 mL of 1.0 M nitric acid was used to completely dissolve the white residue, and the resulting solution was then poured into a 100 mL volumetric flask. After that, the solution was properly neutralized with NaOH solution. The resulting solution was diluted to the mark and adjust the pH to 5.75, and the recommended procedure was followed.

3 Results and discussion

3.1. Spectrophotometric studies

Pd^{2+} has a strong attraction for soft coordination centers like nitrogen and oxygen.[58] The detection systems based on oxygen-containing ligands have generally demonstrated higher selectivity and sensitivity among the many types of palladium optode detection systems.[59] As a result, the possibility of using AHDDO with an oxygen-containing site as an active ionophore for highly accurate and sensitive Pd^{2+} ion detection was explored. By using spectrophotometric titration, the complexation of Pd^{2+} with AHDDO in ethanol solution was studied. Fig. 1 depicts the absorption curves, which peak at about 444 nm due to AHDDO. A reduction in absorbance at this wavelength is seen with the addition of Pd^{2+}. By decreasing the absorbance at 444 nm, a peak at about 567 nm is formed that corresponds to the formation of a Pd^{2+}–AHDDO complex. For the other studied metal ions (Mn^{2+}, Cd^{2+}, Co^{2+} Hg^{2+}, Zn^{2+}, Cu^{2+}, Pd^{2+} , Sr^{2+}, Al^{3+}, Fe^{3+}, Au^{3+}, and Ag^{+}) no effective complexion is detected. The resulting plots of the absorbance (at 567 nm) against metal ion/ligand mole ratios are shown in Fig. 2. From the sharp inflection point observed for Pd^{2+} at a mole ratio of 0.5, it can be immediately concluded that a 1:2 complex of [Pd–$(AHDDO)_2$] is formed in ethanol solution. Using existing formulae and the nonlinear least-squares curve-fitting program KINFIT, the formation constant of the resultant complex between Pd^{2+} and AHDDO was calculated to be equivalent to 4.58 from the absorbance versus [Pd^{2+}]/[AHDDO] mole ratio data.[60,61] Evidently, the curves for the other metal ions in Fig. 2, indicate their negligible complex formation by AHDDO. Thus, based on the results obtained from solution studies, AHDDO was expected to act as a suitable and highly selective ionophore in the preparation of an agarose-based ion-selective optode for Pd^{2+} ion determinations.

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3.2. Ligand immobilization on agarose membranes

The optical characteristics of AHDDO were somewhat altered by its immobilization on an agarose membrane. When AHDDO was immobilized, the absorbance maximum changed from 444 nm to roughly 458 nm in the redshift (Fig. 3), most likely as a result of the ligand's more flattened shape, which would make it easier for electrons to resonant. A similar shift (from 567 to 633 nm) was observed for an absorbance maximum of the Pd^{2+}-AHDDO complex after the ligand immobilization on the agarose membrane (Fig. 3). During the titration, no measurable spectral shift was observed, which is typical for an absorption process involving a strong complex formation. The concentration of AHDDO as an ionophore, pH, and temperature all affect how much AHDDO can be loaded onto the agarose membrane. Due to the membrane-damaging effects of higher temperatures and the unsuitable immobilization at lower ones, 35 ℃ was chosen in this case. The influence of the ionophore concentration was investigated in the range of 5×10^{-5} to 1.5×10^{-2} M at λ_{max} = 458 nm. As it is obvious from Fig. 4, a continuous increase in the membrane absorbance was monitored by increasing the ionophore concentration until 1×10^{-2} M. High loadings, however, may unacceptably decrease the absorbance of the membrane. Thus a concentration of 1×10^{-2} M of the AHDDO was chosen as an appropriate concentration in subsequent experiments. Fig. 5 shows the influence of pH of the reaction solution on the maximum absorbance of the membrane. By adding the proper amounts of universal buffer solution with a pH range of 2.75 to 10.63, the pH of the solution was adjusted. It was discovered that a pH 7.75 solution results in the highest immobilization of the AHDDO.

