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Synthesis, Spectroscopic Characterization of Nickel Complex from $C_{16}H_{19}N_3O_3S$ and Photo Degradation Using Prepared Nano TIO_2 By Sol-Gel as Catalyst.

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ABSTRACT

Nickel (II) complex with $C_{16}H_{19}N_3O_3S$ (L) were synthesized and identification by phesio-chemical procedures elemental analysis C.H.N.S, metal analysis A. A, UV-Vis, FTIR, magnetic susceptibility and conduct metric measurements. From this analysis the ligand behaves as a bidentate through oxygen carbonyl group and nitrogen atom of β-lactase group. Octahedral geometry was suggested for the Ni (II).The photo degradation of complex were study using photoreaction cell and prepared TiO_2 nano catalyst in different condition such as concentration, Temperature, pH, light, catalysis amount and sun light. The results show that the action is first order with activation energy equal to (7.98144 kJ/mol).

Keywords: Amoxicillin derivation, photo degradation, Sol-Gel, TiO_2nanopowder

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INTRODUCTION

Metal-drug play important roles in biological processes and the playing field of information concerned with the use of inorganic chemistry to therapy or diagnosis of disease is medicinal inorganic chemistry [1]. The field of inorganic science in medication may conveniently be isolated into two principle classifications. First ligand as drug target metal ion in some form, whether free or protein –bound. Second, metal-based medications and imaging specialist where the center ion is classically the key component of the instrument of action [2].Transition metals have a significant position in medical inorganic chemistry. Transition metals exhibit unlike oxidation state which can interact with a sum of negative charged molecules [3]. This movement of transition metals led to the recent development of medication depends on metals and are thought to be potential contender for pharmacological and helpful applications [4]. It has been examined that there is a probability of utilizing some inorganic complexes by considering them as a helpful operators and entering them in pharmaceuticals [2], and additionally the impact of the mineral son the living cells and tissues, hence a large number of investigations and explores to control the toxic and non-toxic concentrations of metal ions in living organisms by changing them into metal complexes. Amoxicillin Antibiotics, ($C_{16}H_{19}N_3O_5S$) a semi synthetic penicillin's sis symmetric of ampicillin, with a broad spectrum of bactericidal activity against many gram positive and gram negative microorganisms [5].

Titanium dioxide (TiO_2) is a white pigment [6], it is the popular materials used in various applications because of its semiconducting, photo catalytic, energy converting, electronic and gas sensing properties [7] TiO_2 has favorable characteristics include biological and chemical inertness, environmentally friendly, non-toxic and cheaper, availability, transparency ,a the molecular level, a wideband gap, strong oxidizing power. The synthetic methods developed for the preparation of nanostructure TiO_2, a wide variety of approaches including flame synthesis, ultrasonic irradiation, chemical vapor deposition, sol–gel method has been adopted. Among them, compared to other methods, sol-gel route is regarded as a good method to synthesis ultrafine metallic oxide and has been widely employed for preparing titanium dioxide (TiO_2) particles [8]. M.A. Hussein, *et al* [9] (2009) studied Cu(II), Co(II), Ni(II) and Fe(III) chelates of amoxicillin (AMX) antibiotic drug proved that dentate chelates was through $–NH_2$,–that AMX acts with mentioned metal chlorides as a tri –NH, and oxygen of carbonyl β-lactam groups. K.D. Radosavljevic, *et al* [10] studied TiO_2synthesized by sol-gel applied in the photo catalytic degradation of amoxicillin, the effect of the pH value of the photo degradation AMX was studied at five different pH values. The adjustments of acidic (pH 3 and 5) and alkaline medium (pH 9 and 11).

EXPERIMENTAL

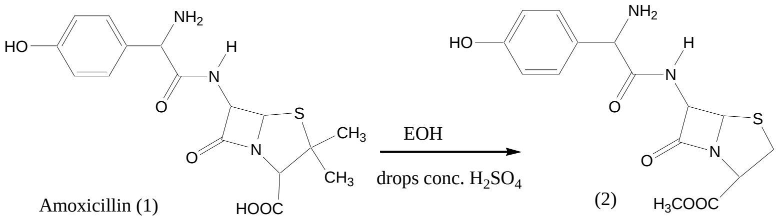
Materials and Instrumentation

The metal salt $NiCl_2.6H_2O$ in this work were obtained from Fluka, FTIR were recorded on Shimadzu 8400 Fourier transform infrared spectroscopy, wavelength range of (4000-400) cm^{-1} and UV-Vis 160 A Shimadzu was used to record the electronic spectra at wave length range of (190-1100) nm. The metal analysis was conducted via a Perkin Elmer 500 Atomic Absorption Spectrophotometer. Conductivity Meter 220 with Gall encamp was used to calculate the molar conductivity in ethanol as a

Solvent at room temperature.M.F.B-6000.01 was used as a melting device .Magnetic susceptibility balance model MSB-MKT was used for magnetic moment measurement.

