

Synthesis, Spectroscopic and Thermal Study of Azo Dye 7-[2-(Benzimidazolyl)Azo]- 8-Hydroxy Quinoline and its Gold(III) Complex

Qusay A. Nema¹, Hassan A. Alshamsi²

Department of Chemistry, Education College, University of Al-Qadisiyah

Abstract: This work involves synthesis and spectral identification of azo ligand 7-[2-(Benzimidazolyl)azo]-8-Hydroxy quinoline (BIAHQ) and prepare of its complex with Au (III). The ligand and its complex were examined using UV-Vis spectroscopy, FT-IR spectroscopy, and photoluminescence spectroscopy (PL). In order to reach the optimal conditions for the degradation of the complex, impact of several factors on photodegradation were studied which include: Study the effect of the complex concentration, temperature range 20-35°C, and acidic function within range 4-10.

Keywords: Azo imidazole, Metal Complexes, Identification, Metal: Ligand Ratio, Infrared Spectra, Electronic Spectra, PL spectra, Photo degradation of complex

1. Introduction

The gold compounds contain some unique properties like unique electronic properties⁽¹⁾. Gold metal has the ability to form strong gold-gold bonds (sometimes called aurophilic interactions)⁽²⁾. The most important oxidation states of gold are Au(I) and Au(III)⁽³⁾. In the presence of strong ligands such as azo dye ligands, gold can undergo easy oxidation⁽⁴⁾. The ligand prevents gold from being reduced to metal. In general, the gold (III) compounds are very toxic, so less research has been done on them⁽⁵⁾. Gold(III) has a d⁸ configuration and square planar tetra-coordination⁽⁶⁾. The gold(III) complexes have many structural chemistries such as [gold(III) porphyrin, dinuclear gold(III) complexes, classical mononuclear gold(III) complexes and organogold(III) compounds]⁽⁷⁾. Gold compounds can be used in several ways such as anticancer drugs⁽⁸⁾. The imidazole ligands and their derivatives azo dyes of heterocyclic compounds can be used in a broad range of applications. They play an important role in organic and inorganic chemistry⁽⁹⁾. The azo dye heterocyclic compounds have a large size in this reaction⁽¹⁰⁾ because they contain one or more active groups that have a tendency to form colored chelate complex compounds that can be specialized with metal ions like Au(III) by using UV-Vis, IR radiation spectrum techniques⁽¹¹⁾. We can see in the [Au(BIAHQ)]Cl.H₂O complex that the ligand behaves like a bidentate tri-azo ligand coordinated from the imidazole ring nitrogen atom (N₃) and the far azo group to the ring nitrogen atom and the oxygen hydroxyl group of quinoline. This leads to the formation of complexes with hexagonal chelate symmetry⁽¹²⁾. [Au(BIAHQ)Cl]Cl.H₂O complex is characterized by having a distinctive color and a fixed dye, so it can be used in industrial areas and medical areas like pesticides, antifungal and antibiotic, or can be used as additives to lubricating oil through high efficiency. In the inhibition of corrosion processes in machines and equipment⁽¹³⁾. The important thing in azo imidazole ligands is that they contain acidic and/or basic groups which increase the chromatic intensity of the ligand and their complexes such as (-Br, -Cl, OCH₃, -CH₃)⁽¹⁴⁾, but sometimes these groups

increase sensitivity, mostly when used in analytical chemistry⁽¹⁵⁾. The imidazole azo is very reactive with transition elements such as Au(III) or other metals.

2. Experimental

2.1 Materials

All chemical materials and solvents were used in this work of high purity from commercial sources such as Merck, Fluka and Aldrich and others. All chemicals were used without any further additional purification. We used Imidazole (C₃H₄N₂) from Sigma-Aldrich. Ammonium acetate (CH₃CO₂NH₄) from FLUKA. Sodium hydroxide (NaOH) from B.D.H. Sodium nitrite (NaNO₂) from B.D.H. Hydrochloric acid (HCl) from B.D.H. Ethanol absolute (C₂H₅OH) from J.T.BAKER. 2-Amino benzimidazole (C₇H₇N₃) from Sigma-Aldrich. 8-hydroxy quinoline (C₉H₇NO) from Sigma-Aldrich. Hydrogen tetrachloroaurate (III) [AuCl₄].4H₂O from Sigma-Aldrich. CaCl₂ from FLUKA. Distilled water.