3.3. Effect of pH of test solution on the sensor response

The response of the suggested Pd^{2+} ion-selective optode is illustrated in Fig. 6 as being affected by the pH of the tested solution. The optode membrane's response characteristic was very pH dependent. Changing the pH from 3.56 to around 5.75 caused an immediate increase in absorbance, but pH values higher than 7.51 caused a drop in absorbance (Fig. 6). The diminished response at the low pH region may be explained by the extraction of H^+ from the test solution into the membrane, via protonation of the nitrogen atom of AHDDO, resulting in an expected change in the formation of a Pd^{2+}– AHDDO complex. On the other hand, the reduced optical response of the proposed sensor at pH >7.51 could be due to a possible hydroxide formation of Pd^{2+} ions {$Pd(OH)^+$ and $Pd(OH)_2$}. Thus, in subsequent experiments, pH 5.75 was used for absorbance measurements.

3.4. Effect of temperature on the sensor reaction

The effect of temperature on sensor performance is investigated. The absorption spectra were recorded at 633 nm at a range of temperatures between 25 and 60 °C (Fig. 7). The absorbance at 633 nm rises with increasing Pd^{2+} sample temperature up to 35 °C, then falls due to thermal quenching associated with rising ion lattice vibrations[58] and declining complex formation with membrane. Increasing temperature to ≥ 60 °C; there in no variation in absorbance indicating no complex formation between Pd^{2+} and AHDDO. The best temperature to obtain highly sensitive and selective results was 35 ± 2.0 °C.

3.5. Effect of stirring

The response of the produced sensor is significantly influenced by stirring the Pd^{2+} solution. When the Pd^{2+} solution was stirred in comparison to the non-stirred solution, an improvement of almost seven times was obtained (Fig. 8).

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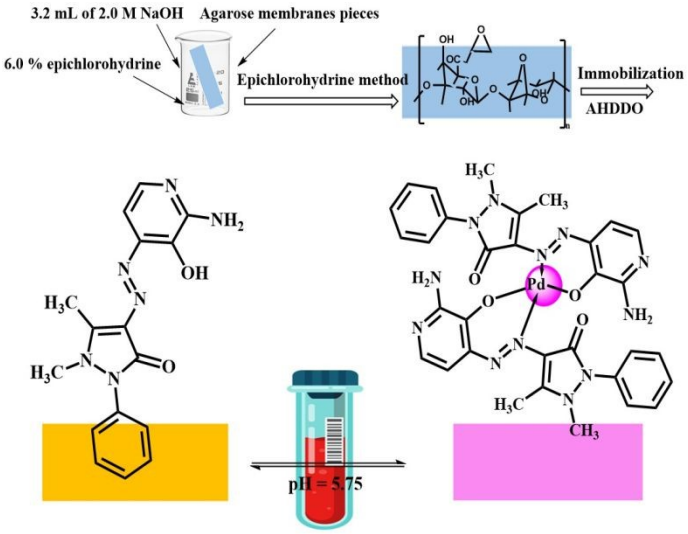
This observation can be explained by the movement of Pd^{2+} ions towards the immobilized AHDDO. The stirring process has accelerated the Pd^{2+} ion-AHDDO reaction as well as the Pd^{2+} ion diffusion across the membrane to the AHDDO (Fig. 8). The concentration gradient is the only variable that affects the diffusion of Pd^{2+} ions across the membrane during the non-stirring procedure.[62]

3.6. Effect of membrane thickness

Various membrane thicknesses were tested to choose the optimum ones. The absorption spectra were recorded at 633 nm at a membrane thickness between 15 and 50 mm. The thickness of the membrane was exactly assessed during the experiments by a digital microscope (Ray Vision Y 103) that was connected to a video camera (JVC TK-C 751EG). The absorbance at 633 nm rises with increasing thickness up to 25 mm, and constants until it reaches to 35 nm, then falls after 35 nm due to the extraction mechanism[63] and declining complex formation with the membrane. The optimum thickness of sensor membrane prepared was established to be 25 ± 2 mm. This is because the membrane is not too thick (>100 mm) and/or not too thin (<5.0 mm) and is reasonable to be applied as a transducer for sensor membrane depending on the extraction mechanism.[63]

3.7. The sensor response time

It is clear that for 150 ng mL^{-1} Pd^{2+} at pH 5.75, the time required to reach the 97% steady state response is less than 5.0 min. The concentration of the analyte ion, membrane thickness, membrane diffusion, the rate of complex formation between the Pd^{2+} ion and AHDDO, and the rate of complex dissociation are some of the factors that affect this type of optode membrane's reaction time. At high concentrations of Pd^{2+} ions a rapid response was achieved, which resulted in a large change in response (3.0 min for 1.0 µg mL^{-1}). The optode membrane's response time was shown to be slower at low Pd^{2+} ion concentrations (5.0 min for 150 ng mL^{-1}). The response time typically ranged between 4.0 and 6.0 min and decreased as the analyte concentration increased. With a thicker membrane, it took noticeably longer to get a lower Pd^{2+} concentration.[64,65] The proposed mechanism for the preparation and interaction between the AHDDO sensor and the Pd^{2+} ions and its complexation is depicted in Scheme 1.