Preparation of ligand$C_{16}H_{19}N_3O_3S$ (L)

The ligand was prepared as reported in the literature [11] 6-(2-amino-2-(4-hydroyphenyl) acetamido-2-2 diethyl -5-oxo-1-thia-4-azabicyclo (3.2.0) Oct –hebtane 3 carboxyl ate. A mixture of amoxicillin (0.02mole) and an excess of absolute methanol (50ml) with (1-2) drops of concentrate sulfuric acid was placed in 100 ml round bottom flask. The mixture was refluxed in a bath water (50°C) for 3 hrs. The solution was cooled and poured into crushed ice. The obtained precipitate was filtered, dried and recrystallized from ethanol.



Preparation of complexes

Amount of (0.236 g) of $NiCl_2.6H_2O$was dissolved in 10 ml of ethanol and mixed with (0.93) g of ligand dissolved in (15 ml) ethanol in molar ratio 1:2 (M: L) in a round bottom flask under heating and refluxed for 3 hrs. The colored precipitate was filtered then washed with ethanol and dried by using desiccators.

Preparation of (TiO_2) Nano particles by (Sol-Gel) method

Five milliliters of glacial acetic acid (99.5%) were added drop wise to 50 ml of distilled ethanol (99.9%) and vigorously stirred for about 1 hr., then (6.3) ml of Titanium tetra isopropoxide (TTIP 99%) were added drop wise to the clear cooled glacial acetic acid- ethanol solution with continuous stirring for about 1 hr. drying for 1 hr. at 50 ^{o}C and calcinating at 400 ^{o}C for 3 hrs [12].

Photolysis Procedure

Thermostatic cylinder photo cell (75 ml) and a medium mercury pressure lamp were used. A series of standard solutions were prepared with a concentration of (1-3.5) $\times 10^{-4}$ M and the absorption values were recorded at a wavelength of 427 nm.

RESULTS AND DISCUSSION

The physic-chemical properties of ligand and Ni- complex were summarized in Table (1).The complex was colored powder stable at room temperature. A molar ratio of (1:2) (M: L) for this prepared complex, can be suggested according to the analytical data.

Table 1: Some of the physical properties and molar conductivity of the ligand (L) and Ni-complex

Compounds	Elemental analysis Found (cal.)				M.P °C	Color	Yield %	μ_s cm^{-1}
	C%	H%	N%	M%				
$C_{16}H_{19}N_3O_3S$ (L)	48.04 (49.1)	5.26 (5.30)	18.2 (19.3)	-	196	Light yellow	87	-
$NiC_{32}H_{42}N_6O_8S_2Cl_2$ (NiL_2)	39.52 (40.5)	4.50 (4.61)	12.99 (14.01)	4.91 (5.51)	236	Greenish yellow	76	81

Infrared spectra

The FTIR spectra of ligand exhibits a strong band at (1778) cm^{-1} due to the presence of carbonyl group of ester that appears usually around (1700) cm^{-1}, [13] β-lactam carbonyl group occurred at a significant value about (1724) cm^{-1}, the band of the ν(NH) group appeared at (3178.5) cm^{-1} in the spectrum. The band of carbonyl group of ester did not shift in the complex which means that the carbonyl did not participate in coordination. The bands attributed to the β-lactam were shifted to higher wave number in complex about (11.9) cm^{-1} indicating that β-lactam carbonyl group was involved in complex formation [14]. The bands of ν(NH) group were shifted to higher wave number in complex about (23) cm^{-1}so the ligand behaves as a bidentate through the coordination via oxygen and nitrogen atoms are further supported by the occurrence of M-O and M-N bands in the spectrum of the complex at the range mentioned in literatures [15,16]. The other important characteristic peaks in the FT-IR spectrum are listed in Table (2).

