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Research Paper

Enzymatic Activity and Photo-Kinetic Study of Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) Complexes with Tetradentate Schiff Base Ligand

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Abstract

The Photo kinetic studies for five metal complexes of tetradentate Schiff base ligand were studied. These complexes were Chrome, Manganese, Cobalt, Nickle and Copper complexes. The kinetic values were achieved for the photoreaction and it referred to first order by in terms of complexes concentration. Three concentrations of these complexes to determined rate constant value which were determined by calculation the slope (-k) of relationship between radiation time on X-axis and natural logathirm of concentration changing on Y-axis. Values of rate constant were (0.0317min-1) for Cr-complex, (0.054min-1) for Mn-complex, (0.0706min-1) for Co-complex, (0.133min-1) for Ni-complex and (0.1211min-1) for Cu-complex. Relation between concentration on Y-axis and radiation time were showed the decreasing of concentration with time. Enzymatic study for the five complexes were achieved and showed that Cr-complex and Mn-complex showed competitive reactions and uncompetitive for Co-complex, Ni-complex and Cu-complex.

Keywords: *Photochemistry of Schiff base, enzymatic activity for Schiff base, enzymatic activity of metal complexes, Schiff base complexes, Photochemistry of transition metal complexes.*

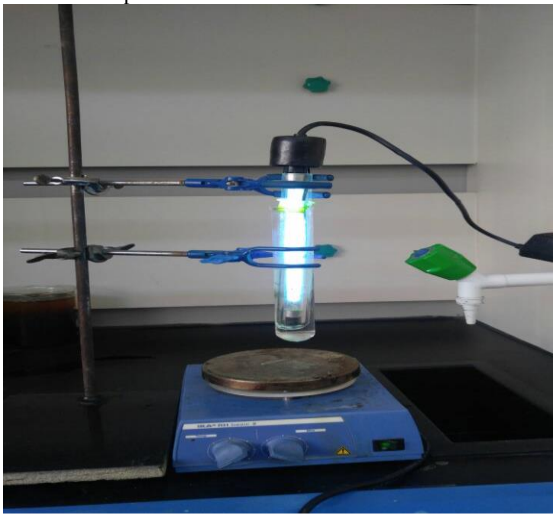
1. Introduction

There are many studies that have been interested in studying of Schiff bases, its complexes with the transition metals elements. This interesting is due to the ease of making ready of these complexes and their high thermal stability and their uses in various applications of life as well as analytical-reagents [Vandna Nishal et al, 2015]. One of the applications of the Schiff base-transition metal complexes is its use in the making ready of oxygen storage devices, molecular-architectures, OLED employments, lasers, transistors and fluorescent-sensors[Pampa Mukherjee etal 2009, Alexey Gusev Elena et al 2016, Wail Al Zoubi etal 2017, Farnoush Faridbod etal 2008, Giovanna Farruggia etal 2006, Navneet Kumar Gondia etal 2016, Sridhar.G et al 2017, Chi-Ming Che etal 2010]. The mineral complexes of the Schiff base are versatile and widely used in various biochemical, pharmaceutical and medical fields for their ability and effectiveness in all biological activities. Metallic complexes can be assembled from a proteolytic base with metal ions such as binary copper, eg 6-diacetylpyridine bis (benzoylhydrazone) (DAPBH) and 2,6-diacetylpyridine bis (benzene sulfonyl hydrazide) (DAPBSH with related metal chlorides and on the otherside of the Schiff complex many other uses in industrial fields[Elaine M.Conner etal 2017]. In recent years, many scientists have studied the viability and efficacy of Schiff Bases complex in the treatment of gastrointestinal diseases and the design of these treatments on the basis of these complexities, and such a type of drugs is designed in a way that makes them biodegradable and releasing their biologically active components in the gut Intestinal. Studies on the development of bipolar compounds, which are made up of the base with either copper and zinc, have been tested in the treatment of colitis in mice[P. Dhanakodietal etal 2018]. In the study of the Methyl-orange photo-degradation, there were two complexes from the Schiff base(N-[2-oxy-acetate] benzyl-2-aminothanol) with copper ion from chloride and bromide metal salt as photo-catalyst at pH=7 and the results proved that this complex has a catalytic properties in Photoluminescence process of organic orange dye through photo-phenon-reaction[Bao-Li Fei etal ,2014]. By using the potentiodynamic polarization and electrochemical impedance spectroscopy, the ability of Schiff base compounds to corrode the compounds on a hard surface and in the hydrochloric acid solution was studied. These compounds showed the ability to inhibit in a mixed manner and gave high resistance to the flow of electrons across the electrolytic electrolytic surface. The stomachs are followed by isothermal Langmeyer [Elias E.Elemike etal, 2017]. In recent years, scientists have been able to use the transition zinc metal complexes with the Schiff base compounds as materials that are used to manufacture or install devices that supply white light. Of these complexes of zinc ion with each of bis salicylidene hexylene, diamine, n-bis, salicylidene ethylene diamine, and salicylic acid-bis (salicylidene), it gave high electroluminescent emission capacity[Dumur,F.,,2014]. In a scientific study, heterocyclic compounds of Schiff bases were obtained by reacting with salicylaldehyde/2-Hydroxy-1-naphthaldehyde with different heterogen -eous aromatic amines. These compounds showed photo-efficiency and capability of light intake. The study of the polarity of these compounds has proved to be effective and sensitive to the micro-environment where the study was conducted using different solvents. At the same time, the study proved that the two composites prepared had light stability against loss of color by a pigment [Hadi M.Marwani etal, 2014].