Scheme 1. Schematic representation for the preparation, and complexation of the formed optode.

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3.8. Reproducibility, short-term stability and lifetime

When assessing a membrane optode's appropriateness for selectively determining an interest ion, reproducibility and stability are two crucial factors to consider. The numerous applications of the optode for Pd^{2+} monitoring in test solutions at two concentration levels of 100 and 150 ng mL^{-1} were used to assess the reproducibility of the response. Following each absorbance test, the membrane was restored in less than 2.0 minutes by soaking in a solution of 0.03 M EDTA and 0.02 M HCl, respectively. A good reproducibilities were obtained at both Pd^{2+} concentration levels. The calculated relative standard deviation (RSD) values from the results were 1.68% and 1.82%, respectively, which are satisfactory and highly accurate. The short-term stability of the optode membrane was investigated by monitoring its absorbance values during its contact with a 150 ng mL^{-1} solution of Pd^{2+} at pH 5.75 over a period of 12 h. From the absorbance measurements in 30 min intervals (n = 24), it was found that the response was almost unchanged with only 3.5% increase in absorbance at 633 nm after the 12 h period. Meanwhile, it was found that the membrane optode could be stored in 20% ethanol at 4 °C, without any measurable change in its absorbance value at 633 nm over a period of one months. Therefore, there is no ionophore leaching from the membrane during this period and it is quite stable over at least one months.

3.9. Efficient sensor membrane regeneration

Complete recovery of the sensor membrane's absorbance was not achieved upon transitioning from high to low concentrations of Pd^{2+} ions. To restore a sensor membrane previously immersed in Pd^{2+}, various reagents, including NaOH, H_2SO_4, HCl, HNO_3, and EDTA, were evaluated. Notably, among these options, a 0.15 M HNO_3 proved to be the most effective, fully regenerating the sensor after a brief 2.0-min treatment. It's important to note that following the regeneration step, and before subsequent analyses, the sensor membrane must be immersed in a buffer with a pH of 5.75 for a minimum of 3.0 min.

3.10. Selectivity

A membrane optode's selectivity, which indicates its relative response for principal ion over various ions present in solution, maybe one of its most crucial properties. Thus, it was investigated how several common metal ions affected the absorbance of the proposed Pd^{2+} sensor. To study the selectivity of the proposed Pd^{2+} sensor membrane, the absorbance of a fixed concentration of Pd^{2+} ion, at 150 ng mL^{-1} level, in a solution of pH 5.75 was recorded before (A_o) and after (A) addition of some potentially interfering ions such as Ag^+, Cd^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+} Hg^{2+}, Cu^{2+}, Ni^{2+} , Sr^{2+}, Al^{3+}, Fe^{3+}, Au^{3+}, and at concentrations up to 400 times of the analyte ion. The resulting relative error is defined as $RE(\%) = [(A - A_o)/A_o] \times 100$. The findings recorded in Table 1, clearly show that the relative error for all of the metal ions under investigation is less than 4.0%, which is regarded as tolerable. Further investigation revealed that anions such as $C_2O_4^{2-}$, NO_3^-, NO_2^-, CO_3^{2-}, IO_3^- and CH_3COO^- present at high concentrations up to 200 µg mL^{-1} also do not show an obvious interfering effect on the Pd^{2+} assay (Table 1). The represented results demonstrated the tolerance limits of the ions concentrations added resulting in less than ± 5.0 % relative error. The results show that the suggested optode membrane is extremely selective towards Pd^{2+} ions and may be used to detect levels of Pd^{2+} ions in natural environmental samples, even when other co-existing cationic and anionic species are present.

