



Synthesis, Characterization and Theoretical Study of Azoimine and Using for Analysis of Palladium (II) Ion by Turbidimetric Method in Environmental Samples



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Sajda .S. Affat*

*Department of Chemistry, College of Science, University of Thi-Qar, Iraq.

Abstract

In the present study, simple and rapid efficiency using the turbidity method acting for the pre-concentration and estimation of Pd (II) in environmental samples was investigated by using turbidity meter device detection. In the proposed approach, 2-(((2-E-2-hydroxy-4-((E)-o-tolyldiazenyl)benzylidene)amino)benzyl)imino)methyl-5-(o-tolyldiazenyl)phenol (A₃) was synthesized and characterized by UV-visible, FT-IR, ¹H-NMR and Mass spectra. Additionally, the structure of chemical compound (A₃) was studied the Frontier Molecular Orbitals (FMOs) of (A₃) were computed at the B3LYP/6-31G(d,p) level of theory. The synthesized compound was used as a complexing agent with as a surfactant (SDS). Parameters provide optimum reaction conditions were studied such as the effect of order addition, the effect of reagent concentrations, the effect of surfactant concentration (SDS), the impact of pH solution, and finally the effects of equilibrium temperature, and time. A linear calibration curve was found to lie between 0-60 μg.L⁻¹ with a correlation coefficient of 0.999, the limit of quantification (LOQ) 0.40 μg.L⁻¹, and the detection limit (LOD) 0.12 μg.L⁻¹. The accuracy of the method were found to be RSD 2.80%. The method was applied successfully to determine palladium ion concentrations in various environmental samples, was found the recovery in the range 99.0-102.44%.

Keywords: Pd (II) ion; Analytical reagent; Turbidity; Complex; Environmental Samples

1. Introduction

Determination of ultra-trace metals such as palladium in environmental and food samples has been more severe in recent years owing to significantly lower limitations set on the quality of trace metals in these samples. Palladium is used for a variety of uses such as medicine, dentistry, electrical devices, electronics, chemical, automotive and glass industry, and jewelry, etc because of its attractive physical and chemical properties such as high melting point, corrosion resistance and, special particular catalytic properties [1]. In the catalytic converter, noble metals are used to reduce air pollution. Pd (II) compounds can be released into the aquatic environments due to solid air suspension, sediments, soils and road dust [2]. Consequently, monitoring of Pd (II) in industrial and environmental samples is essential for the human health protection

[3,4]. Although of the essence of corrosion resistance, the palladium content of earth crust is 0.01–0.02 μg.ml⁻¹, and it presents is in different natural minerals, soil, and rocks. Palladium and its alloys have a wide variety of uses in both the chemical industries and instrument making. This is used in fine devices, such as watches and certain medical instruments to purify medical instruments to purify hydrogen gas [5]. Therefore, the complex structure is a common way of estimating low Pd (II) concentrations using various techniques. In literature, the cloud point extraction (CPE) [6-8], solid phase extraction [9-11], co-precipitation [12,13], column extraction [14], ion-selective electrode [15,16], liquid-liquid extraction [17-19], electrothermal atomic absorption spectrometry [20], flame atomic absorption spectrometry [21], ultraviolet-visible spectrometry [22], In the present study, an attempt

*Corresponding author e-mail: sajida.j_mschem@sci.utq.edu.iq (Sajda .S. Affat).

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was made to establish a new approach for Pd (II) ion analysis using the turbidity method. The process is based on the formation of the complex between Pd (II) ion and Azoimine as a synthesized reagent and the presence of SDS that keeps the complex suspended in solution for a long time. The suggested procedure has been applied for the determination of Pd (II) ion in different environmental samples.

2. Experimental

2.1 Instrumentation

The UV-Vis spectrophotometer model T 60, PG Instruments Ltd, (Germany). Water bath Thomas Sc. Ap. (England). The FT-infrared measurements were recorded by using FT-IR affinity Spectrophotometer (Shimadzu) Japan, Mass spectra are recorded of compounds using Agilent Technology (HP)/MS Model 5973 network mass selective detector in the university of Tehran, Iran. The $^1\text{H-NMR}$ with using DMSO as a solvent in Tehran, Iran, and a Lovibond turbidimeter (Germany) device was used to measure the turbidity of the solution.