Table 2: Selected IR data for Ligand (L) and Ni-complex

Comp	νNH	ν(C=O) Est.& Amid	ν(CH) Alpha Aroma	ν(C=O) B-acetum	ν(C=C)	ν(C-O)	ν(M-N)	ν(M-O)	$\nu(H_2O)$
L	3032	1778 1689	2970 3151	1724	1616	1242	----	-----	3444
NiL_2	3055	17788 1685	2900 3186	1735.9	1616	1238	555	428	3410

Electronic spectra

The electronic absorption spectrum is used to predict the geometry according to the shape and number of observed peaks beside those calculated once depending on the information of Reach parameter (B), 10Dq and nephelauxetic factor (β) using Tanabe Sugano diagram. The electronic spectrum of the ligand shows three main bands, the first and the second absorption bands appeared at (42372 and 36363) cm^{-1} due to $(\pi-\pi^*)$ transitions located on (C=C) group. The third absorption appeared at (31250) cm^{-1} attributed to $(n-\pi^*)$ may be located on the (C =O) group [17].

Ni L$_2$Complex

The electronic spectrum shows two bands at (16260 and 23419) cm^{-1}which attributed to the $^{3}A_{2}g \rightarrow {}^{3}T_{1}g$ (f) and $^{3}A_{2}g \rightarrow {}^{3}T_{1}g$ (p) transitions respectively. The transition (ν_1) $^{3}A_{2}g \rightarrow {}^{3}T_{2}g$ was calculated and found to be (8499) cm^{-1} from these band indicate an Octahedral structure around Ni (II) ion [18]. The magnetic moment of the complex (2.86) BM. The ligand field parameters were estimated and can be shown in Table (3). .From these results the proposed structure of the complex is Octahedral Fig. (1).

Table 3: Electronic spectra and their assignment of the prepared ligand and its Ni-complex

Comp.	Band cm^{-1}	Assignment	B^{0}cm^{-1}	Dq/B$^-$	B	10Dq cm^{-1}
L	67613 42372 31250	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	-	-	-	-
Ni L_2	8499 16260 23419	$^{3}A_{2}g\rightarrow{}^{3}T_{2}g$ $^{3}A_{2}g \rightarrow{}^{3}T_{1}g(F)$ $^{3}A_{2}g \rightarrow{}^{3}T_{1}g(p)$	1035	1.2	0.68	8499

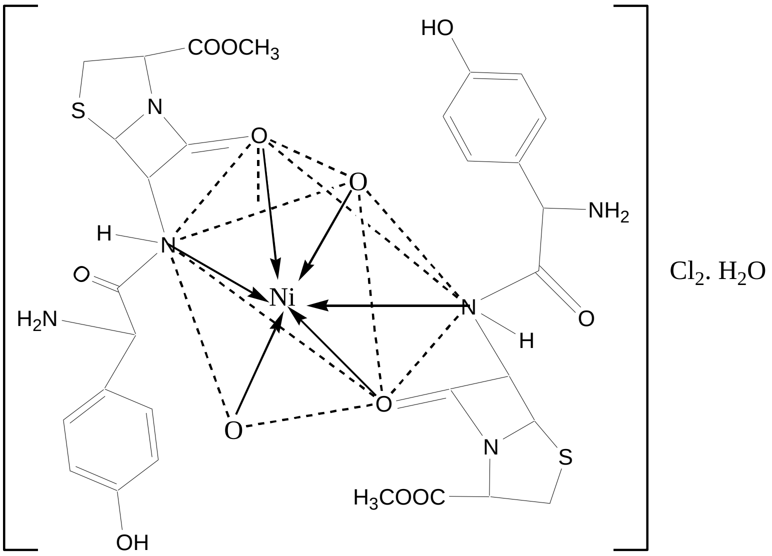


Figure 1: Proposed structure for the prepared metal complex.

Characterization of Nanostructure TiO_2

Atomic force microscope was used to detect (TiO_2) nanoparticles structure and to get morphological information Fig. (2) show typical surface AFM image (in three and two dimensions). The nano particle are spherical in shape [19] and has an average diameter of (52.21) nm.

