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Synthesis, Characterization of new azo-Schiff base chelating complex with new azo-base ligand by Template method and study the photo-decolorization of their complex with Pd(II) using $NiCo_2O_4$/Uv-A System

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ABSTRACT

In this work, a new Azo-Schiff base complex of Pd(II) ion prepared by Template method. The prepared metal complex characterized by analytical techniques *viz.*, FT-IR, XRD, UV-visible, CHN elemental. The FT-IR spectra regions of the (M-O), (M-N) and (N=N) vibration stretching bonds indicate the coordination form of NPs prepared complex, while the XRD data allowed to calculate the mean crystallite size this NPs complex that equals to 26.4 nm**.** The analytical data demonstrated that the ratio of metal ion to ligand in this prepared complex is 1:2 with Octahedral structure. The maximum photo-decolonization efficiency of 7 ppm for Pd(II) complex in $NiCo_2O_4$ suspension solution under UV-A light found to be 96.87% with half time 7.941min. The impact rising temperature on photo-decolonization process of this complex was enhanced the positive value of enthalpy. The negative activation energy value of this photoreaction may be attitude to happen several steps on $NiCo_2O_4$ surface leads to low positive value before happened the high negative value via series of chain reactions. On the other hand, the photo decolonization process for this complex is fast, less random and non-spontaneous.

Keywords: Template method, Schiff bases; azo compounds; *chelating complex,* UV-A light; $NiCo_2O_4$.

1. Introduction

Azo-Schiff base compounds represent a novel category of chemical entities garnering heightened interest in scientific research. These organic compounds are notable for possessing two functional groups in their structures: (CH=N) and (N=N). These significant compounds can interact with various metal ions to form coordinated complexes [1], due to the possession of a variety of substituents with distinct electron-donating and/or electron-withdrawing groups, resulting in intriguing chemical characteristics[2–4]. Azo dyes have exceptional optical transmission among organic photoactive substances [5]. Palladium Schiff bases have significant reactivity and selectivity, leading to their development in recent years [6]. The reciprocal influence of both groups provided personnel engaged in spectroscopic investigations with considerable interpretative flexibility [7–9]. Conducting experiments related to photo-organic sensitization and devising innovative storage system designs was a seldom traversed avenue [10]. These ligands and their complexes with transition metals have proliferated significantly, including a vast array of organometallic compounds and a varied spectrum of bioinorganic chemistry, due to the presence of heteroatoms such as O, N, P, S, and heavy metals [11]. Schiff base ligands were investigated for their diverse biological activities due to the azomethine linkage, enabling various applications such as antibacterial, antifungal, and analytical functions [12–14]. Conversely, metal complexes containing nitrogen and oxygen as donor Schiff bases attract particular attention because to their potential for atypical geometries [15]. There are many benefits and importance for photo-catalytic process which are, the brilliant efficiency, little by product, affordability and can be consider as environmentally friendly process, the degradation process by photo-catalysis need photo-catalyst to remove any pollutant under the radiation of light [16, 17]. Palladium nanoparticles are significant among metal nanoparticles due to their versatile catalytic properties in several processes. Recently, several modifications have been developed for the encapsulation of palladium catalytic species within the porosity of mesopores [18, 19]. Because of Palladium ions have good ability to give strong complexes with both organic and inorganic ligands, that cause a high potential to impact on pollutant equilibrium during interact it with its functional groups, this technique provides an opportunity for developing novel hybrid inorganic-organic encapsulating agent for Pd NPs and effective catalysts for many reaction types, including photo-catalytic and redox processes [20]. Herein, the aim of this work focuses on synthesizing complex palladium nanoparticles and then studying their properties, including electronic spectra., UV–Vis, FT-IR and X-ray diffraction analysis. The photo-decolorization of Schiff base complex NPs for palladium will estimate via $NiCo_2O_4$/ UV-A system with different complex concentrations and temperature. The kinetic and thermodynamics functions for this complex will investigate. Furthermore, the hybrid organic-inorganic nature of these encapsulating systems allows for precise tuning of the nanoparticle's electronic environment, which can significantly improve selectivity in asymmetric catalysis and photocatalytic degradation reactions.