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3.11. Calibration curve

As recorded in Table 2; the sensor response, in the form of a change in absorbance at 633 nm, towards Pd^{2+} ions concentration was obtained within 15–225 ng mL^{-1}. The blank absorbance at 633 nm was assessed after equilibrating sensor sample with blank solution at pH 5.75. The absorbance linearly differs as a function of Pd^{2+} ions concentration range of 15–225 ng mL^{-1}. The equilibrating solution's minimum Pd^{2+} ion concentration was found to be 4.25 ng $mL^{-1,}$ which was sufficient to generate a distinct color change in the sensor. A larger amount of aqueous sample, however, can further reduce the detection limit of Pd^{2+} ions concentration. The detection and quantification limits,[66] defined as $C_L = 3S_B/m$ *and* $C_Q = 10S_B/m$ (where C_L, C_Q, S_B, and m are the detection limit, quantification limit, standard deviation of the blank and slope of the calibration graph, respectively), was 4.25 and 14.25 ng mL^{-1}.

The intra-day and inter-day precision and accuracy analytical results show that the attained approach is highly repeatable and reproducible, with coefficients of variation ranging between 1.88 and 2.15 %.

Table 3 contains the findings of a comparison between optical sensor detection of Pd^{2+} ions and spectrophotometric methods.[67–78] [84–95] Unfortunately, there aren't many publications on optical sensors for evaluating Pd^{2+} ions. It was established that the achieved optode is significantly better than a number of available sensors for the monitoring of Pd^{2+} ions. In addition, the suggested sensor has a lower detection limit than spectrophotometric techniques. The use of AHDDO as a chromophoric reagent for an optode membrane for the preconcentration and evaluation of Pd^{2+} ions is described here for the first time.

3.12. Analytical applications

The suggested approach was used to determine the presence of Pd in various road dust, soil, water, food, and biological materials after digestion in order to demonstrate its reliability. In order to measure the matrix effect, the samples were spiked. The results showed good agreement between the amounts of added and measured analytes. Table 4 presents the outcomes. It is clear from the results of three analyses of each sample that Pd was successfully recovered. Table 4 lists all the results that were obtained. The recoveries between 97.74% and 102.29% that were obtained, as demonstrated in this table, validated the correctness of the developed procedure. The statistical analysis of these results using the Student's t-test showed that there was no significant difference between the experimentally measured and captured/detected concentrations at the 95% confidence level.[79] [96]

4. Conclusion

In this study, a highly selective optical sensor for the measurement of Pd^{2+} was created by immobilizing 4-(2-amino-3-hydroxypyridine-4-ylazo)1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one (AHDDO) on an agarose membrane. The proposed sensor has excellent optical properties that make it suitable for use as an optical sensor, including good selectivity, low cost, appropriate lifetime, rapid and reproducible regeneration, and ease of manufacture and handling. The sensor also demonstrated a rapid response time, a suitable linear calibration curve, and low detection and quantification limits. By the means of an easy and low-cost methodology, satisfactory experimental results were achieved for the determination of Pd^{2+} ion by the prepared sensor. Without any significant interference from other metal ions, the suggested sensor can be used for the quantitative and qualitative measurement of Pd^{2+} ions in various real samples.

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CRediT authorship contribution statement

Adil Bahathiq and Ahmad Babalghith: Conceptualization, Data curation, Investigation, Methodology, Visualization, Validation, Writing - original draft, Writing - review & editing. **Alaa Amin:** Conceptualization, Methodology, Data curation, Investigation, Supervision, Validation, Writing -original draft, Writing - review & editing. **Abdelrazek Askar**: Conceptualization, Investigation, Methodology, Validation, Writing - original draft, Writing - review & editing

Conflicts of interest

There is no potential conflict of interest.

Ethical Approval

This article does not contain any studies with human participants or animals performed by any of the authors.