2.2 Measurements

We used a hot plate LMS-1003, Labtech, Korea. pH-meter 211-Instrument Hanna, Romania. Electronic Balance BL 2105 Sartorius Ag Gottingen, Germany. Oven Memmert LDO-080N Labtech, Korea. Ultrasound bath 405 power sonic Hwashin Korea. Water bath WB 710M Optima, Japan. Melting point apparatus Electrothermal 9300 M.P. Japan. Source light 400 W Osram German. FT-IR spectra were recorded using KBr discs in the range (400-4000) cm⁻¹ on a FT-IR spectrophotometer by Shimadzu model 8400 S FT-IR test scan series (Japan). Electronic spectra were obtained on a UV-vis by Shimadzu model 1650 pc (Japan). Fluorescence spectrophotometer by Agilent Technologies.

2.3 Synthesis of the Azo Dye Ligand:

The heterocyclic azo dye ligand (BIAHQ) has been synthesized by the diazotization coupling reaction by using the Shibata method with some modification (Scheme 1). 2-Amino benzimidazole (1.33 gm, 0.01 mole) was dissolved in a mixture

30 ml distilled water and 5 ml of concentrated hydrochloric acid and 20 ml ethanol. The filtered solution was diazotized at 0-5 °C with (0.75 gm, 0.01 mol) sodium nitrite in 25 ml distilled water drop wise, and stirred for 20 min at 0-5 °C. The resulting diazonium chloride solution was added drop wise with cooling and stirring continuously at 0-5 °C to alkaline solution of 8-hydroxy quinoline (1.45 gm, 0.01 mol), dissolved in mixture of 150 ml absolute ethanol and 30 ml of 8% sodium hydroxide solution in the mixture was stirred continuously for 1 hour

at 0-5 °C in ice bath and allowed to stand over night. The mixture was acidified with dilute hydrochloric acid until pH=6. The precipitate was filtered and washed several times with cold distilled water as well as with 10 ml absolute ethanol to remove the excess of unreacted substance. The isolated dark red crystals were recrystallized from hot ethanol and dried in oven at 60 °C for several hours and stored in a desiccator over anhydrous calcium chloride. The yield was 83% and melting point found to be 238.2 °C⁽¹⁶⁾.



Scheme 1: Synthesis of azo dye ligand 7-[2-(Benzimidazolyl)azo]-8-Hydroxy Quinoline (BIAHQ)

Preparation Metal Complex

The metal complex which prepared using metal salt (hydrogen tetrachloroaurate(III) $H[AuCl_4] \cdot 4H_2O$) and the azo dye ligand (BIAHQ). The amount of 0.45 gm (0.002 mol) from azo dye ligand was added dissolved in 50 ml hot ethanol which was added in drops with stirring continuously to (0.001 mol), 1:1 [M:L] for $H[AuCl_4] \cdot 4H_2O$ dissolved in 40 ml hot buffer solution (ammonium acetate) at pH=7. The mixture was heated to 70 °C for 30 min., then left over night. The separated solid complexes were filtered off, washed with distilled water and then little warm ethanol to remove any traces of unreacted materials. The complex obtained was finally dried under vacuum desiccators over fused $CaCl_2$ ^(17,18).

Table 1: Molar absorptivity (ϵ) of (BIAHQ) ligand and its Au(III)-complex

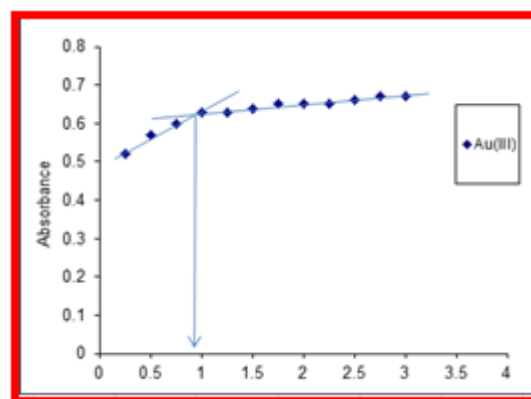
M : L	Absorbance of complexes Au(III)
M : Optimal Conc. $\times 10^{-4} M$	Molar Absorptivity $\times 10^3 (\epsilon) L \cdot mol^{-1} \cdot cm^{-1}$
01:00.3	0.521
01:00.5	0.57
01:00.7	0.6
01:01.0	0.63
01:01.3	0.63
01:01.5	0.64
01:01.8	0.65
01:02.0	0.65
01:02.2	0.651
01:02.5	0.66
01:02.8	0.67
01:03.0	0.67

3. Result and Discussion

3.1 Metal: Ligand Ratio

To finding the expected structure formula of prepared complex were studied by molar ratio method at (λ_{max}). The solution of prepared complex increase the intensity of the color as approach of point intersection ratio. (M:L) and colors continuous constant at passing this point which indicate that the complex formed in constant. Solution⁽¹⁹⁾.