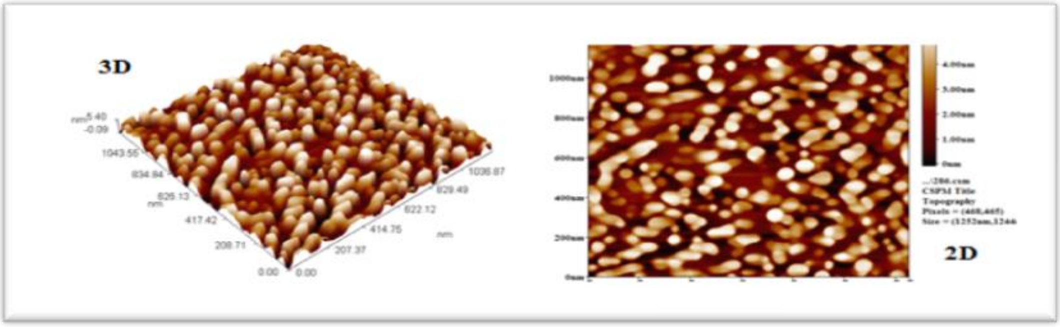


Figure 2: The AFM imges-2 and 3D view

The Scanning electron microscope (SEM) shows the surface morphology Fig.(3) of synthesized TiO_2nano powder by sol- gel after calcinations at (400°C) which illustrate the small size of the particles indicating that the synthesized nano particles are spherical and have homogenous morphology [19, 20].

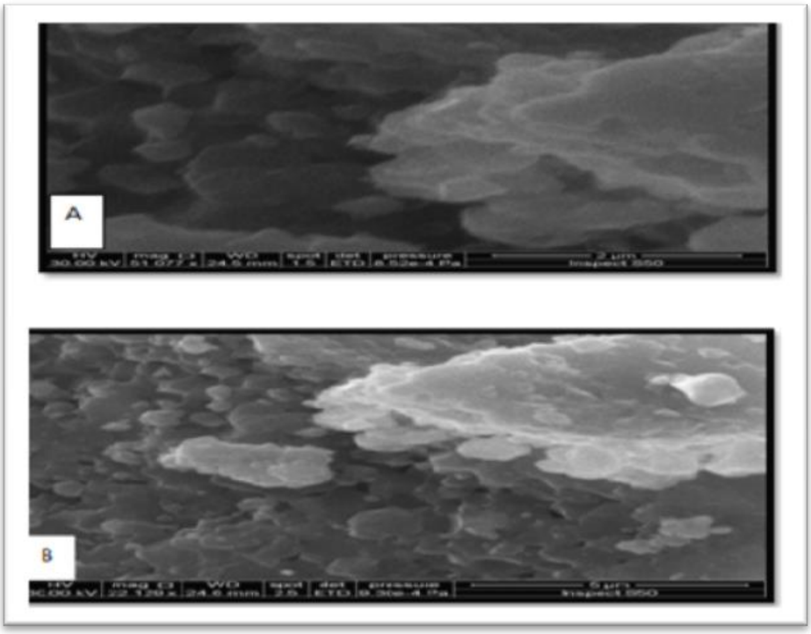


Figure 3: SEM images of synthesized TiO_2nano powder by Sol- Ggel after calcinations at 400°C. (A) 2µm, (B) 5 µm

X-ray DIFFRACTION

X-ray-D Technique was used to investigate the phase transformation of the prepared sample, Fig. (4), show the X-Ray diffraction pattern for the calculated sample calcinations at (400 °C) for (2hr), the atase phase was only observed. The main diffraction peaks were at 2θ =25.30, 37.83 and 48.05 corresponding to (101), (004), (200) planes respectively [21, 22].Crystalline sizes 10.23 nm calculated by using the Scherer formula.

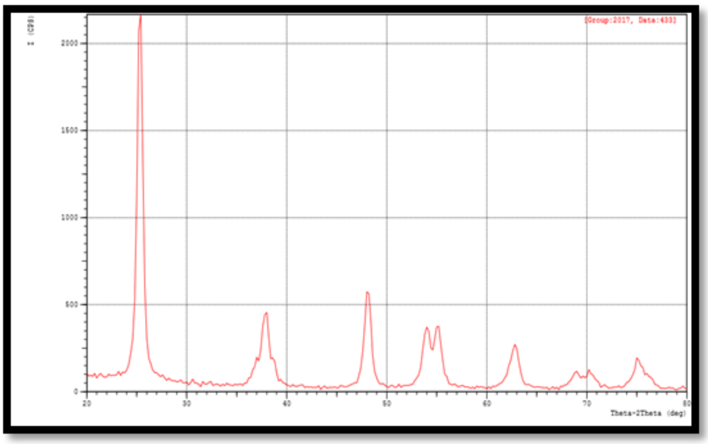


Figure 4: The X-Ray diffraction of TiO_2nano particles at calcinations temperature, 400°C.