2.2 Materials

Both analytical grade reagents were used as received from various companies, without further purification. Palladium chloride (II) (99%) from Merck, Germany, O-toluidine (99%), NaOH (99%), HCl (37%) and NaNO_2 (99%) were purchased from BDH, 2-aminobenzylamine (98%) and salicylaldehyde (99%) from sigma Aldrich.

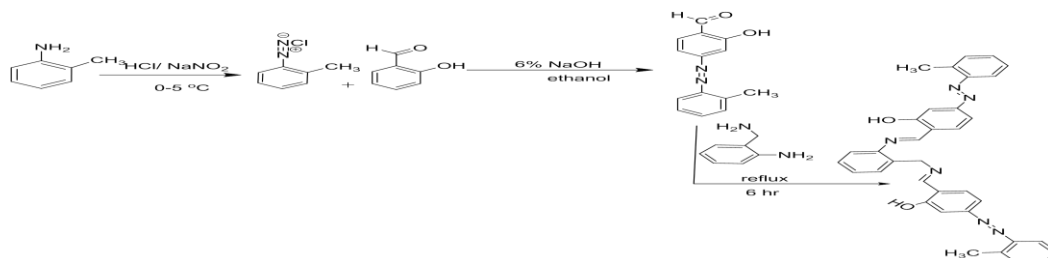
2.3 Solutions preparation

Analytical reagent (A_3) 1mmol.L^{-1} was prepared by dissolving 0.0566gm of the reagent in DMSO (25ml) and then transferring the solution to a volumetric flask 100ml. A standard stock solution of PdCl_2 (0.5mmol.L^{-1}) was prepared by dissolving 0.0089gm of PdCl_2 in 100ml of water acidified with 0.5ml of concentrated hydrochloric acid. Sodium dodecyl sulphate stock solution (SDS) (288.3g.mol^{-1}

4%w/v) was prepared by dissolving 10gm in 250ml of deionized water.

2.4 Preparation of analytical reagent (A_3)

Azo dye (2-hydroxy-4-(o-tolyldiazenyl) benzaldehyde) was prepared by dissolving (2.143 gm, 0.02 mole) of O-toluidine in a mixture of 30ml distilled water and 5ml of concentrated hydrochloric acid. The mixture was cooled to $0-5^\circ\text{C}$. The solution was diazotized at $0-5^\circ\text{C}$ with (1.38gm, 0.02mole) sodium nitrate was dissolved in 20ml distilled water was added drop wise to amine solution and stirring continuously at $0-5^\circ\text{C}$ and left to stand for 30 min. This diazonium solution was added to salicylaldehyde (2.442gm, 2.13ml, and 0.02mole), then the mixture was dissolved in 25ml ethanol and 30 ml of 6% sodium hydroxide. The mixture was stirred continuously for 2h. at $0-5^\circ\text{C}$ in ice-bath and allowed to stand in the refrigerator overnight and acidified with dilute hydrochloric acid to $\text{pH} = 6$. The precipitate was filtered and washed with distilled water and ethanol solution to remove the excess of unreacted substances chemicals and recrystallized from ethanol and dried in an oven at 50°C for two hours [23,24]. The purity was confirmed by the TLC technique and the yield was 85.58%, mp $122-123^\circ\text{C}$. The imine was prepared by the condensation reaction by dissolving (2.703gm, 0.01mol) of (2-hydroxy-4-(O-tolyldiazenyl)benzaldehyde) in (20ml) absolute methanol. Then the raw materials were mixed with a solution of (0.611gm, 0.005mol) of (2-aminobenzyleamine) dissolved in (10ml) of the same solvent with the addition of four drops of glacial acetic acid as a catalyst followed by reflux for 6 hours. The reaction was followed using TLC [25,26]. The brown precipitate was formed and it was filtered, dried, and recrystallized using absolute ethanol. The reaction is shown in Scheme 1.



Scheme 1. Preparation of analytical reagent (A_3)

2.5 Turbidity Method

Analytical reagent (A_3) the compound used as a standard compound to calibrate a turbidimeter, so it is used as the same unit of attenuation of source light.

2.5.1 Palladium-Analytical reagent complex formation

For the complex appearance, the viscosity cloud formation was obtained by 10ml solution contain 0.5 mmol.L⁻¹ of Pd (II) ion added to 0.5ml of 1 mmol.L⁻¹ of analytical reagent then mixed with 0.5ml of 0.1% w/v SDS was adjusted to related pH 4.0. The miscellanea mixture was shaken for 5 min and left to stand in a thermostatic bath at 60 °C for 20 min, The precipitate was formed as Pd (II)- A_3 -SDS system the bulk aqueous phase was readily evaluated by utilizing turbidity meter to measure the attenuation of the incident light.