The physical properties of (BIAHQ) ligand and $[Au(BIAHQ)Cl]Cl \cdot H_2O$ can be show in table(1)



Scheme 2: Molar ratio curve of Au(III)-(BIAHQ) complex with ligand

Table 2: Some physical properties for ligand (BIAHQ) and its Au(III) complex

Compound	m.p.(°C)	Colour	m.f(m.wt)
L=BIAHQ	238	Dark red	C ₁₆ H ₁₁ N ₅ O (289.266)
[Au(L)Cl]Cl.H ₂ O	275	Earthy	C ₁₆ H ₁₂ N ₅ O ₂ Cl ₂ Au (710,917)

3.2 Infrared Spectra

The infrared spectroscopic data of the azo dye ligand and its Au(III)-complex have been studied in lab. The comparison between spectra of the ligand with the coordination Au(III)-complex have apparent, characteristic differences of some of these main shifts along with conclusion are give below.

1) The spectrum of free ligand (BIAHQ) show abroad a weak absorption band around at 3380cm⁻¹ due to $\nu_{(OH)}$ ⁽²⁰⁾. This abroad due to strong inter molecular hydrogen bonding⁽²¹⁾. The spectrum of Au(III)-complex show abroad a weak band around at 3218 cm⁻¹

- ¹ which evidence to the coordination of water molecculer⁽²²⁾.
- 2) In the spectrum of free ligand Two weak bands had been observed at 3047cm⁻¹ and 2661cm⁻¹ because of $\nu_{(CH)}$ aromatic and aliphatic respectively⁽²³⁾. These bands are the same location in Au(III)-complex.
 - 3) In The free ligand shows a medium band at 1572cm⁻¹ because of $\nu_{(C-O)}$ of 8-hydroxy quinoline⁽²⁴⁾. This band ambulant at 1562 cm⁻¹ in Au(III)-complex⁽²⁵⁾.
 - 4) In ligand The $\nu_{(C=N)}$ of benzimidazole 8-hydroxy quinolin shows recpetively two absorption bands at 1580 cm⁻¹ and at 1505cm⁻¹. In the spectra of Au (III)- complex these bands shift to lower frequences at 1516cm⁻¹ and 1606 because of linkage with nitroge of hetero cyclic benzimidazole ring^(26,27).
 - 5) The spectrum of free ligand shows two absorption bands at 1473 cm⁻¹ and 1411cm⁻¹ due to azo group $\nu_{(N=N)}$. The position of these bands in Au (III) -complex are shifted to a lower frequencies at 1465 cm⁻¹ and 1419 cm⁻¹. this indicates that it have been effected on coordination with Au (III)⁽²⁸⁾.

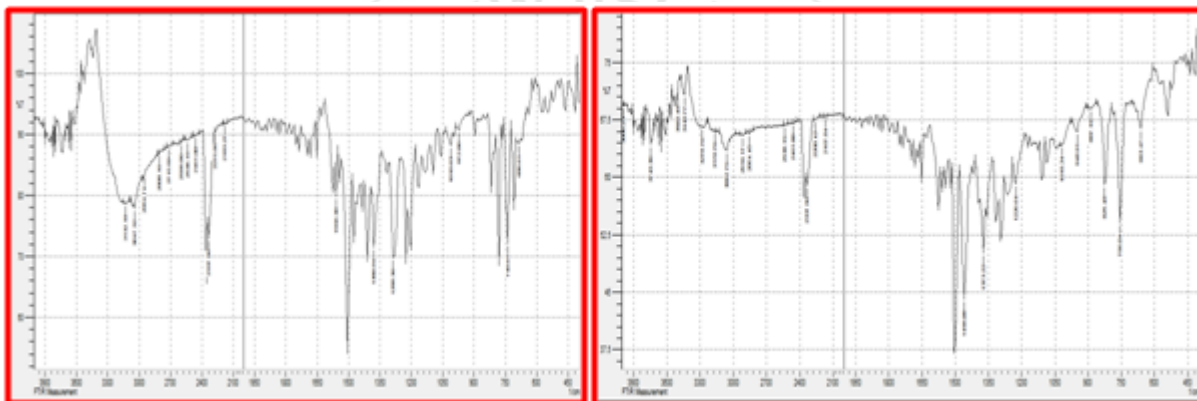


Figure 1: Infrared spectrum of ligand (BIAHQ) and its complex with Au (III)-complex in cm-1 unit (KBr)