Photo degradation of Ni-complex

The removal efficiency of Ni-complex was defined in Eq. (1). Removal of Degradation (%) = $[(C_0 \_ C_t)/ C_0] \times 100$ (1) Where C_0 is the initial concentration and C_t is the concentration at irradiation time. The calibration curve used to calculate C_t is shown in Fig. (5).

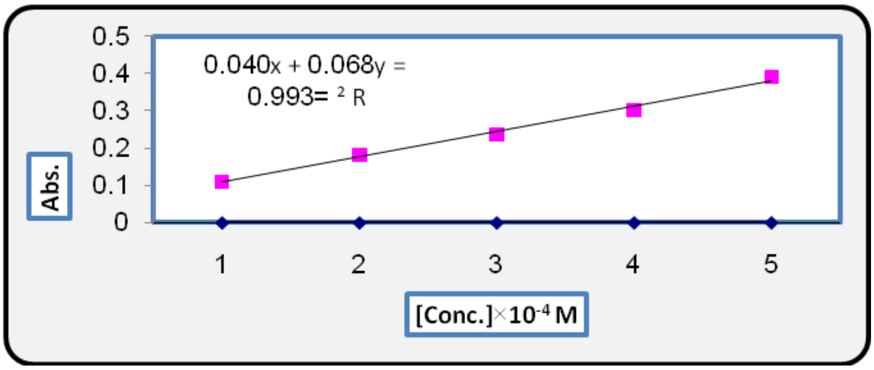


Figure 5: The Calibration curve for Ni-complex a wavelength (427) nm.

The Effect of Light

According to the results, Fig. (6) Show no photo-degradation for complex in dark and get photo-degradation in UV, whereas UV plays an important role in photo degradation by effect in TiO_2. Reactions are initiated when a photon of higher energy level or equal to the band gap energy is absorbed by TiO_2 catalyst promoting an electron (e^-) from the valence band to the conduction band with simultaneous generation of a positive hole (h^+) in the valence band. The mechanism of radical's generation ($^{\bullet}OH$ and $\bullet O_2^-$) is presented as in the following equation

$TiO_2 + hv \rightarrow TiO_2\,(e^- + h^+)$ …………..2
$H_2O + TiO_2\,(h^+) \rightarrow TiO_2 + {}^{\bullet}OH + H^+$ ……3
$O_2 + TiO_2\,(e^-) \rightarrow TiO_2 + \bullet O_2^-$ …………….4

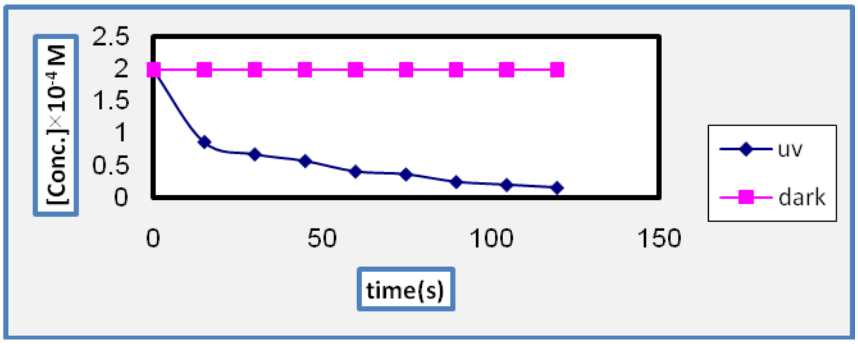


Figure6: **The effect of light and dark condition on photo degradation of Ni-complex with TiO_2 nano particles (0.003g) at 25°C.**

Effect of Catalyst amount

Fig. (7) Includes the results obtained for the [2×10^{-4} M] Co-complex where using a lamp of type (MPML) and different amounts of the nano-photo catalyst (TiO_2) from (1 -5 $\times10^{-3}$) g keeping all other parameters fixed.

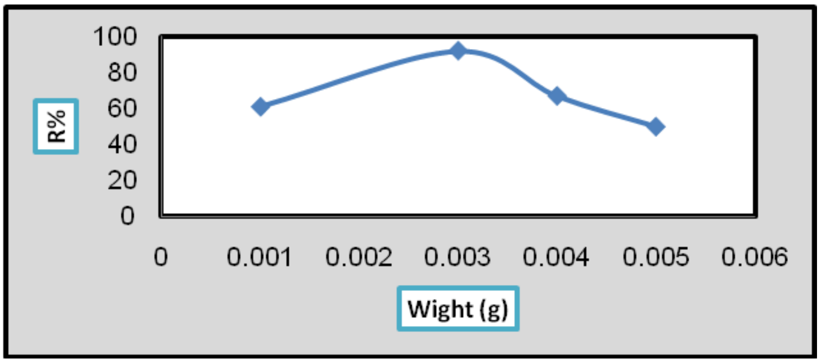


Figure 7: Influence of catalyst loading (TiO_2) on Ni- complex (2×10^{-4}) M photo degradation at 25°C.