2. Materials and Methods

All Chemicals and pure solvent were provided by Fluka, BHD.

1. All investigation measurements were achieved in Al-Mustansiryah University / College of Science /Chemistry Department.
2. **Preparation of Metal Complexes:** All Complexes, which were investigated previously, were prepared at Inorganic Lab-Chemistry Department /College of Science/Al-Mustansiryah University. They were prepared by taking of 1mmole of metal Chloride of the five metals and dissolved in 20 ml of ethanol . This solution mixed with solution of Schiff base ligand of 1mmole in ethanol absolute as illustrated in literature[S.M.Al-Bayati, 2017].
3. Photo-recording were achieved in Al-Mustansiryah University/College of Science/Chemistry Dept.–physical chemistry Lab. by using Uv-vissible (Uv-1650)PC Shimadzu spectrophotometer at standard condition and complexes conce -ntration of 1×10^{-4} ,0.5×10^{-4},1×10^{-5} Molarity. Photo-radiation light was supplied by using source of Uv-light with 125 watt covered by cell of quartz (like quartz tube).
4. Photo-kinetic study: Solution of Metal-Schiff base complexes from (1×10^{-4}, 0.5×10^{-4} ,1×10^{-5})M concentration with (25ml) of absolute methanol were prepared respectively. This concertation was exposure to Uv-light for 24hrs to test its Uv-light sensitivity. Then different concentrations of metal complexes of (1×10^{-4}.05×10^{-4}.1×10^{-5})M were prepared and exposure to Uv-light at different times set with (0min) and continue at every 15min to follow the changing with its Uv absorbance at (λ of 320 nm) for Mn^{+2} complex, (λ of 305 nm) of Co^{+2} complex, (λ of 305nm) of complex, (λ of 306 nm) of Ni^{+2} complex and (λ of 305 nm) of Cu^{+2} complex. The gained data were reported and used to illustrate the relationship between the time of radiation at X-axis and concentration at different times at Y-axis by which the photoreaction order and reaction constant were gained. The below Figure refer to -system which consist from stirring device, Cell of quartz cover the source of Uv-light, tube of quartz which radiation contain the solution of metal complex.



The radiation device

5. Enzymatic activity of the prepared complexes: Enzymatic activity study of the Five complexes against MAO enzyme (which were its solution and reagent prepared manually) were achieved and from its data, the order of enzymatic reaction , rate enzymatic constant (K_m) and the max rate (V_{max}) values were obtained by using the relationship between 1/[S] at x-axis and 1/V at Y axis.MAO activity was determined according to Mewen way[Mcwen C. etal,1963].

3. Results and Methods

Photo-degradation study: At Photo – degradation study for prepared complexes, order of reaction and rate constant were achieved to check the photo-stability of prepared complexes and determined the order of reaction by which depend in it and to check any materials concentration by which the reaction depend on it. At this research, studying the effect of various concentrations of metal complexes with constant of other factors like temperature and pressure were determined. Rate of photo-degradation was increasing with the increasing of metal complexes concentration where the maximum rate of photo-reaction was be at the maximum concentration. This results deals with the previous photo-study which illustrated the proportionality between the rate and concentration according to Kinetic theories. Number of excited molecules increased (because of its absorbing Uv-light) where Speed of collisions were increasing between complexes molecules[Waseem Naqasha ,201٥, R.Flukiger etal 2013, Emad Yousif etal 2015]. The rate of reaction rate, whether light interaction or thermal reaction depends in one way or another on the concentration of the reactants and also depends on the concentration of the resulting materials, where the speed of the reaction is estimated either by the concentration of the reaction or by the concentration of the products. Mathematical expression in an equation formula is representing the law of rate speed[Kapral, Styliani Consta,1998]. Below, it is show the data which were gained and discussed for photo-study.