3. Results and discussion

3.1 UV-Vis Spectrum

The UV-Vis spectra for the analytical reagent [2-((E)-((2-((E)-2-hydroxy-4-((E)-o-tolyldiazenyl)benzylidene)amino)benzyl)imino)methyl)-5-(o-tolyldiazenyl)phenol] (A_3) is shown in Figure1. Two absorption are shown in the figure, the first at wavelength 282 nm due to π - π^* in the aromatic ring [24,27] and the second peak at 475 nm due to interior intramolecular charge transfer n - π^* [24,28] which belongs to the $-N=N-$ and $C=N$ groups.

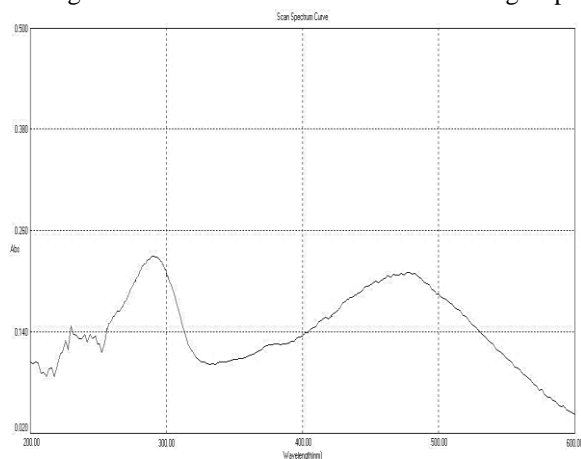


Figure 1. UV-Vis spectrum for analytical reagent (A_3)

3.2 FT-IR spectrum

The IR spectrum was obtained for analytical reagent prepared as KBr is shown in Figure 2. The spectra shows absorption band in 3263 cm⁻¹ and

belongs to OH [29]. The absorption band at 1612 cm⁻¹ belongs the stretching vibration of $C=N$ of imine [28] and a strong band in the range at 1549 cm⁻¹ due to the stretching vibration of the $(N=N)$ [30]. The $C=C$ appear stretching vibration at 1563 cm⁻¹ [30-32] is shown stretching vibration for the $C-H$ aromatic appear weak band at 3024 cm⁻¹ [30-33], the absorption band at 2920 cm⁻¹ due to $C-H$ aliphatic [28].

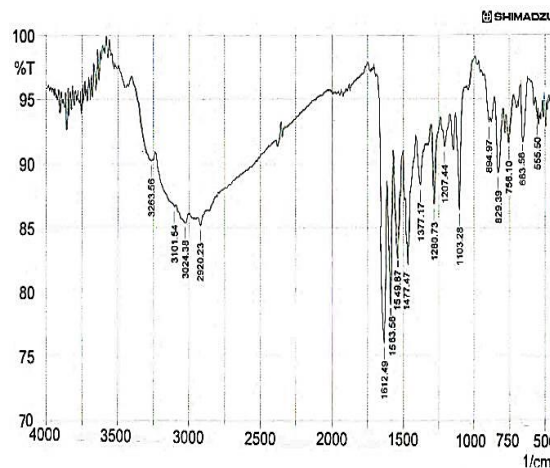


Figure 2. FT-IR spectrum for analytical reagent (A_3)

3.3 ¹H-NMR spectrum

The ¹H-NMR spectrum of the analytical reagent (A_3) was recorded in DMSO as solvent in figure 3. The chemical shift δ ppm at 6.55-7.72 (m, 18H, aromatic rings) [29], δ at 3.35 (s, 6H, CH₃) [34], δ at 7.78 (m, 2H, 2OH) [29], δ at 3.82 (s, 2H, CH₂) [35] and 7.76 (s, 2H, 2 CH=N) [29].