Table 3: Characteristic IR absorption bands of the ligand (BIAHQ) and its metal complex in cm⁻¹ units (KBr disc)

Sample	Assignment									
	$\nu_{(O-H)}$	$\nu_{(N-H)}$ Imidazole	$\nu_{(C-O)}$	$\nu_{(C=N)}$ Imidazole Hydroxyl	$\nu_{(N=N)}$	$\nu_{(C=C)}$	$\nu_{(C-N=N-C)}$	$\nu_{(C-N)}$ imidazole $\nu_{(C-N)}$ quinol	$\nu_{(M-O)}$	$\nu_{(M-N)}$
BIAHQ	3301 w.br.	3170 m.br	1573 m.	1620 m. 1504 s.	1473m. 1380 s.	1380s.	1288 s.br	1226 s. 779 s.	-	-
[Au(L)Cl] Cl. H ₂ O	3350 m.br.	3255m.br	1629 m.	1605 w. 1577 s.	1465v.s. 1419 m	1373s.	1280 s. 779 s.	1242 w 1110 s.	570 w.	510 m.

3.3 Electronic Spectra

The electronic Spectra of azo dye ligand and its Au (III) – complex were studied in absolute ethanol as a solvent (10⁻³M). The free ligand (BIAHQ) spectrum gives three absorption bands, the first band show at 517 nm (19342 cm⁻¹) for $n \rightarrow p^*$ transition of the azo group ($N=N$)⁽²⁹⁾. The second band is observed at 310 nm (32258cm⁻¹) due to $p \rightarrow p^*$ transition to the (C=C) group in

heterocyclicbenzimidazole and hydroxyl quinoline rings⁽³⁰⁾, the third band show at 241 nm (41494cm⁻¹) for $n \rightarrow \sigma^*$ transition to the (C=N) group in the ligand structure⁽³⁰⁾. The electronic Spectrum of Au(III)-complex show band at 385nm(25974cm⁻¹) is assigned to $^3A_{2g} \rightarrow ^3T_{1g}$ transition. So the Square Planer geometry and hybridization dsp^3 are suggested. Fig.2 show the spectra of ligand and its complex with Au(III) ion⁽³²⁾.

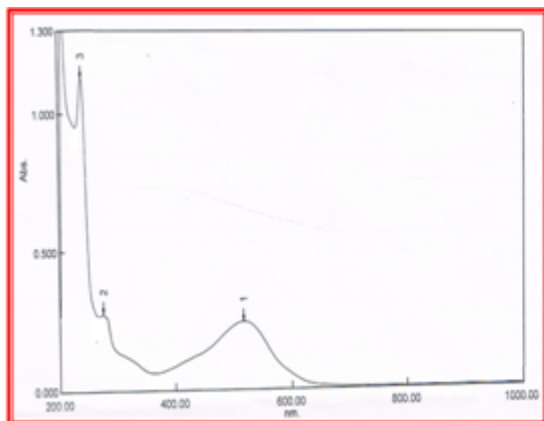


Figure 2 (a): UV-Vis spectrum of ligand

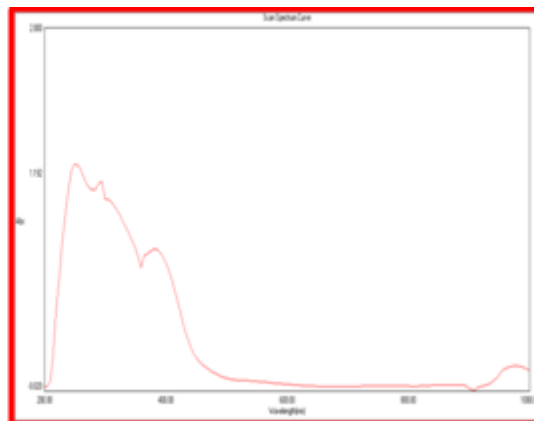


Figure 2 (b): UV-Vis spectrum of Au(III)-complex

3.4 PL spectra

The room-temperature PL spectra are showed in Fig. 4a and 4b. Each spectrum of the ligand and its complex consists of some sharp bands in the visible region of spectra⁽³³⁾. The peak centered at approximately 3.2 eV known as the green defect luminescence⁽³⁴⁾. The

(BIAHQ)ligand and its complex generally attributed to oxygen vacancies, other assignment was also proposed in the literature⁽³⁵⁾. The peak centered at 3.49 eV for the ligand spectrum appeared in 355 nm, show in Fig 4a. While in the Au(III)-complex, the peak centered at 3.22 eV appeared in 385nm⁽³⁶⁾.