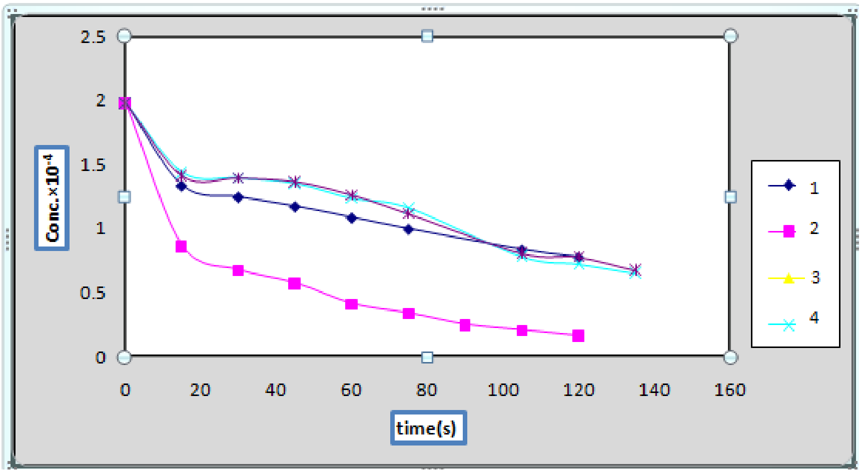


Figure8: Relationship between time and different concentration for TiO_2nano particles for Ni- complex.1. TiO_2 (0.001g), 2.TiO_2 (0.003g).3. TiO_2. (0.004g), 4. TiO_2 (0.005g).

The best amount of the catalyst was (0.003 g) used in a series of experiments to study the photo-degradation of different concentration of the Ni-complex and the results obtained show in Fig.(8).The results from Fig (5, 6) show that the best concentration of photo catalyst led to higher photo-degradation was (0.003) g. Increasing the concentration of the photo catalyst (TiO_2) higher than (0.003)g the degradation process decreases in mineralization rate due to aggregation of TiO_2 nano particles at high concentration causing a decrease in the number of surface active sites and an increase in the opacity and light scattering of the falling light [23].

Effect of temperature

A series of experiments were carried out at different temperatures (278K -318K), a rate constant (k) was calculated for each temperature, and the values were (0.011, 0.010, 0.016, 0.014, 0.015) at (278, 288, 298, 308,318) temperature respectively. The degradation of Ni-complex [2×10^{-4} M Conc. and 0.003 g TiO_2]. The results show no significant change in the rate of complex.

The effect of pH

The photo degradation of Ni-complex was studied at five different pH values under UV-light. PH value of the solution was adjusted before irradiation. The adjustments of acidic (pH 2and 4) and alkaline medium (pH 6and 10) were made using dilute HCl or NaOH respectively shown in Fig. (9). And the result show Complex and TiO_2 are both positively charged in more acidic conditions. These should hinder the adsorption of complex on TiO_2 surface and slow the reaction [10]. In alkaline medium the charge of complex and TiO_2 is neutralized no attraction forces between the catalyst and complex.

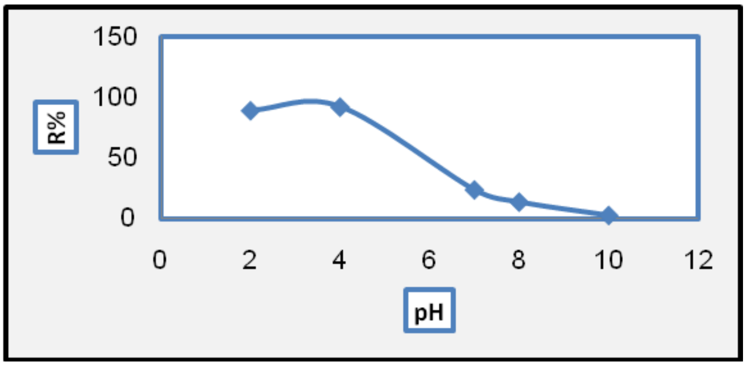


Figure 9: The effect of pH value on the photo catalytic degradation of Ni-complex with [TiO_2 (0.003) g] at 25 °C.