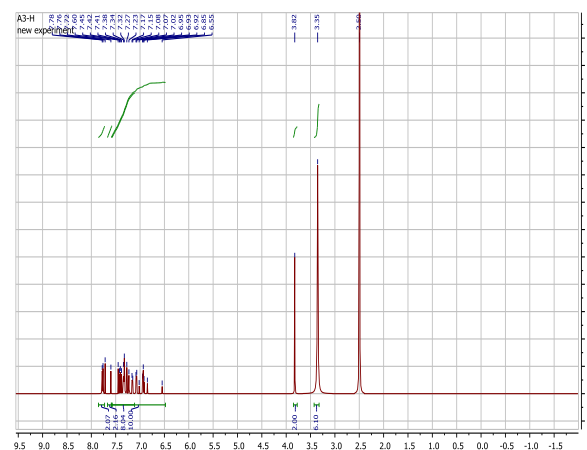


Figure 3. ¹H-NMR spectrum for analytical reagent (A_3)

3.4 Mass spectrum

The mass spectrum of the analytical reagent (A_3) was recorded and the obtained molecular ion (m/z) peaks confirm its proposed formula and the

geometry. The ligand shows a peak at $M^+ = 566$ corresponding to the molecular ion peak ($C_{37}H_{30}N_6O_2$) in the Figure 4. It also showed a series of peaks at $m/z = 330, 316, 301, 284, 226, 197, 182, 120, 106, 91, 77$ and 65 corresponding to $[C_{21}H_{20}N_3O]^+, [C_{20}H_{18}N_3O]^+, [C_{19}H_{15}N_3O]^+, [C_{19}H_{14}N_3]^+, [C_{13}H_{12}N_3O]^+, [C_{12}H_9N_2]^+, [C_{12}H_{10}N_2]^+, [C_7H_6NO]^+, [C_7H_6O]^+, [C_7H_7]^+, [C_6H_5]^+$ and $[C_5H_5]^+$ respectively.

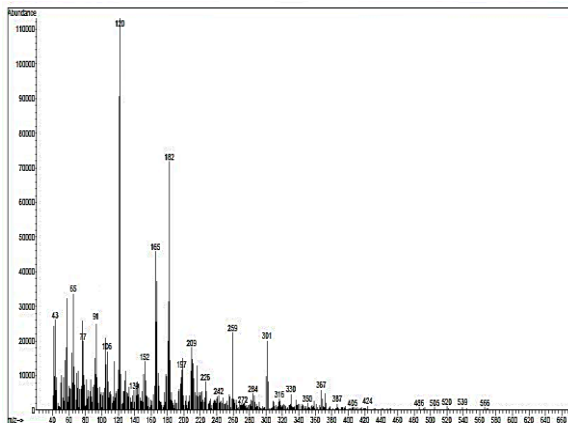


Figure 4. Mass spectrum for analytical reagent (A_3)

3.5 Theoretical studies on [2-(((2-((E)-2-hydroxy-4-((E)-o-tolyldiazenyl)benzylidene)amino)benzyl)imino)methyl)-5-(o-tolyldiazenyl)phenol](A_3)

The Frontier Molecular Orbitals (FMOs) of (A_3) were computed at the B3LYP/6-31G (d,p) level of theory. The results are shown in Figures 5 (a) and 5 (b). The HOMO orbitals of A_3 are delocalized on the N-benzylmethanimine and the 2-azanylidene methyl phenol. The LUMO orbitals are delocalized on N-benzylmethanimine, 2-azanylidene methyl phenol, and O-tolyldiazenyl. Additionally, the energy gap between HOMO and LUMO (ΔE) was calculated and was found to be 1.8 eV (Table 1). This large gap between HOMO and LUMO infers good stability, high excitation energies, and large chemical hardness of this molecule. Two energetic parameters correlated with the frontier orbitals were calculated, Ionization potential (I), and electron affinity (A). The high ionization potential of (A_3) indicates that it is a good electron donor, and the relatively low electron affinity shows it is not highly reactive (Table 1). We have calculated the global chemical reactivity was calculated and show in Table 1. The electronic chemical potential (Π), the absolute electronegativity

(χ), the global hardness (η), the global softness (S), and the global electrophilicity index (ω). The results show that this compound has good stability, high excitation energy, and high electrophilicity[36].