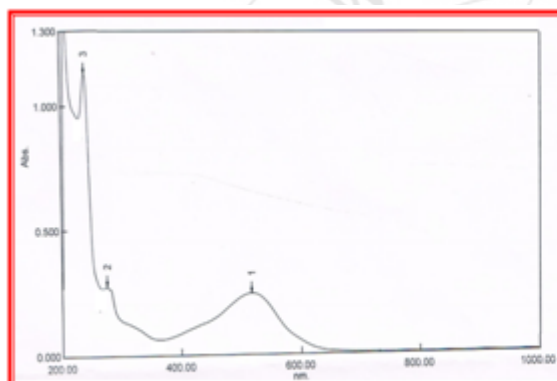


Figure 4(a): The Photoluminescence Spectra of ligand (BIAHQ) complex

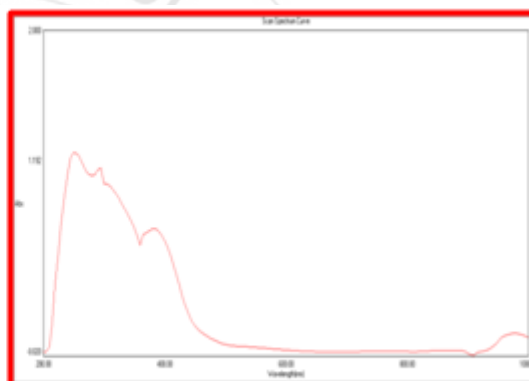


Figure 4(b): The photoluminescence Spectra of Au(III)-complex

3.5 Photodegradation of complex

3.5.1 The effect of irradiation time in Dark Reaction (Adsorption Reaction)

This experiment was carried out in the absence of U.V by using 0.4 gram of Au- (BIAHQ) complex . We show the result in the plot(AbsorptionEffect) in figure 5. The result indicate that there is now reaction in the absence of UV, because the wavelength was small change with increase the time.this indicate that the Au-(III) complex is high stability⁽³⁷⁾.

3.5.2 Effect of irradiation time and concentration of complex

We studied the irradiation time on the complex dissociation rate with 1×10^{-4} M concentration, 298 K temperature and 400Watt light intensity.

We observed in figure 5 that the absorption spectrum curve of complex decrease in increase of irradiation time.

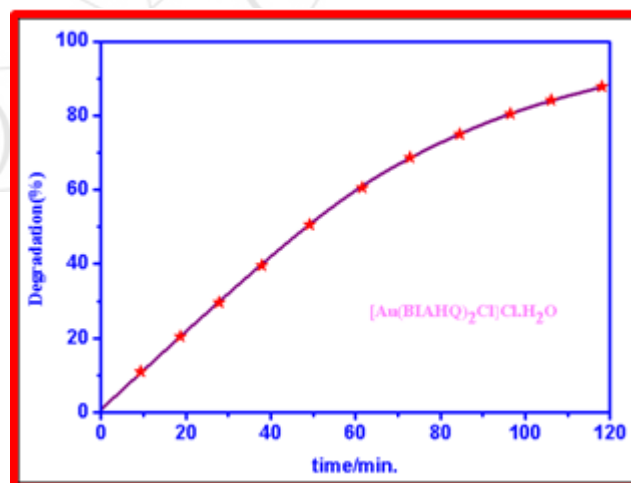


Figure 5: The change of Adsorption time in existence irradiation of $[Au(BIAHQ)_2Cl]Cl.H_2O$

3.5.3 Effect of concentration of Au-(BIAHQ) complex

In this experiment we used different dosages of Au-(BIAHQ) complex. as we show in figure 6. The other factors kept constant like (initial pH solution 7, light intensity 400Watt and temperature 298 K. According to the result, we found that 0.3

gram of Au-(BIAHQ) complex gives optimum photocatalytic activity.