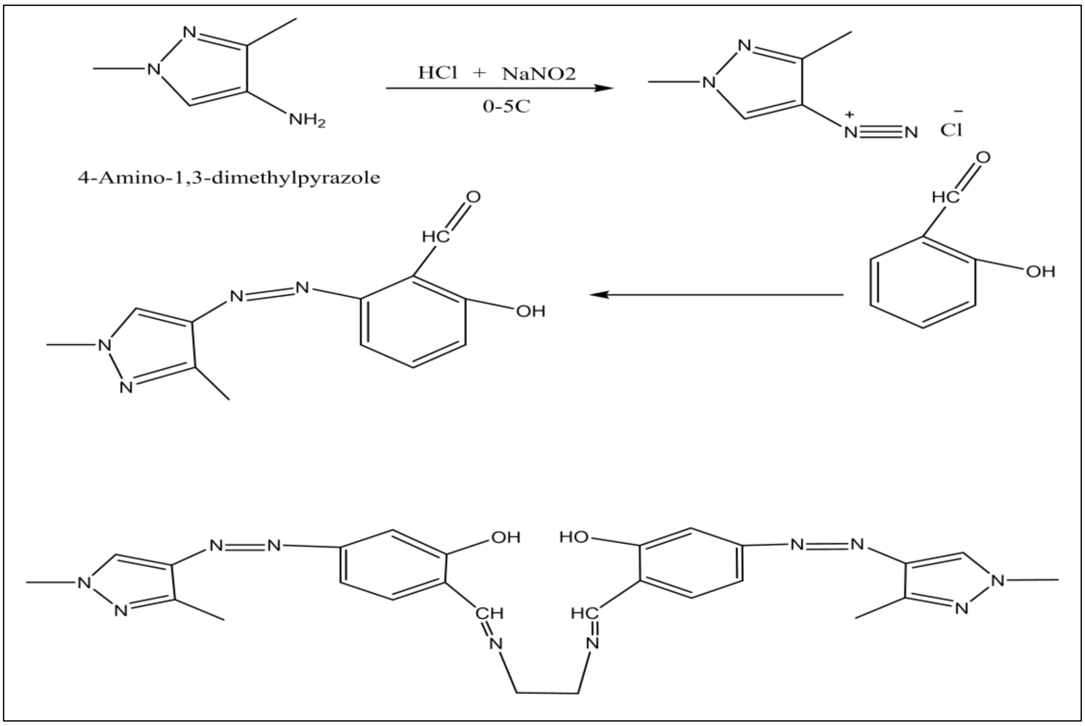
2. Experimental

2. 1. Materials and Reagents

All the chemicals and solvents for the prepared compound were of analytical grade. The ethanol, glacial acetic acid and other solvents used were of high purity and supplied by BDH. 1,3-dimethyl pyrazole, salicylaldehyde, 1,3-dibromo propane and metals salt $Pd(NO_3)_2$ was supplied by BDH and Sigma-Aldrich. A Euro EA Elemental Analyzer was used to perform CHN elemental analysis on the ligand and complexes. The ligand and complexes' infrared spectra were captured using a Shimadzu Corporation 8000S Fourier transform-infrared (FT-IR) spectrometer with a KBr disk in the frequency range of (4000–400) cm^{-1}. All electronic spectra of the prepared compounds have been recorded in the region of (200–1100) nm using a Shimadzu UV-240 UV-visible recorder spectrometer using dimethylformamide (DMF) as a solvent at the concentration of ($1x10^{-3}$) M Because it has low absorption in the spectral range required to prepare this complex, and also does not participate in coordination with the palladium ion, unlike other solvents alternative solvents such as DMSO and other solvents. A magnetic Susceptibility Balance-MSBMKI was used to determine the complexes' magnetic susceptibilities at room temperature. Molar conductivity was assessed utilizing a Jen way Ltd-4071 Digital conductivity meter employing DMF as a solvent at the concentration of ($1x10^{-3}$) M which is a suitable medium for conductivity measurements. The melting points were determined utilizing a Stuart melting point apparatus. The ligand synthesis is illustrated in Scheme1.

2. 2. Preparation of Ligand

The ligand was prepared by coupling reaction of diazonium salt with appropriate amount of salicyladehyde as coupling component in alkaline solution. [21, 22] A diazonium solution was prepared at 1:1 mole ratio (to ensure high efficiency of this salt formation, minimize side reactions such as oxidation, and achieve high yield and purity of the desired azo ligand) by dissolving (0.5 g, 0.2 mol) of 4-amino-1,3-dimethyl pyrazole in 25mL distilled water with 5mL of concentrated HCl with continuous shaking [22, 23]. To this mixture a solution of (2.5 g, 0.2 mol) of sodium nitrate in 25 mL of distilled water was added drop wise to the Diazonium solution with shaking and stirring to complete the aromatic amine Azotization process [24, 25]. At (0-5) ºC, and left to stand (30 min). This diazonium solution was added drop wise to (1mol) of the salicyladehyde dissolved in (30 mL) of ethanol and (50 mL) of (2N) sodium hydroxide at (0-5) ºC that is to increase yield by increasing diazonium stabilization and reducing loss of them at high temperatures above 5 °C, and to increase the purity of the azo bond in the ligand by reducing side reactions and decomposition, making the reaction more selective and efficient. A drop by a drop was observed to change the color. The azo compound (azo dye) was neutralized by adding drops of dilute HCl until reached to the acidic function pH~ 7 [26–29]. After that, the mixture was allowed to stand overnight and then the solution was filtered off. The precipitate produced was washed with distilled water, and then dried in oven at 40 ºC for 1 hours. Finally obtained product was re-crystallized from ethanol and dried. The steps of synthesis ligand are shown in Scheme 1.



Scheme1. The synthesis of the Azo ligand

2. 3. Preparation of Pd-complex NPs.

The new azo-Schiff base complex was prepared by dissolving (2 mol) of pure azo dye dissolved in absolute alcohol (50 mL), then mixing it with (1 mol) (ethylenediamine) dissolved in absolute alcohol with (1 mol) 1,3-dibromo propane. Next, a suitable volume of ethanol solution of palladium salt $Pd(NO_3)_2$ was added in a ratio of 2:1:1:1, (L: ethylene diamine,1,3-dibromo propane: Metal salt).