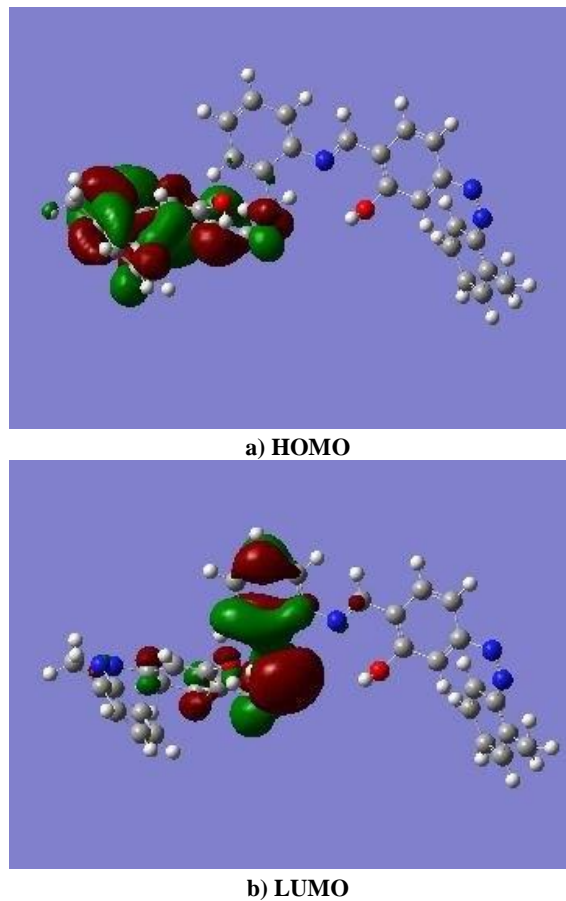


Figure 5. HOMO and LUMO of analytical reagent (A_3)

Table 1. The electronic data of (A_3)

Parameter	Value
EHOMO (eV)	- 4.406
ELUMO (eV)	-2.606
ΔE (eV)	1.8
I (eV)	4.406
A (eV)	2.606
Π (eV)	-3.506
χ (eV)	3.506
η (eV)	0.9
S (eV)	0.555556
ω (eV)	5.531416

Table (2): Order addition effect [Conditions: 0.5 mmol L⁻¹ Pd (II) ion; 1 mmol L⁻¹ aqueous analytical reagent (A₃); 0.1 % (w/v) SDS]

No. of solution	Order addition	Turbidity (NTU)
1	Pd + A ₃ + SDS	66.42
2	Pd + SDS + A ₃	45.54
3	A ₃ + Pd + SDS	31.05
4	A ₃ + SDS + Pd	17.63
5	SDS + Pd + A ₃	22.28
6	SDS + A ₃ + Pd	18.80

3.6 The conditions of measurements turbidity

To maximized extraction efficiency of complex Pd-A₃ using the turbidity method. The most important effects were found to be the order of addition to the organic reagent concentration, SDS concentration, pH of the solution, and effects of temperature and time.

3.6.1 The effect of order addition

The orderly arrangement of the reactants has been analyzed through the varied arrangement of the addition to obtaining the rich phase substance in the experimental options. The findings are shown in Table (2) from which solution number 1 arrangement seems to be the best choice due to the most significant affectability.

3.6.2 The effect of reagent concentration

The effect of the analytical reagent concentration on incident light attenuation has been calculated ranging from 0.02 mmol L⁻¹ to 0.15 mmol L⁻¹. Table (3) outlines the outcomes obtained that 0.08 mmol L⁻¹ of the analytical reagent is the ideal focus.

Table 3. The effect of analytical reagent concentration (A₃) on the turbidity measurement [Conditions: 0.5 mmol L⁻¹ of Pd (II); 0.1% w/v SDS]

Concentration of A ₃ mmol L ⁻¹	Turbidity measurement (n=3)	RSD %	Confidence interval at 95% $\bar{y} \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$ (n=3)
0.02	24.15	0.77	24.15 ± 0.28
0.04	32.23	0.71	32.23 ± 0.86

0.06	58.11	0.54	58.11 ± 0.92
0.08	66.45	1.10	66.45 ± 1.44
0.1	42.08	0.68	42.08 ± 1.12
0.15	28.10	0.82	28.10 ± 1.06

3.6.3 The effect of surfactant concentration

The concentration of surfactant used as a part of the turbidity calculation is a vital variable of SDS surfactant. SDS was selected because of its commercial availability in a highly purified homogeneous, low toxicological product, and low cost material as well as the strong density of the surfactant rich phase. Additionally, it gives a richly complex phase in a suspended state. The effect of surfactant concentration on the measurement of turbidity was evaluated after surfactant was added to increase the homogeneity of the turbid solution. Table (4) shows the signal of attenuation of incident light of the rich phase with an increasing grouping of the SDS molecules 0.2% is indicating the best concentration could be chosen because of the number of turbid product increases [37].