Effect of sun light

The impact was identified of sunlight radiation on the amount of photo degradation of Ni-complex with and without TiO_2nano powder and irradiated by sunlight (2 hours), where the intensity of the sun light 1.425×10^{-8} Ein.l^{-1}.sec^{-1}.was observed that photo-degradation did not happen in absence of TiO_2nanopowder,but occurred when use TiO_2 in solution inside the cell. Fig. (10) shows the effect of sunlight on Ni-complex. Note through the fig. (10) that the amount of photo degradation of the sunlight radiation is at a slow rate compared to the effect of ultraviolet radiation, which increases the speed of photo-degradation and can be explained by the low intensity of sunlight radiation. This wavelength has a significant effect on TiO_2 by stimulating electrons from Valence band (V.B) to conduction band (C.B).

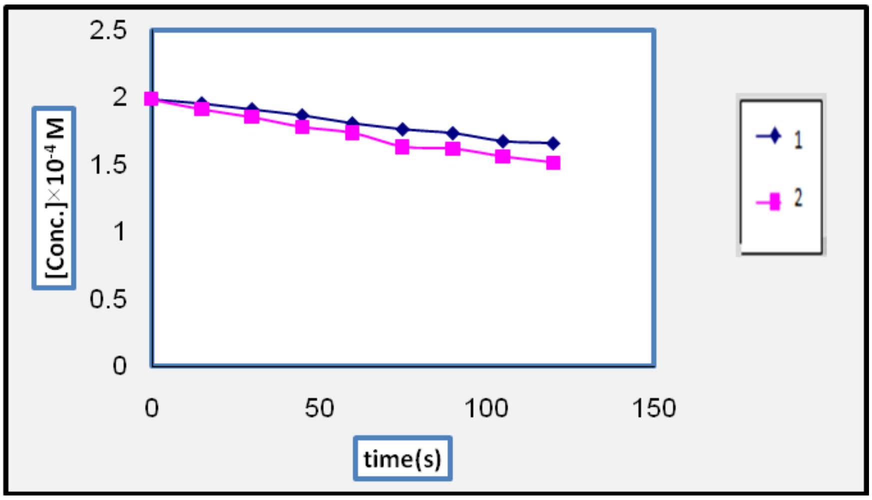


Figure 10: The effect of sunlight on Ni- complex at 25 °C. 1.Without TiO_2, 2.With TiO_2.

Effect of light Sources

Under constant parameters (temperature, catalyst) two different optical sources were used UV lamp and Visible Irradiation. The results one can conclude that photo-degradation occurs when using different sources of light, but the difference between them depends on the intensity or wavelength of the radiation emitted from the light source. Fig. (11) Shows the result of different sources (UV) and (Vis) effect. Comparing the source (UV) and (Vis) since the intensity of the lamp(UV) the largest the amount of photons absorbed per second is greater since the intensity of the radiation in the light source used increases with the increase in wavelength and increase as a result the number of electrons moving from the valence band to equivalent band in TiO_2 because the energy band gap of the TiO_2 is(3.29 ev).When the semiconductor is absorption of light with sufficient energy(≥the band energy) an electron is promoted from Valence band (V.B) to conduction band (C.B).