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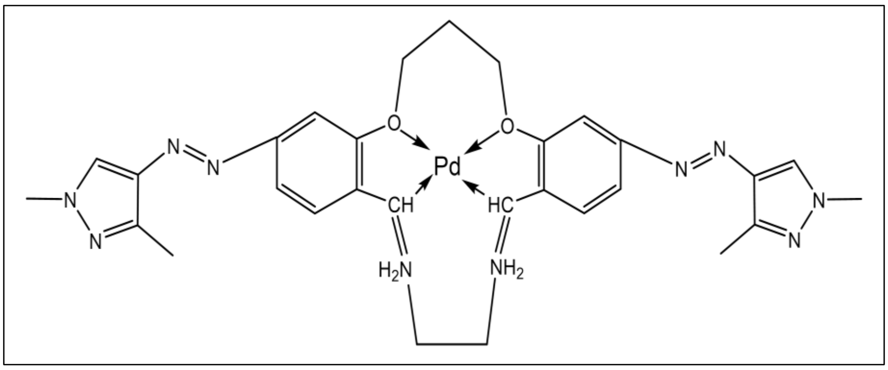


Scheme2. The synthesis of the Pd-complex NPs

2. 4. Method of Photo-Decolorization

Photo-catalytic decolorization reactions of the Pd-complex NPs with $NiCo_2O_4$ were conducted using a homemade photoreactor, as illustrated in Figure 1. The samples were mixed without illumination for 30 minutes, followed by exposure to UV-A light (250 W) for a series of successive intervals [33, 34]. A UV-Vis spectrophotometer set at 417 nm was used to measure the absorbance of the residue complex in solution. Fixed K_{app} rate. The PDE% photo-decolorization efficiency was calculated according to equations 1 and 2, which were approved in references [35].

$$ln\left(\frac{C_o}{C_t}\right) = k_{app} \,.\, t \quad \ldots. \qquad (1)$$

$$PED\ \% = ln\left(\frac{C_o}{C_t}\right) \times 100 \quad \ldots. \qquad (2)$$

where the initial concentration of Pd-complex NPs in dark reaction at 0min of illumination is C_o and the concentration of Pd(II) compound at the time of illumination (t) is C_t. See Figure 1.

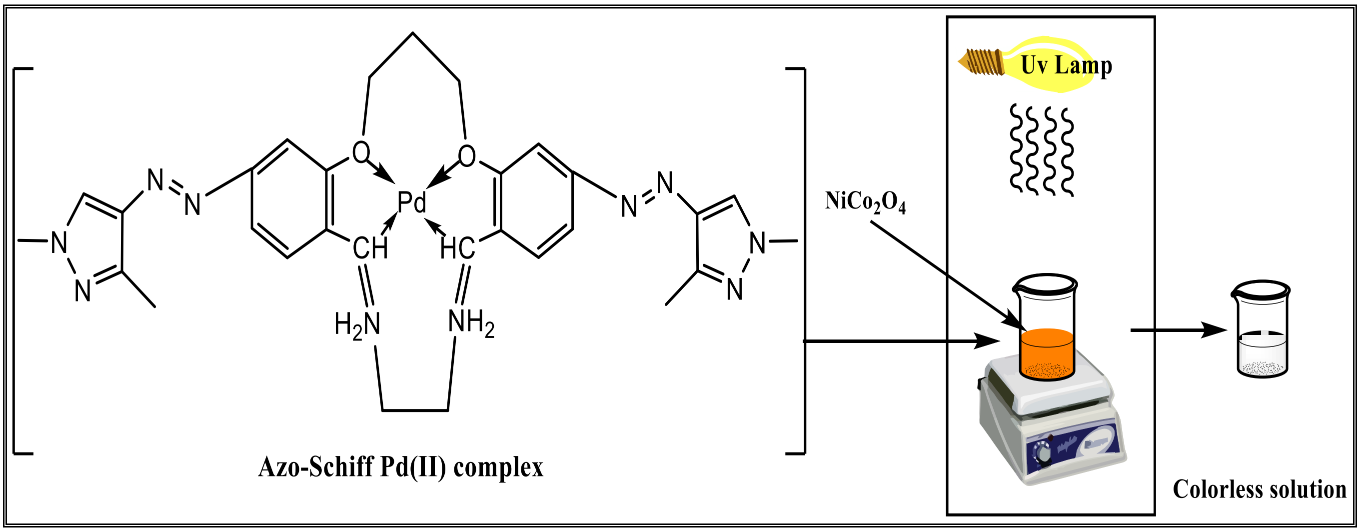


Figure 1: Decolorization of Pd-complex NPs by using A homemade photoreactor

3. Results and Discussion

The azo-azomethine ligand was deep green crystal, but the prepared complexes of this ligand vary in color from green to deep brown. The solid complexes exhibit stability at room temperature and demonstrate solubility in acetone, DMF, and DMSO, while remaining insoluble in water. The elemental analyses and metal content data are summarized in Table 1, demonstrating good agreement with the proposed formula for both the ligand and the complex.