Table 4. Effect of SDS surfactant concentration on the turbidity measurement [Conditions: 0.5 mmol L⁻¹ Pd (II) ion; 0.08 mmol L⁻¹ aqueous analytical reagent(A₃)]

Concentration of SDS (w/v%)	Turbidity measurement (n=3)	RSD %	Confidence interval at 95% $\bar{y} \pm t_{0.05/2, n-1} \sigma_{n-1} / \sqrt{n}$ (n=3)
0.04	31.52	0.77	31.52 ± 0.48
0.08	42.73	0.71	41.88 ± 0.65
0.12	58.45	0.54	58.45 ± 1.32
0.2	82.05	1.10	82.05 ± 1.04
0.28	61.14	0.68	61.00 ± 0.92
0.4	48.22	0.82	48.22 ± 2.16

3.6.4 The effect of pH

The pH is a very critical parameter with the metal ions for both the coacervation of the micelles and the complexation of the ligand. A set of similar experiments was carried out in the pH series of 2-12 by utilizing diverse pH solutions (0.1 M HCl and 0.1 M NaOH). As can be seen from Figure 6, the product's turbidity increased with increasing pH and reached the greatest at pH of 6. The turbidity has gradually decreased because of partial dissociation of the complexes at higher pH, which may produce an unfinished extraction of a complex. Therefore, pH 6 was selected as the optimum working pH for a full

formation of Pd (II)-analytical reagent-SDS complex and consequently a reasonable yield.

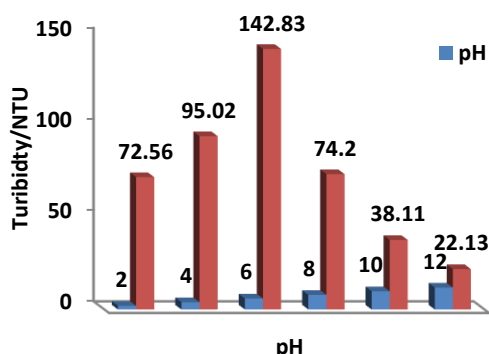


Figure 6. Effect of pH on the measured turbidity [Conditions: 0.5 mmol L^{-1} Pd (II) ion; 0.08 mmol L^{-1} aqueous analytical reagent (A_3); $0.2\% \text{ w/v}$ SDS]

3.6.5 The effects of equilibrium temperature and time

The temperature of equilibration in the range of $10\text{--}90^\circ\text{C}$ has been studied. It has been noticed that a temperature of 60°C has allowed the formation of suspended complexes to be achieved, also when increasing temperature larger than 60°C will cause complex color change and decreasing the value of turbidity due to the decomposition and disturbance of the complex at high temperatures. The incubation time of the solution was also, tested for the interval in the same temperature optimum in a period of 5–45 min. An optimal value was selected for an equilibration time of 20 min. The temperature and time influence on the Pd (II) ion determination by turbidity signal were shown in Figures 7 and 8 respectively.

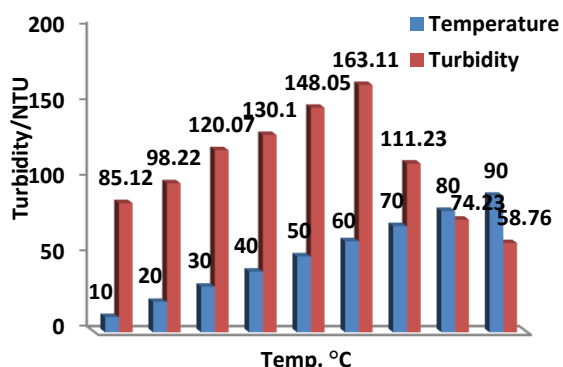


Figure 7. Effect of temperature on the measured turbidity [Conditions: 0.5 mmol L^{-1} Pd (II) ion; 0.08 mmol L^{-1} aqueous analytical reagent (A_3); $0.2\% \text{ w/v}$ SDS at pH 6]