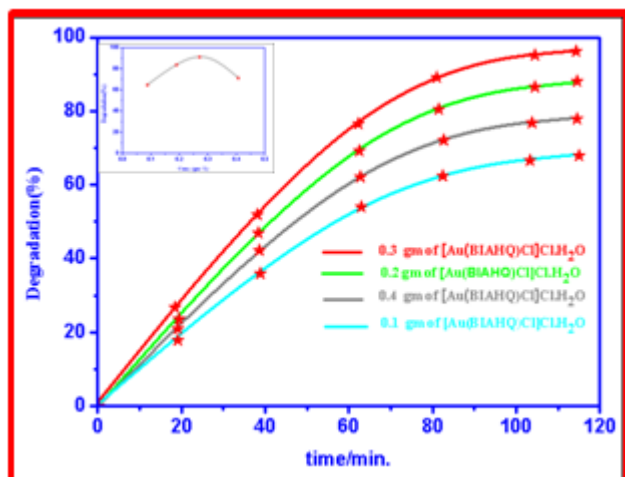


Figure 6: The change of Adsorption time in different concentration with $[\text{Au}(\text{BIAHQ})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$

3.5.4 Effect of Initial pH Solution for Au-complex

The pH play an important role in the production of hydroxyl radical. In this experiments we fix the experimental conditions such as light intensity 400Watt), Au-(BIAHQ) complex concentration (0.4g/200mL of Ethanol) and temperature 298k. **figure 6** show the degradation increase with increase of initial pH solution up to pH 7 and then decrease in pH (9,3,5 and 4). so the best pH of Au-(BIAHQ) complex is pH 7.

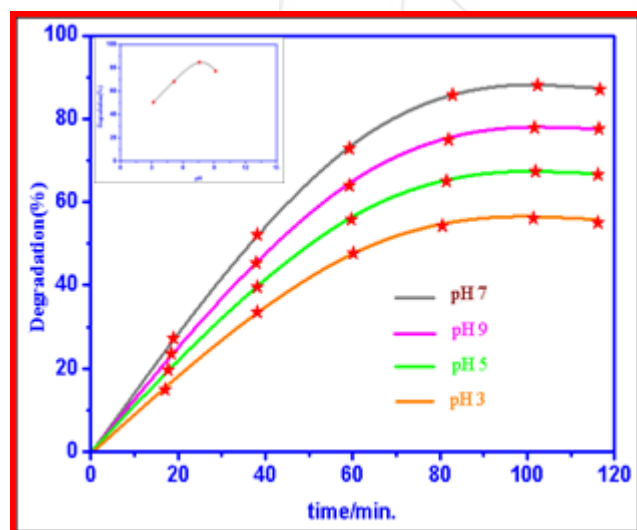


Figure 7: The change of adsorption time in different pH of solution with $[\text{Au}(\text{BIAHQ})_2]\text{Cl}\cdot\text{H}_2\text{O}$

3.5.5 Effect of Temperature on Au-(BIAHQ) complex decomposition

In this experiments we show that the higher temperature can fast the Au-(BIAHQ) complex decomposition when fix other condition such as light intensity 400Watt), Au-(BIAHQ) complex concentration (0.4g/200mL Ethanol), initial pH Solution equal 7 as we show in **figure 15** we used different temperature with Au-(BIAHQ) complex in the range (278–293K). Its found that the complex decomposition increase when the temperature increase. in

figure 6 we show the reaction is pseudo first order according to the Langmuir Hishelwood relationship.

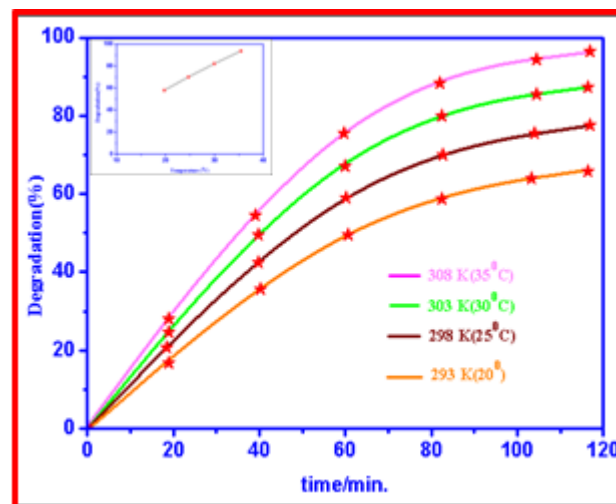


Figure 8: The change of Adsorption time in different temperature of solution with $[\text{Au}(\text{BIAHQ})_2]\text{Cl}\cdot\text{H}_2\text{O}$