3. 1. Physical Properties and Elemental Analysis of azo Schiff base ligand (H_2L) and Pd-complex NPs

The physical parameters and CHN elemental analysis are presented in Table 1, where the final results for the ligand and its compounds coincides closely with what was theoretically computed for the proposed formulas. The physical characteristics, namely the melting point and color, of the azo Schiff base ligand (H_2L) and Pd-complex NPs indicate a color variation between the ligand and the produced complexes.

Table 1. Melting point, Yield percentage and elemental analysis and for the ligand (H_2L) and Pd-complex NPs.

Compounds	Elemental analysis, %						MP, K	Color	Yield %	Molecula r weight, g/mole
	C%		H%		N%					
	Cal.	Found	Cal.	Found	Cal.	Found				
Azo-Schiff (L)	**59.1**	**59.3**	**4.95**	**4.89**	**22.94**	**22.76**	**240k**	**Dark green**	**60%**	**244.10**
Azo Schiff complex	**63.70**	**63.21**	**5.88**	**5.68**	**24.76**	**24.78**	**278k**	**Dark brown**	**50%**	**565.65**

3. 2. FT-IR Spectroscopic Investigations

The FT-IR spectra that represented in figures (2 and 3) explain the basic bands for azo ligand and Pd-complex NPs, respectively. New bands at (457-408) cm^{-1} in the Pd-complex spectrum are assigned to ν(Pd-O) stretching vibrations, confirming oxygen coordination from the Schiff base moiety. [36–41] While, the other band gave a strong red shift in the spectrum of υ(N=N) to 1452 cm^{-1} with presence ν(M-C=N) band at 1598 cm^{-1}, this confirms the coordinate the azo ligand with Pd(II), despite of the blue shift band of ν(C=N) to 1678 cm^{-1}, which attitude to the stability with resonance inside the aromatic ring , this indicate the linkage and the chelate coordinate from this Pd-complex NPs [42–44].

Table 2. The FT-IR data for Schiff base ligand (L) and Pd-complex NPs (cm^{-1}).

Compound	υ(C –H) aliphatic	υ(C –H) aromatic	ν(O-H)	ν(C=O) imd	ν(C=N) shf.	ν(M-C=N)	ν(C=C) Ar	ν(N=N)	υ(COC)	ν(M-O) Pd-O
Azo (L)	**2939**	**3070w**	**3402br**	**1643**	**1643m**	**-**	**1593**	**1583 m**	**-**	**-**
Azo Schiff complex	**2357**	**2980**	**-**	**-**	**1678m**	**1598**	**1379**	**1452**	**1246**	**457w**

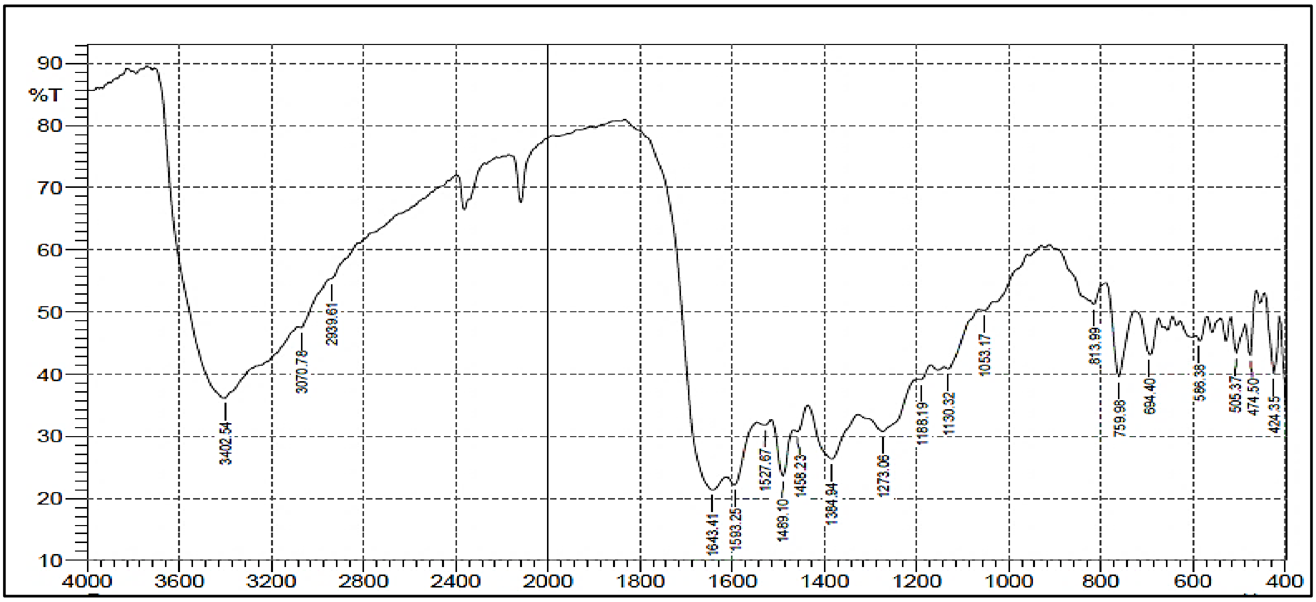


Figure 2. FT-IR spectrum of Azo ligand.