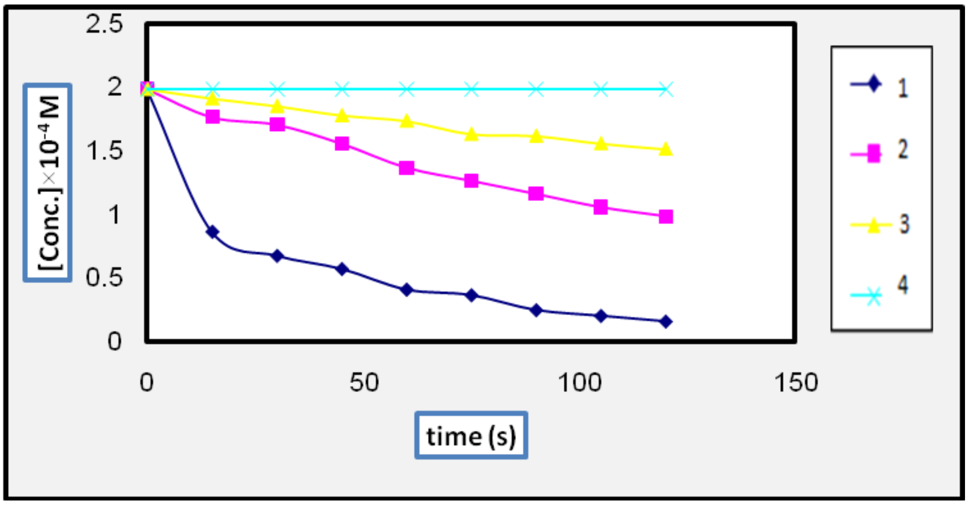


Figure 11: The effect of light sources with TiO_2. 1. UV effect, 2. Vis effect, 3. Sun light effect, 4. Dark effect

Calculation of reaction order& activation energy

The reaction order was determined using the trail method by applying different equation of order reaction 0, 1 and 2

$C = C_O\text{-}kt$ ………….. (5) For zero order
$\text{LnC} = \ln C_O\text{-}kt$ ……… (6) For first order

$\frac{1}{c} = \frac{1}{c_0}$+kt ……….. (7) For second order

The results obtained are shown in Fig. (11).The values of correlate coefficient R^2 obtand from the plotting of the above equation are 0.953, 0.993 and 0.935 for 0, 1, and 2 reaction order respectively, which indicate that the photo-degradation reaction followed the first order reaction. The results obtained are shown in figure Fig. (12).

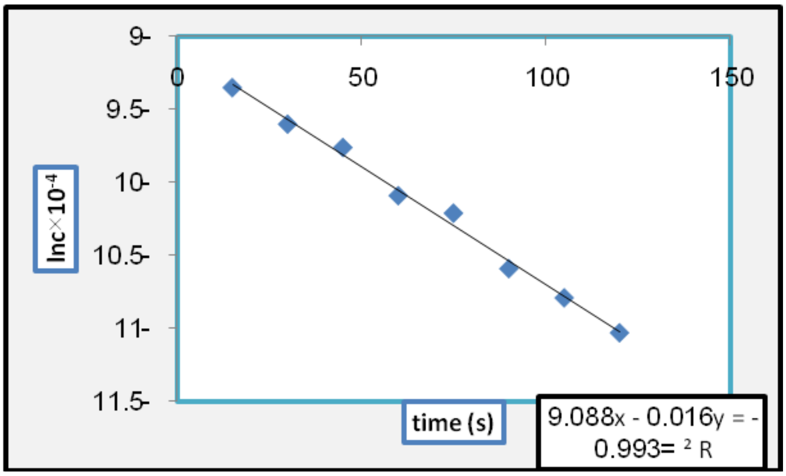


Figure 12: The first-order kinetics of complex Ni-complex at optimum conditions 25°C [2×10^{-4}M Conc. TiO_2 0.003 g].

Calculation of activation energy

Activation energy is calculated by Arrhenius equation:-

$ln\ k = ln\ A - Ea/RT$ …… (8).

The value of $(Ea)$is equal to (7.98144 kJ/mol) that refer the low value indicates that the thermal activation steps are negligible in this photo catalytic process [24].The results obtained are shown in Fig (13).

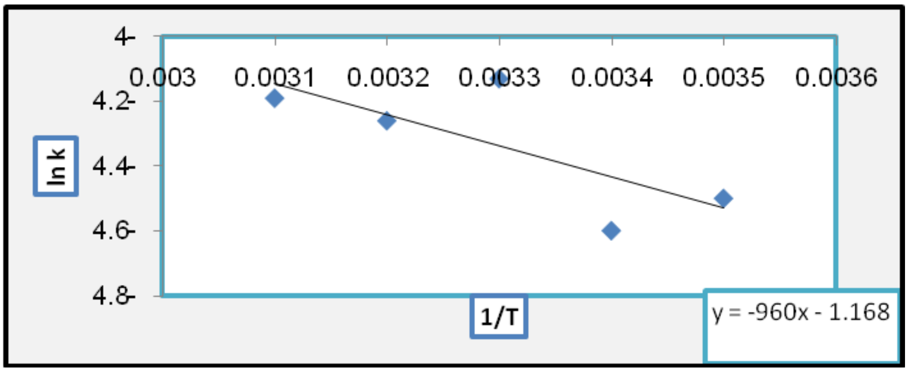


Figure 13: Arrhenius plot for the degradation of Ni-complex, with TiO_2+UV

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