References

- [1] Alves, Leonor and et al., Synthesis and stabilization of subnanometric gold oxide nanoparticles on multiwalled carbon nanotubes and their catalytic activity., Journal of the American Chemical Society., 2011, 133.26, 10251-10261.
- [2] Mubeen, Syed and et al., Plasmonic properties of gold nanoparticles separated from a gold mirror by an ultrathin oxide., Nano letters, 2012, 12.4, 2088-2094.
- [3] Huang, Xiaohua, and Mostafa E., Gold nanoparticles: optical properties and implementations in cancer diagnosis and photothermal therapy., Journal of Advanced Research, 2010, 1.1, 13-28.
- [4] Verma, Ayush, and Francesco S., Effect of surface properties on nanoparticle-cell interactions., 2010, 6.1, 12-21.
- [5] Louis, Catherine, and Olivier P., Gold nanoparticles for physics., chemistry and biology., London, Imperial College Press., 2012.
- [6] Tsukamoto, Daijiro and et al., Gold nanoparticles located at the interface of anatase/rutile TiO_2 particles as active plasmonic photocatalysts for aerobic oxidation., Journal of the American Chemical Society., 2012, 134.14, 6309-6315.
- [7] Kumagai, Michiaki and et al., Enhanced in vivo Magnetic Resonance Imaging of Tumors by PEGylated Iron-Oxide-Gold Core-Shell Nanoparticles with Prolonged Blood Circulation Properties., Macromolecular rapid communications., 2010, 31.17, 1521-1528.
- [8] Zhu, Chengzhou and et al., In situ loading of well-dispersed gold nanoparticles on two-dimensional graphene oxide/ SiO_2 composite nanosheets and their catalytic properties., Nanoscale., 2012, 4.5, 1641-1646.
- [9] Frath, D. and et al., Luminescent Materials: Locking π -Conjugated and Heterocyclic Ligands with Boron (III)., Angewandte Chemie International Edition., 2014, 53.9, 2290-2310.
- [10] Nolan and Steven P., ed. N-Heterocyclic carbenes in synthesis., John Wiley & Sons., 2006.