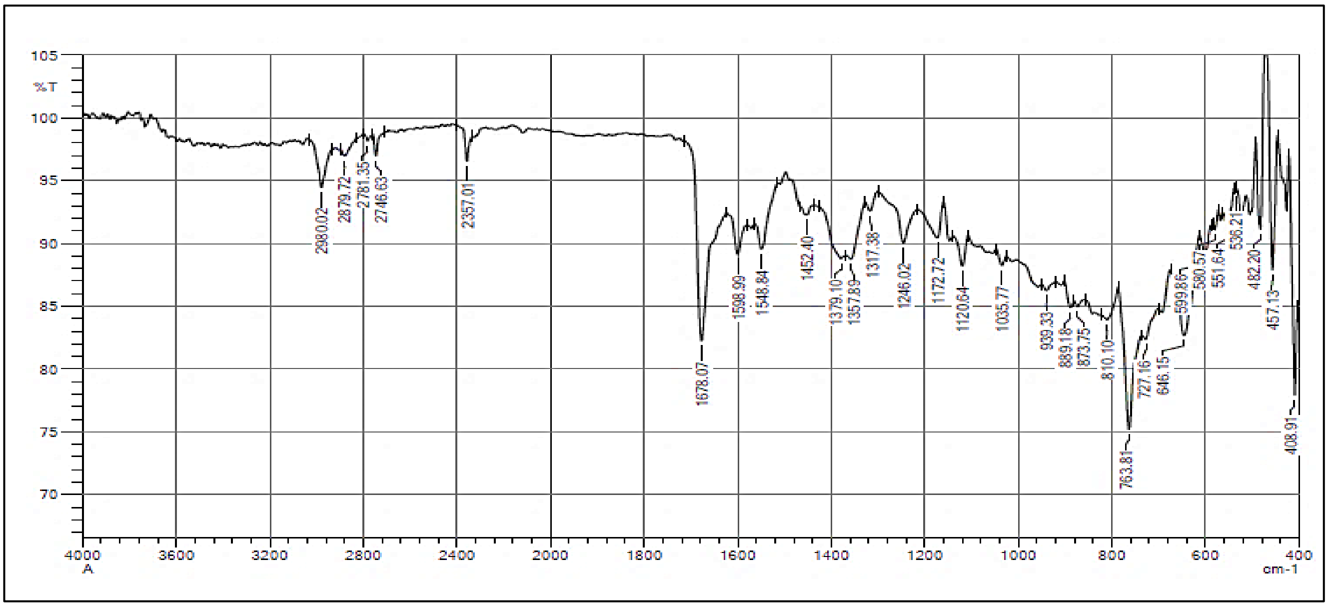


Figure 3. FT-IR spectrum of Pd-complex NPs.

3. 3. Electronic Spectra

Based on figure 4, the (π–π*) transition was represented by the first absorption band at 222 nm in the Azo ligand's electronic spectrum, whereas the (n–π*) transition was represented by the second band at 326 nm [42].

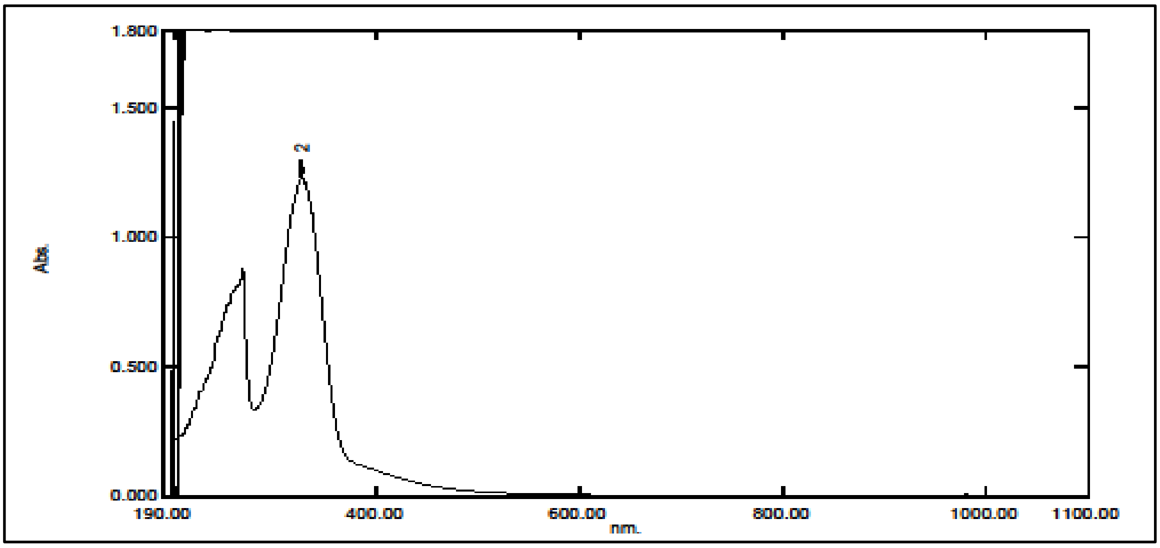


Figure 4. UV-Vis spectrum for azo ligand

A square planar geometry around the Pd (II) ion is indicated by the two peaks in the spectrum of the Azo Schiff complex illustrates in Figure 5, the ligand field transition caused the first high-intensity peak at 249 nm, while the charge transfer transition caused the second peak at 357 nm. The electronic transition for the complex causes the third peak at 395 nm.