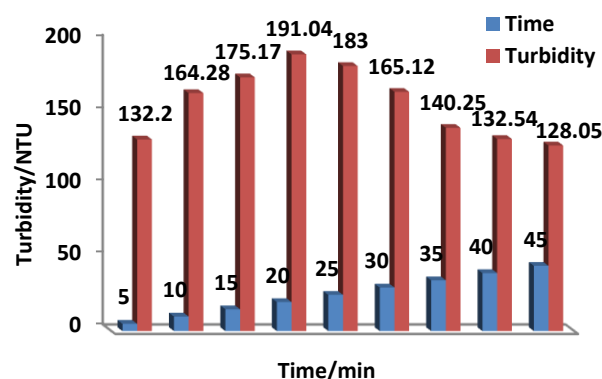


Figure 8. Effect of time on the measured turbidity [Conditions: 0.5 mmol L^{-1} Pd (II); 0.08 mmol L^{-1} aqueous analytical reagent (A_3); $0.2\% \text{ w/v}$ SDS at pH 6; Temp. 60°C]

3.7 Stoichiometric ratio

The absorption spectrum of the Pd- A_3 and Pd- A_3 -SDS in Figure 9 shows the effect of Pd^{2+} cation and SDS on the absorption spectra of the analytical reagent (A_3). Forming a solid ion-association hydrophobic complex depending on the reaction between Pd (II) ion with an azoimine as a synthesized reagent and subsequently extracted into the surfactant SDS at the optimum conditions. The nature of the complex was determined at λ_{max} and at the optimum conditions described above using the molar ratio method. The plot of absorbance versus the molar ratio of A_3 to Pd (II), obtained by varying the A_3 concentration, showed inflection at molar ratio 1.0, indicating the presence of one ligand molecule (A_3) in the formed complex. The results in Figure 10 indicated that the stoichiometric ratio was (1:1) [A_3 :Pd(II)].

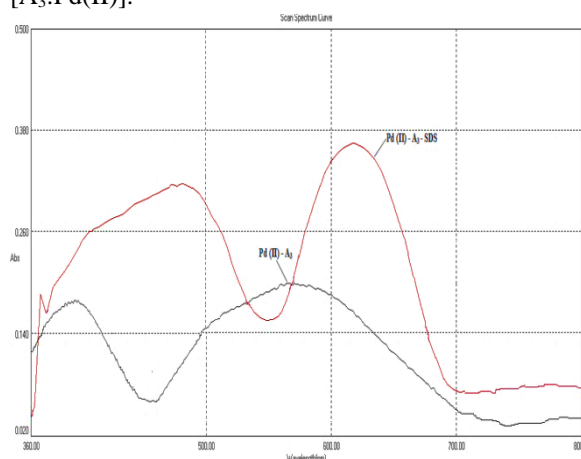


Figure 9. UV-Vis spectrum for Pd- A_3 complex and Pd- A_3 -SDS

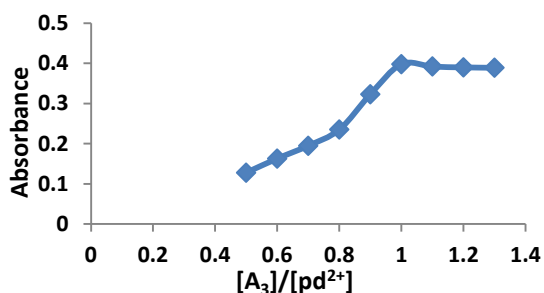


Figure 10. Mole ratio method of the $[A_3: Pd (II)]$

3.8 Calibration Curve

Under optimal experimental conditions above, a calibration curve of turbidness against the concentration of Pd (II) solutions was adjusted by pulling together the turbidity signals of different volumes of Pd (II) standard solutions submitted to the method proposed. Under the optimum conditions, the scatter line for Pd (II) ion is linear from 0-60 $\mu\text{g}\cdot\text{L}^{-1}$ with a correlation coefficient of 0.999. Table (5) gives the parameters of the calibration curve and results of the linear regression analysis.

Table 5. Calibration curve parameters

Parameter	Value
Range of scatter line	0-60 $\mu\text{g}\cdot\text{L}^{-1}$
RSD (n=5)	2.80
LOD ($3 \times \text{SD}/\text{Slope}$)	0.12
LOQ ($10 \times \text{SD}/\text{Slope}$)	0.40
Slope	3.0517
Intercept	0.1835
Correlation coefficient (r^2)	0.999
$t_{\text{calculated}}$	125.23

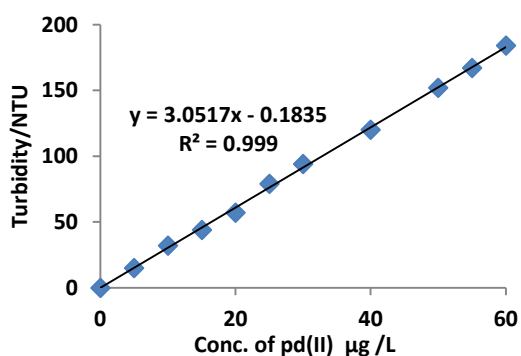


Figure 11. Calibration curve for the variation of Pd (II) ion concentration on NTU

3.9 Repeatability

The relative standard deviation (RSD %) value for Pd (II) $20\mu\text{g}\cdot\text{L}^{-1}$ is tabulated in Table (6). A RSD % of less than 2% was obtained, indicating a consistent measurement can be achieved using the proposed method.