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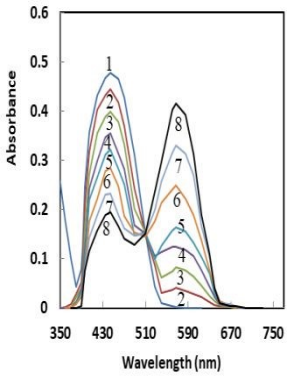

Fig. 1. Absorbance spectra of 1- AHDDO (2×10^{-4} M) in ethanol in the presence of increasing [Pd^{2+}] ion. The color change of solution upon complexation with Pd^{2+} ions. The numbers 2– 8 show the direction of absorbance changes by increasing [Pd^{2+}] from 100–700 µg mL^{-1}

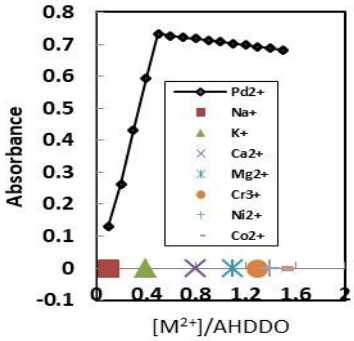

Fig. 2 Absorbance of AHDDO (2×10^{-4} M) in ethanol at 567 nm, as a function of [Pd^{2+}]/ [AHDDO] mole ratio for different metal ions

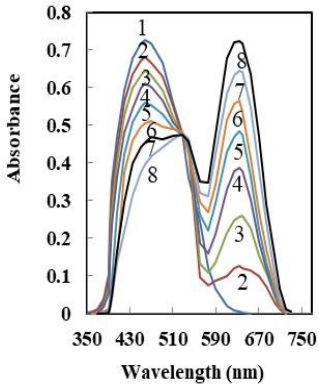

Fig. 3. Absorbance spectra of 1- AHDDO membrane in the presence of increasing [Pd^{2+}] ion 2–8 for 40–225 µg mL^{-1}. The color change upon complexation of AHDDO with Pd^{2+} ions. The numbers show the direction of absorbance changes by increasing Pd^{2+}

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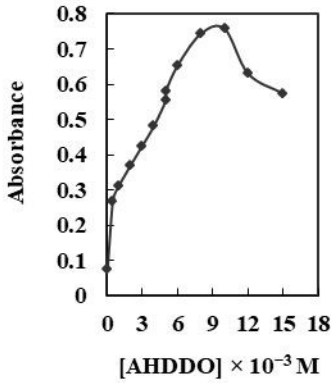

Fig. 4. Effect of [AHDDO] on its loading on the agarose membrane. Experimental conditions: pH, 5.75; wavelength, 458 nm; temperature 35 °C.

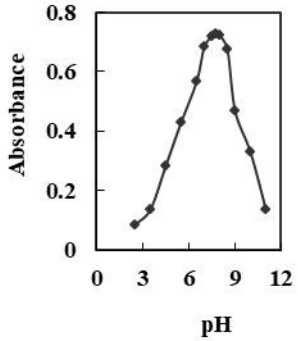

Fig. 5. Effect of pH of the reaction solutions on the immobilization of AHDDO on the agarose membrane. Experimental conditions: [AHDDO], 1.0×10^{-2} M; λmax, 458 nm.

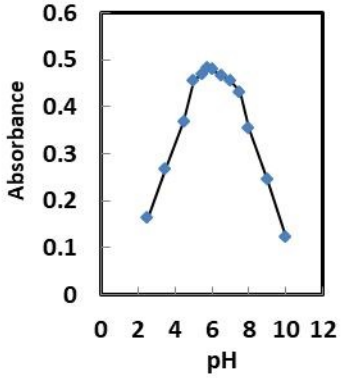

Fig. 6. Effect of pH on the Pd^{2+} ion-selective sensor in the presence of 150 ng mL^{-1} Pd^{2+} at the optimum conditions.

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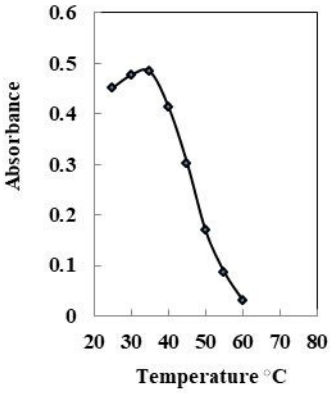

Fig. 7. Effect of temperature on the Pd^{2+} ion-selective sensor in the presence of 150 ng mL^{-1} Pd^{2+} at the optimum conditions

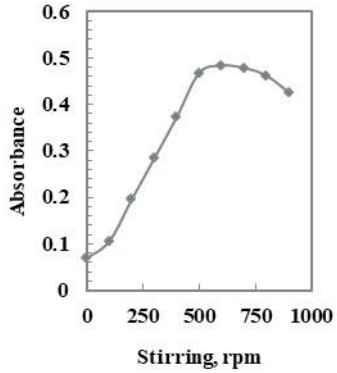

Fig. 8. Effect of stirring on the Pd^{2+} ion-selective sensor in the presence of 150 ng mL^{-1} Pd^{2+} at the optimum conditions

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Table 1 Tolerance ratio (TR = ion/Pd^{2+} mass ratio) for various interfering ions in the determination of 150 ng mL^{-1} of Pd^{2+}.