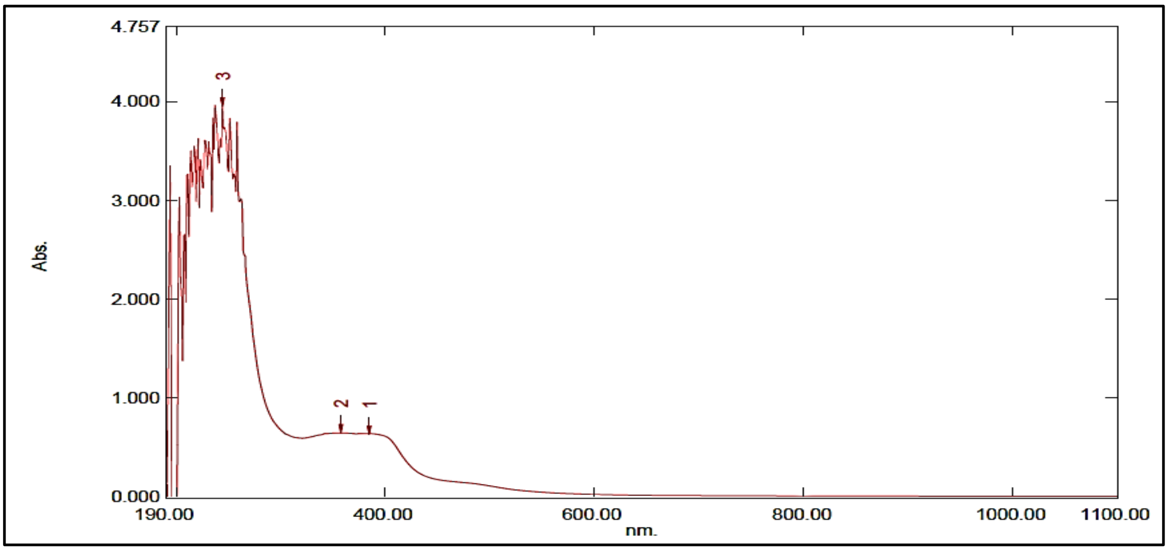


Figure 5. UV-Vis spectrum for Pd-complex NPs.

3. 4. Powder X-ray Diffraction Pattern

The XRD pattern for Pd(II) complex shown in Figure 6. The crystalline structure of the Schiff base complex of pd(II) were measured with the XRD analysis at room temperature. As illustrated in (Figure 5), the XRD pattern exhibited shifted reflection peaks at 2θ = 10.7˚, 18.4˚, 19.5˚, 26.3˚, 27.7˚ and 33.1˚, that are specified to the (011), (102), and (200) to palladium-Schiff base [45–48], and at 2θ = 47.1˚ corresponding for metallic palladium which matching to (200) lattice plane [49].The mean crystallite size for Pd(II) complex NPs was calculated using the Scherer's equation and found to be equal 26.4 nm**.** This value proved the prepared complex is monoclinic plane [50, 51].