- [11] Chianese, Anthony R. and et al., Iridium Complexes of CCC-Pincer N-Heterocyclic Carbene Ligands: Synthesis and Catalytic C–H Functionalization, *Organometallics.*, 29.13, 3019-3026. 2010
- [12] Park, Hee-Jun and et al., Unsymmetric Ru (II) complexes with N-heterocyclic carbene and/or terpyridine ligands: synthesis, characterization, ground-and excited-state electronic structures and their application for DSSC sensitizers., *Inorganic chemistry.*, 2010, 49.16, 7340-7352.
- [13] Hajipour, Mohammad J. and et al., Antibacterial properties of nanoparticles., *Trends in biotechnology.*, 2012, 30.10, 499-511.
- [14] Crees, Rachel S. and et al., Synthesis of a Zinc (II) Imidazolium Dicarboxylate Ligand Metal–Organic Framework (MOF): a Potential Precursor to MOF-Tethered N-Heterocyclic Carbene Compounds., *Inorganic chemistry.*, 2010, 49.4, 1712-1719.
- [15] Gao, Huan-huan and et al., Synthesis of anionic iron (II) complex bearing an N-heterocyclic carbene ligand and its catalysis for aryl Grignard cross-coupling of alkyl halides., *Organometallics.*, 2010, 29.18, 4189-4192.
- [16] Habeeb A., Khalid A., and Suadad J., Synthesis, characterization, thermal and kinetic photochemical decomposition study of new azo dye 7-[2-(Benzimidazolyl) Azo]-8-Hydroxy Quinoline and its zinc (II) complex., *Synthesis.*, 2014, 6.8.
- [17] Alshamsi, Hassan A., Khalid A., and Suadad J., Thermal Decomposition Study on Solid Complexes of 7-[2-(Benzimidazolyl) azo]-8-hydroxy quinoline with Co (III), Ni (II) and Cu (II)., *Oriental Journal of Chemistry.*, 2015, 31.2, 809-818.
- [18] AL-Adilee J., Ahmed A., and Ali T., Synthesis of some transition metal complexes with new heterocyclic thiazolylazo dye and their uses as sensitizers in photo reactions., *Journal of Molecular Structure.*, 2016, 1108, 378-397.
- [19] Guibaud, Gilles and et al., Sorption of Cd (II) and Pb (II) by exopolymeric substances (EPS) extracted from activated sludges and pure bacterial strains: modeling of the metal/ligand ratio effect and role of the mineral fraction., *Bioresource Technology.*, 2009, 100.12, 2959-2968.
- [20] Sulway, Scott A. and et al., Iron (II) Cage Complexes of N-Heterocyclic Amide and Bis (trimethylsilyl) amide Ligands: Synthesis, Structure, and Magnetic Properties., *Inorganic chemistry.*, 2011, 50.6, 2521-2526.
- [21] Adhikary, Sirsendu D. and et al., Au (I)- and Pt (II)-N-heterocyclic carbene complexes with picoline functionalized benzimidazolylidene ligands; synthesis, structures, electrochemistry and cytotoxicity studies., *New Journal of Chemistry.*, 2012, 36.3, 759-767.
- [22] Pal, Amlan K., and Garry H., Design, synthesis and excited-state properties of mononuclear Ru (II) complexes of tridentate heterocyclic ligands., *Chemical Society Reviews.*, 2014, 43.17, 6184-6197.
- [23] Grubbs, Robert H., and Daniel O., *Handbook of Metathesis, Volume 2, Applications in Organic Synthesis.*, John Wiley & Sons., 2015.
- [24] Kuwata, Shigeki, and Takao I., β -Protic Pyrazole and N-Heterocyclic Carbene Complexes: Synthesis, Properties, and Metal–Ligand Cooperative Bifunctional Catalysis., *Chemistry–A European Journal.*, 2011, 17.13, 3542-3556.
- [25] Tomás M., Eder and et al., Water-Soluble Gold (I) and Gold (III) Complexes with Sulfonated N-Heterocyclic Carbene Ligands: Synthesis, Characterization, and Application in the Catalytic Cycloisomerization of γ -Alkynoic Acids into Enol-Lactones., *ACS Catalysis.*, 2013, 3.12, 3086-3098.
- [26] Bantreil, Xavier, and Steven N., Synthesis of N-heterocyclic carbene ligands and derived ruthenium olefin metathesis catalysts., *nature protocols.*, 2011, 6.1, 69-77.
- [27] Romain, Charles and et al., Synthesis and Structural Characterization of a Novel Family of Titanium Complexes Bearing a Tridentate Bis-phenolate-N-heterocyclic Carbene Dianionic Ligand and Their Use in the Controlled ROP of rac-Lactide., *Organometallics.*, 2010, 29.5, 1191-1198.
- [28] Crees, Rachel S. and et al., Synthesis of a Zinc (II) Imidazolium Dicarboxylate Ligand Metal–Organic Framework (MOF): a Potential Precursor to MOF-Tethered N-Heterocyclic Carbene Compounds., *Inorganic chemistry.*, 2010, 49.4, 1712-1719.
- [29] Dakiky M., and Nemcova L., Aggregation of o, o'-Dihydroxy azo Dyes III. Effect of cationic, anionic and non-ionic surfactants on the electronic spectra of 2-hydroxy-5-nitrophenylazo-4-[3-methyl-1-(4"-sulfophenyl)-5-pyrazolone]., *Dyes and Pigments.*, 2000, 44.3, 181-193.
- [30] Bauer, Christophe, Patrice J., and André K., Photooxidation of an azo dye induced by visible light incident on the surface of TiO₂, *Journal of Photochemistry and Photobiology A, Chemistry.*, 2001, 140.1, 87-92.
- [31] Akiyama, Hidenari and et al., Synthesis and properties of azo dye aligning layers for liquid crystal cells., *Liquid Crystals.*, 2002, 29.10, 1321-1327.
- [32] Irick J., Gether and Pacifici J., Solvent and Substituent Effects on the Ultraviolet-Visible Absorption Spectra of Azo Dyes., *Textile Research Journal.*, 1972, 42.7, 391-397.
- [33] Yu, Ying and et al., Enhancement of adsorption and photocatalytic activity of TiO₂ by using carbon nanotubes for the treatment of azo dye., *Applied Catalysis B., Environmental.*, 2005, 61.1, 1-11.
- [34] Feng, Jiyun and et al., Degradation of azo-dye orange II by a photoassisted Fenton reaction using a novel composite of iron oxide and silicate nanoparticles as a catalyst., *Industrial & engineering chemistry research.*, 2003, 42.10, 2058-2066.
- [35] Sorof, Sam and et al., Zonal electrophoresis of the soluble proteins of liver and tumor in azo dye carcinogenesis., *Cancer research.*, 23.6 Part 1, 1963, 864-882.
- [36] Wilcoxon, J. P. and et al., Photoluminescence from nanosize gold clusters., *The Journal of chemical physics.*, 1998, 108.21, 9137-9143.