Ion	TR	Error%	Ion	Error%	TR
Na^{+}, K^{+}, Li^{+}, Acetate	7500	+ 2.4	Al^{3+}, Fe^{3+}, CO_3^{2-}	– 2.9	2500
Ca^{2+}, Mg^{2+}, Succinate	6000	– 1.8	Fe^{2+}, Oxalate	– 3.0	2000
Ag^{+}, Tl^{+}, Citrate	5500	– 3.1	Cu^{2+}, Ni^{2+}, SO_4^{2-}	+ 4.0	1750
Sr^{2+}, Ba^{2+}, NO_2^{-}, Cl^{-}	5000	– 2.7	Hg^{2+}, Co^{2+}, HCO_3^{2-}	– 3.5	1300
Ge^{4+}, Ti^{4+}, NO_3^{-}	4500	+ 3.8	Sn^{4+}, Sn^{2+}	+ 3.9	1000
Bi^{2+}, Mn^{2+}, IO_3^{-}	4000	– 3.3	Zn^{2+}, Pb^{2+}, SCN^{-}	+ 3.9	750
Zr^{4+}, Cr^{6+}, $S_2O_3^{2-}$	3500	+ 3.6	Au^{3+}, La^{3+}, Cr^{3+}	+ 2.4	500
Mo^{6+}, W^{6+}, Br^{-}	3250	– 3.0	Se^{4+}, Te^{4+},	– 3.2	200
Th^{4+}, UO_2^{2+}, $B_4O_7^{2-}$	3000	+ 3.5	Cd^{2+}, Pt^{4+}	+ 4.0	60

Table 2 Analytical characteristics of the offered sensor membrane

Parameters	Proposed sensor	Parameters	Proposed sensor
pH	5.75	Quantification limit (ng mL^{-1})	14.25
λ_{max} (nm)	633	Reproducibility (RSD%)[b]	1.82
Beer's range (ng mL^{-1})	15–225	Regression equation	
Ringbom range (ng mL^{-1})	40–200	Slope	3.82
Molar absorptivity (L mol^{-1} cm^{-1})	3.23×10^{7}	Intercept	– 0.11
Detection limit (ng mL^{-1})	4.25	Correlation coefficient (r)	0.9975

[a] For six replicate determination of 150 ng mL^{-1} Pd^{2+}.

Table 3
Comparison of the proposed optode method with spectrophotometric methods for Pd(II) determination.