$$D = \frac{K\,\lambda}{\beta\,\cos\theta} \qquad \dots (3)$$

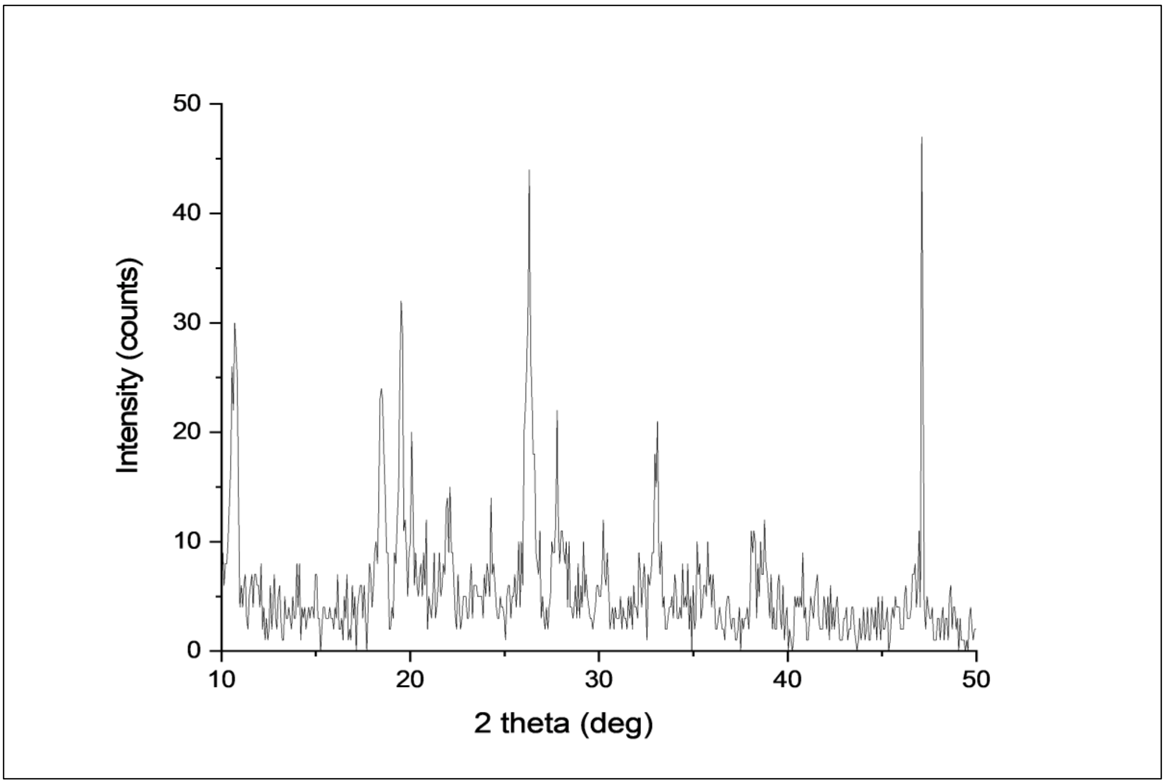


Figure 6. XRD pattern for Pd-complex NPs

4. Photo-decolorization reaction of Pd-complex NPs.

The effect of the concentration of Pd-complex NPs in the decolorization process under $NiCo_2O_4$/ UV-A light shows in (Figure 7), that illustrates the steady rate and efficiency ratio of photo-decolorization progressively increasing as the concentration of Pd(II) compound increases from 5 ppm to 7 ppm. By increasing the number of intermediates in the solution, this behavior seeks to increase the rate and efficiency of the studied photoreaction while cutting its duration in half [52, 53].The peak efficiency of this photochemical reaction is observed at 7ppm, achieving a value of 96.8% after 27 minutes. Table 3 displays the minimal half-time, which was determined using Equation 3 [52] and is equivalent to 8.994 minutes for a 7 ppm Pd(II) compound. However, when concentrations are increased from 10ppm to 15ppm, acted as a “screen” leading to decrease the efficiency and the half-time increases from 85.821% to 68.468% and 13.535 minutes to 16.951 minutes, respectively, because less UV-A light reaches the solution. The hydroxyl radical then limits the so-called screen effect [52, 54].

$$t_{1/2} = \frac{0.693}{k_{app.}} \quad .... \qquad (4)$$

Table 3. The adsorption function results of Pd-complex NPs with $NiCo_2O_4$/UV-A light.

Pd-complex NPs Conc./ppm	**PDE%**	**Half time $t_{1\backslash 2}$ / min**	**Apparent rate constant k app./ min-1**
5	91.589	8.994	0.077051368
7	96.87	7.941	0.087268606
10	85.821	13.535	0.051200591
15	68.468	16.951	0.040882544

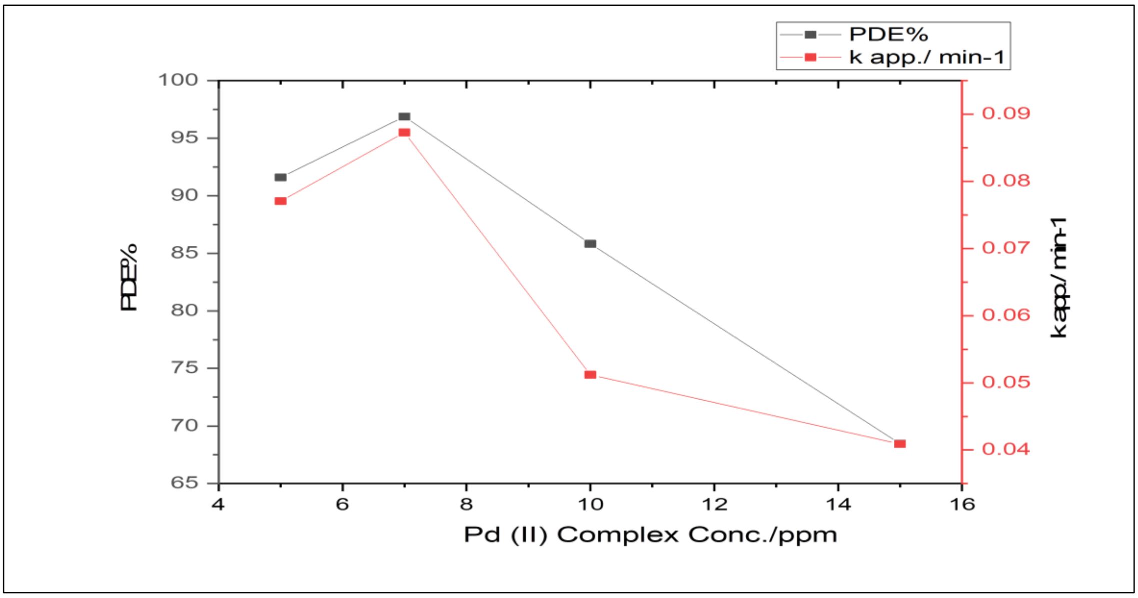


Figure 7. The k_{app} and PED% of photoreaction of Pd-complex NPs with $NiCo_2O_4$.