Table 6. Repeatability of Pd(II) determination at experimental parameters

[Pd] $\mu\text{g}\cdot\text{L}^{-1}$	Average response (n=5)	RSD%	Confidence interval at 95% $\bar{y} \pm t_{0.05/2, n-1} \sigma_{n-1}/\sqrt{n}$
20	141	1.66	141 \pm 0.09

3.10 Application of the Proposed Method

To test the applicability and accuracy of the method devised above, it was applied in the determination of the amounts of Pd (II) ion in different samples. Good recoveries (99.0-102.44%) were achieved for all analyzed samples by adding Pd (II) standard solution into the sample solution. On applying the proposed procedure, the results of samples were shown in Table (7).

Table 7. Determination of amounts of Pd(II) ion in environmental samples

Sample	Conc. added of Pd(II)	Conc. founded	Recovery%
Road dust ^a	0	0.16	-
	0.2	0.357	99.17
Soil ^a	0	0.25	-
	0.2	0.461	102.44
Maineral water ^b	0	BDL	-
	0.2	0.198	99.0
Sea water ^b	0	0.121	-
	0.2	0.323	100.62
Dam Water ^b	0	0.182	-
	0.2	0.380	99.48

a: $\mu\text{g}\cdot\text{g}^{-1}$, b: $\mu\text{g}\cdot\text{L}^{-1}$

3.11 Comparison of turbidity method with other preconcentration methods

A comparison of the proposed method with other reported methods for the determination of Pd (II) is shown in table 8. As can be concluded from Table 8, the proposed method has a low detection limit, good linear dynamic range, and RSD, which are better in most cases or comparable with several reported methods. The proposed turbidity method can be used for several environmental samples. All these results demonstrate that the method is needed simple, quick efficient, easy to use, and environmentally friendly involving minimum usage of organic solvents. In addition, this methodology is a reproducible, simple,

and low-cost technique for laboratories.

Table 8. Comparison of proposed turbidity with published preconcentration methods

Method	LOD μgL^{-1}	RSD %	Volume sample ml	Liner range μgL^{-1}	Ref.
Coprecipitation	2.1	<10	20	-	[38]
DLLME	0.02	3.5	5	0.05-1	[39]
CPE	0.12	3.4	50	0-125	[40]
DLLME	0.6	2.4	10	0.88-124	[41]
DLLME	1.65	2.52	10	30-230	[42]
IT-UAA-LLME	0.94	2.6	50	5-800	[43]
DES-AA-ELLME	1.2	3.6	10	4-500	[44]
Turbidity	0.12	2.80	10	0-60	This work

4. Conclusion

A simple, rapid accurate, and low-cost method was used to determine the concentration of palladium (II) in environmental samples based on preconcentration palladium ion by turbidity method. This was performed by forming a solid ion-association hydrophobic complex depending on the reaction between palladium ion with an azoimine as a synthesized reagent and subsequently extracted into the surfactant SDS at the optimum conditions. Short time analysis and low cost were the main advantages of this method for routine quantity analysis.

5. Conflict of interest:

The author declares no conflict of interest, financial, or otherwise.

6. Formatting of funding sources: Self-funding.

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Highlighted

1. Synthesis, characterization and theoretical study of Azoimine using complex reagent were performed in the present study.
2. Short time analysis and low cost, and environmentally friendly results were obtained with this method.
3. Forming a hydrophobic complex depending on the reaction between palladium ion with an Azoimine as a synthesized reagent and subsequently extracted into the surfactant SDS at the optimum conditions.
4. Concentration of palladium (II) in water and soil samples based on pre-concentration palladium ion by turbidity method was determined.

Determination of gold and palladium in environmental samples by FAAS after dispersive liquid-liquid microextraction pretreatment. *Journal of Industrial and Engineering Chemistry*, **20**: 4059 (2014).

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