Reagen	Conditions	λ_{max}, nm	ε_{max}, L·mol^{-1}·cm^{-1}	M : L	Linear range, μg·mL^{-1}	Interfering ions	Ref.
3,4-Dihydroxy-benzaldehydeisonicotinoyl hydrazone	pH = 3.0, acetate buffer	380	5.3×10^3	1 :1	0.5–20.0	Cu^{2+}	67
4-(4'-Antipyriyl azo)-2-bromophenol	pH = 4.0–7.0	498	2.1×10^3	1 : 2	0.2–3	Cu^{2+}, Co^{2+}, V^{5+}, Ag^{+}, Fe^{3+}	68
A-Furildioxim	0.1–1.4 M HCl, $CHCl_3$	380	2.2×10^4	1 : 2	1–3	–	69
4-(2'-Furalidene-imino)-3-methyl-5- mercapto-1,2,4-thiazole	pH = 5.4, n-butanol	410	1.4×10^3	1 :1	17–50	Cu^{2+}, Cr^{+6}, Mn^{+7}, $S_2O_3^{2-}$, CH_4N_2S	70
Sulphochlorophenol-azorhodanine	8 M H_3PO_4+ 5 M H_2SO_4; 1 M HCl, 1–2 h	520; 520	1.2×10^5; 5.0×10^4	–	–	Pt^{4+}, Rh^{3+}	71
2-(2-Quinolylazo)-5-diethylaminobenzoic acid	1.0 M HCl, 1% CETAB	625	1.51×10^5	1 : 2	0.01–0.6	Co^{2+}, Ni^{2+}	72
4-(6-Bromo-2-benzothiazolylazo)pyrogallol	Dimethylformamide	580	–	–	0.6–15.0	–	73
1-(2-Benzothiazolyl-azo)-2-hydroxy-3- naphthoic acid	5.0 M HCl and CETAB	669	2.61×10^5	1 : 2	0. 0–0.9	Ni^{2+}, Co^{2+}	74
Benzyloxybenzaldehydethiosemicarbazone	pH = 5.0, cyclohexanol	365	4.0×10^3	1 :1	5–60	Ni^{2+}, Cu^{2+}	75
4-(N'-(4-Imino-2-oxo-thiazolidine -5-ylidene)-hydrazino)-benzoic acid	pH = 7.0, universal buffer	450	4.3×10^3	1 :1	0.6–10.6	Pt^{4+}, Ru^{4+},	76
4-(N'-(4-Imino-2-oxo-thiazolidin-5-ylidene)-hydrazino)-benzene-sulfonic acid	pH = 7.6–8.3	438	7.5×10^3	1 : 2	0.2–2.2	Ir^{4+}, Ru^{4+}	77
Cefixime	pH = 2.6 Na_2HPO_4-citric acid buffer	352	1.22×10^4	2 :1	0.8–16.5	Cu^{2+},Zn^{2+},Cd^{2+}, Ni^{2+}	78
AHDDO	pH = 5.75,	633	3.23×10^7	1:2	15-225	-----	PW

CETAB: cetyltrimethyl ammonium bromide PW: Present work

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Table 4 Results of Pd^{2+} determination in real samples after digestion (95% confidence level; n=6)

Samples	Added [ng mL^{-1}]	Found[a] [ng mL^{-1}] Sensor	ETAAS	Recovery (%)	t-test[b]	F-value[b]
Free Benha-Cairo	–	<DL*	<DL*			
road	75	75.7±0.08	74.0.00±0.77	100.93	1.89	
	150	148.6±0.13	153.2.00±1.05	99.07		3.71
Benha-Zagazig	<DL*	<DL*	<DL*			
road	100	98.8±0.11	102.5±1.20	98.80	1.62	
	200	201.6 ±0.18	196.5±.95	100.80		3.96
Soil – 1	–	<DL*	<DL*			
	60	60. 5±0.09	61.0±1.05	100.83	2.18	
	120	118.8±0.10	123.6±1.30	99.00		4.04
Siol – 2	–	<DL*	<DL*			
	90	88.9±0.07	91.7±0.80	98.78	1.85	
	180	182.3±0.12	177.2±1.00	101.28		3.96
Sea water	–	<DL*	<DL*			
	80	80.5±0.08	78.8.00±1.25	100.63	1.44	
	160	158.3±0.13	163.6±0.75	98.94		3.78
underground water	–	<DL*	<DL*			
	70	69.1.25±0.16	72.0 ±.95	98.71		4.07
	140	143.2± 0.20	137.4±0.85	102.29	1.93	
Tap water	–	<DL*	<DL*			
	110	107.5 ± 0.21	106.4±1.45	97.73		3.71
	220	223.7 ±0.13	217.0±0.95	101.68	2.07	
Serum	–	<DL*	<DL*			
	85	84.1±0.11	86.5±1.30	98.94	1.83	
	170	167.8±0.17	173.0±1.55	98.71		3.79
Urine	–	<DL*	<DL*			
	65	65.7±0.14	64. 0±1.00	101.08	2.17	
	130	128.6±0.19	132.3±1.35	98.92		4.18
Green tea	–	<DL*	<DL*			
	105	106.6±0.11	103.2±2.05	101.52	2.08	
	210	214.0±0.13	215.0±1.85	101.90		3.85
	–	<DL*	<DL*			
Black tea	55	55.5±0.18	54.0±0.19	100.92	1.81	
	110	108.7.7±0.20	112.4±0.19	98.81		3.68

* DL. Detection limit; [a:] Mean ± SD.

[b]: Theoretical values for t- and F- values at 95% confidence level for five degrees of freedom are 2.57 and 5.05, respectively.[79]

[c]: µg kg^{-1}