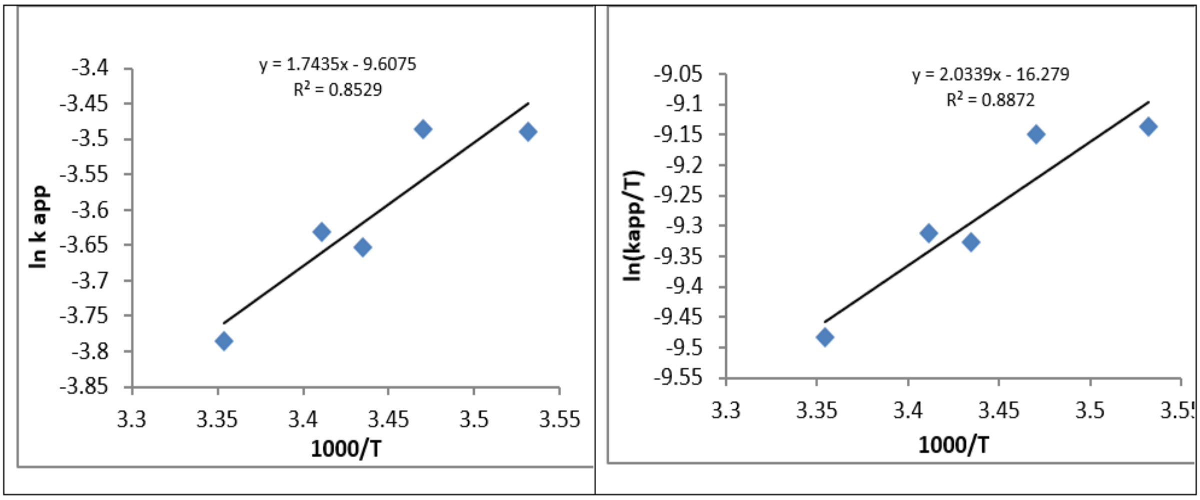
5. Temperature-dependent decolorization mechanism for Pd-complex NPs.

An increase in the temperature of the Pd-complex NPs solution, within the range of 283.15 K to 296.15 K, improves the decolorization process in the $NiCo_2O_4$/ UV-A system, as shown in Figure 7 [55].

$$\ln k_{app} = \frac{-E_a}{RT} + \ln A \qquad \ldots . (5)$$

$$\ln \left(\frac{k_{app}}{T}\right) = \frac{-\Delta H^{\#}}{RT} + \left(\ln \left(\frac{k_B}{h}\right) + \frac{\Delta S^{\#}}{R}\right) \qquad \ldots . (6)$$

Where: R is the gas constant, T : temperature, k_{app} : apparent rate constant of Pd-complex NPs (min^{-1}), A : frequency constant , k_B : Boltzmann constant and h : Plank constant.



(a) **(b)**

Figure 8. The photoreaction of the Pd-complex NPs in a $NiCo_2O_4$/UV-A light system at different temperatures ranging from (283.15-296.15) K is illustrated by: (a)Arrhenius equation (b) Eyring -Polanyi equation.

The activation energy (E_a) and the thermodynamic parameters, $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$, were determined using Gibbs equation that shown below- [56]:

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad \ldots . (7)$$

Table 4. Decolorization of Pd-complex NPs in a $NiCo_2O_4$/UV-A light system with kinetic and thermodynamic activation factors.

Ea kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ kJ mol^{-1} K^{-1}	$\Delta G^{\#}_{288.15}$ kJ mol^{-1}
-14.495	16.909	-0.004	18.297

Table 4 indicates that the low activation energy value supports the conclusion that the decolorization reaction for the Pd-complex NPs in the $NiCo_2O_4$/ UV-A light system will take place in several steps, one of which may be exothermic, before converting at very low positive activation energy through several of chain reactions [17, 55]. The endothermic and non-spontaneous nature of the photo decolorization reaction for Pd-complex NPs is indicated by the positive values of $\Delta H^{\#}$ and $\Delta G^{\#}$, that result from increasing the transition state between Pd-complex NPs molecules and the chemical intermediates, namely hydroxyl radicals [57]. Moreover, the negative value of $\Delta S^{\#}$ signifies that the resultant complex is unstable, displaying higher order than the Pd-complex NPs molecule and experiencing rapid degradation [58, 59].

6. Conclusions

The research study involved the synthesized of Azo-Schiff base complex with Pd(II) ion molar ratio of (2:1), it proved synthesized using U.V-Vis spectra, FT-IR spectra, and CHN analysis, The Photocatalytic decolorization of synthesized Pd-complex NPs solutions were executed in the $NiCo_2O_4$/ UV–A light system was applied inside of a photo reactor. The best results of Pd-complex NPs solutions decolorization demonstrated significant effectiveness at (7 ppm) in color removal. The Arrhenius equation and the Eyring-Polanyi equation demonstrated a strong linear fit for the decolorization experiments conducted within the temperature range of 283.15 to 296.15K indicating that this reaction is endothermic and non-spontaneous. Furthermore, this photoreaction is pseudo-first order based on the constructed Pd-complex NPs structure.

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