١).Constant reaction Calculation and Discussion [*JESSIE A.KEY etal 2012*]: By using the Integral methods, order of photo-reaction were calculated by supposing that the reaction was from the first order and using the equation:

$\ln[A] = \ln[A]_o - k_t$

If the plot between the radiation time at X-axis and the various concentration of complex at different radiation time at Y-axis is linear and rate constant of the reaction have the same or approximate value, then the reaction should be from the order if not, then another order equation should be applied. For all prepared complexes, the equation of Zero, second and third order were applied which give unequal rate constant value of three different concentration. This gives us evidence that the reaction was not from these order and focus on the first order reaction [Vallance, C etal, Hanan Muhyialdeen Ali Malibari etal,2016].

Chrome – Schiff base complex: By using integral methods for calculated the order reaction and supposed that reaction was from zero reaction and the results gave non equal values of rate constant at Fix the other effects like temperature and pressure[Hussain Ismail Abdullah etal,2017]. The same thing was done for second and third order equation which enhanced that reaction was not from the three previous order. This led us to use the first order reaction equation which gave data apply and compatible with first order equation. A slope of the plot between time radiation and the natural logarithm of the quantity (A_o-A_t/A_o-$A_α$) referred to the value (-K) by which rate constant calculated. Value of rate constant were (0.0317)min^{-1} for the complex concentration of(1×10^{-4}) M,(0.0309)min^{-1} for concentration of ($0.5x10^{-4}$)M and the value with (0.0312)min^{-1} of complex concentration ($0.1x10^{-4}$)M. At the same time, the relationship between the time and complex concentration was drawn. This relationship showed that concentration decreased with by the time of photo-degradation reaction[Hussain Ismail Abdullah etal 2017]. Table(1,2,3) illustrated the gained data for radiation of Chrome complex and the method for rat constant calculation. Fig(1) refer to the way of rate constant obtained by significance of radiation time and natural logarithm of (A_o-A_t/A_o-$A_α$), Fig.(2) showed the relationship between the concentration and time of radiation.

Table1: Values of initial rates for photo-degradation at ($1x10^{-4}$) for Cr - complex:

C_∞ =0.4	C^{0}-C^{∞} =1.56	C_o =1.96	
Time (min).	[reactant] (Ct)	Ct-Cα/Co-Cα	lnCt-Cα/Co-Cα
35	0.92	0.4317	-0.84
40	0.84	0.333	-1.1
45	0.773	0.281	-1.271
50	0.745	0.239	-1.43
55	0.721	0.221	-1.51
60	0.669	0.206	-1.58
65	0.622	0.1721	-1.76
70	0.566	0.1422	-1.95
75	0.547	0.1065	-2.24
80	0.289	0.094	-2.365

Table2: Values of initial rates for photo-degradation at ($0.5x10^{-4}$) for Cr complex:

C_∞ =0.24	C^{0}-C^{∞}=1.4	C_o = 1.64	
Time (min).	[reactant] (Ct)	Ct-Cα/Co-Cα	lnCt-Cα /Co-Cα
35	0.916	0.483	-0.728
40	0.697	0.3263	-1.12
45	0.586	0.247	-1.4
50	0.544	0.217	-1.529
55	0.528	0.2058	-1.58
60	0.498	0.184	-1.693
65	0.4623	0.1588	-1.84
70	0.45	0.15	-1.9
75	0.4115	0.1225	-2.1
80	0.367	0.0907	-2.4

Table3: Values of initial rates for photo-degradation at ($0.1x10^{-4}$) for Cr complex:

C_∞ =0.17	C^{0}-C^{∞}=0.794	C_o = 0.964	
Time (min).	[reactant] (Ct)	Ct-Cα/Co-Cα	lnCt-Cα /Co-Cα
35	0.687	0.651	-0.43
40	0.642	0.595	-0.52
45	0.512	0.431	-0.842
50	0.493	0.407	-0.9
55	0.469	0.376	-0.978
60	0.387	0.273	-1.3
65	0.364	0.244	-1.41
70	0.349	0.225	-1.492
75	0.334	0.206	-1.58
80	0.289	0.15	-1.9

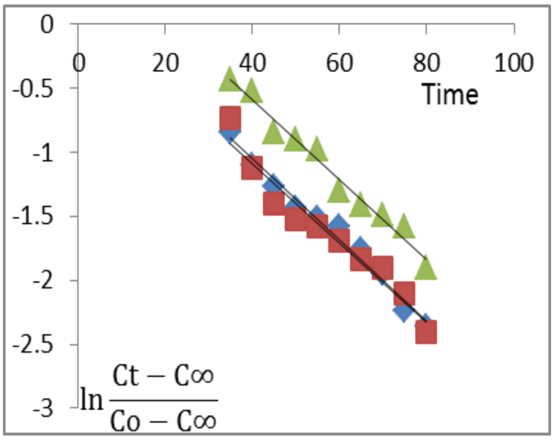


Fig.1: Referred to rate constant calculation for three concentration of Chrome-Schiff base complex for the three concentration

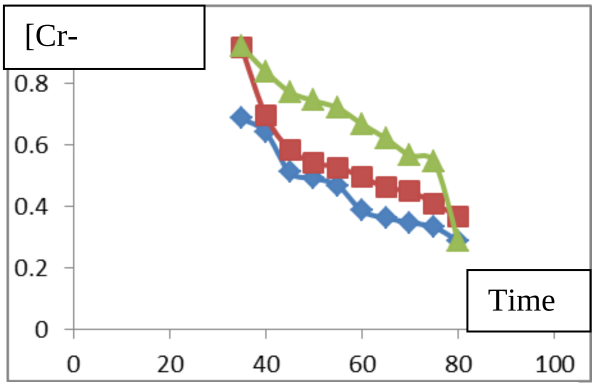


Fig.2: Referred to relationship between Time and Concentration of Chrome complex

Manganese – Schiff base: After ensuring that the interaction is not from second, third or zero order reaction. So the assumption was that the Photo-degradation reaction was from the first order. The equation of first order was applied to determine the value of rate constant (K) for three concentration of Manganese – Schiff base complex with($1×10^{-4}$,$0.5×10^{-4}$,$1×10^{-5}$)M. A slope of the plot between time radiation and the natural logarithm of the quantity (A_o-A_t/A_o-$A_α$) referred to the value (-K) by which rate constant calculated. Value of rate constant were (٠,٠٥٤٤min^{-1}) for the complex concentration of ($1×10^{-4}$)M, (٠,٠٥٤١min^{-1}) for concentration of ($0.5x10^{-4}$)M and the value with (٠,٠٥٤min^{-1}) of complex concentration ($0.1x10^{-4}$)M. These approximate rate constant values for different concentration of complex at constant condition of temperature and pressure gave us the evidence of reaction being from the first order by significance of complex concentration. Relationship of decreasing of complex concentration with time was achieved. Table (4, 5, 6) showed the gained data for initial rates of the three concentration of Manganese-Schiff base complex and Fig (3) refer to the relationship between radiation time and natural logarithm of (Ao-At/Ao-Aα)[A. Cornish-Bowden etal 2017]. Fig (4) refer to the relation between concentration of complex and time radiation.

Table4: Show the values of initial rates for photo-degradation at($1x10^{-4}$) for Mn-Complex:

C_∞ = 0.25	C^{0}-C^{∞}=1.65	C_o = 1.9	
Time (min).	[react.] (Ct)	Ct-Cα/Co-Cα	Ct-Cα/Co-Cα
35	1.571	0.801	-0.2219
40	1.35	0667	-0.405
45	1.1	0.515	-0.664
50	0.94	0.4182	-0.872
55	0.8	0.333	-1.0996
60	0.64	0.2364	-1.442
65	0.53	0.1697	-1.774
70	0.42	0.17	-1.772
75	0.31	0.06	-2.58
80	-------	--------	---------

Table 5: Show values of initial rates for photo-degradation at ($0.5x10^{-4}$) for Mn-Complex:

C_∞ = 0.21	C^{0}-C^{∞}=1.65	Co-C^{∞}=1.54	
Time (min)	[react.] (Ct)	Ct-C^{∞}/ Co-C^{∞}	lnCt-C^{∞}/ Co-C^{∞}
35	1.7	0.968	-0.0325
40	1.45	0.8052	-0.2167
45	1.15	0.6104	-0.494
50	1	0.513	-0.6675
55	0.84	0.4091	-0.894
60	0.71	0.325	-1.124
65	0.58	0.2403	-1.426
70	0.46	0.1623	-1.82
75	0.31	0.1	-2.304
80	--------	------------	----------

Table.6 **:**Show the values of initial rates for photo-degradation at(1x10^{-5})for Mn - Complex:

$C\infty =$0.1		$Co - C\infty = 1.4$	
Time(min).	[react.] (Ct)	Ct-Cα/Co-Cα	Ct-Cα/Co-Cα
0	1.68		
35	1.5	0.9900	
40	1.486	0.887	-0.01
45	1.342	0.738	-0.12
50	1.1332	0.606	-0.304
55	0.9484	0.432	-0.501
60	0.7048	0.332	-0.84
65	0.565	0.22	-1.103
70	0.408	0.156	-1.5
75	0.3184	0.134	-1.86
80	------	-------	----------

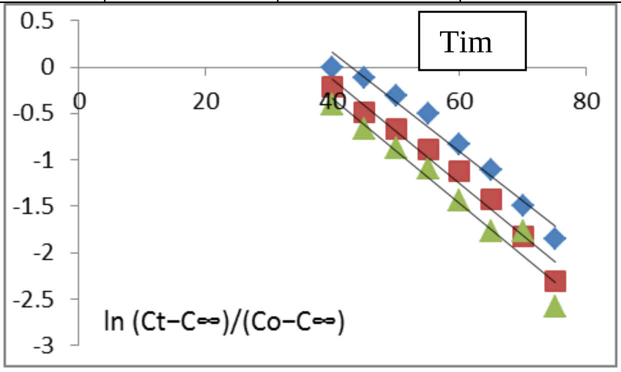


Fig.3: Referred to rate constant calculation for three conc. of Mn-Schiff base complex

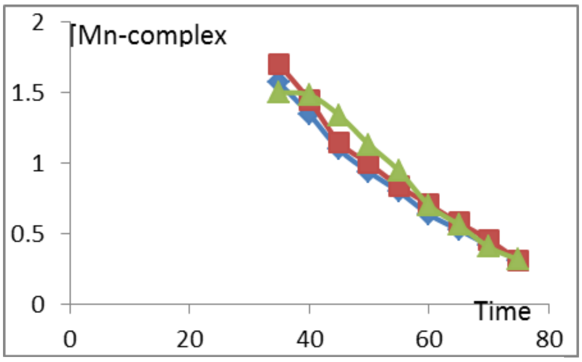


Fig.4: Referred to relationship between Tim and Conc. of Mn complex

Cobalt – Schiff base complex: Cobalt – Schiff base complex showed results of rate constant which have approximate equal values of three different concentrations by using first order equation. These values were (٠,٠٧١١)min^{-1} for (1×10^{-4})M,(٠,٠٧٠٩)min^{-1} for (0.5×10^{-4})M and (٠,٠٧٠٦)min^{-1}for (0.1×10^{-4}) M. This result led us that photo-degradation reaction depends on one concentration of the reactant represented by Cobalt – Schiff base concentration. Like Chrome and Manganese complexes, the relation showed that concentration of Cobalt complex diminished with the time of radiation[Omer A.Hassan etal 2008, Dmitry V. Fomitchev etal 2000, Savitri Lodha etal 2008]. Fig.(5) showed the relation between radiation time and natural logarithm of (A_o-A_t/A_o-A_α) [A. Cornish-Bowden etal 2008] when Fig.(6) refer to the relation of concentration decreasing with the radiation time.

Table 7: Show the values of initial rate for the photo-reaction at (1×10^{-4}) for Co-complex:

$C\infty =$0.532		$Co - C\infty = 1.468$	
Time (min).	[react.] (Ct)	$Ct - C\infty / Co - C\infty$	ln$Ct - C\infty / Co - C\infty$
35	1.861	0.905	-0.1
40	1.338	0.549	-0.6
45	1.3	0.52	-0.654
50	1.047	0.351	-1.047
55	0.905	0.254	-1.37
60	0.808	0.188	-1.67
65	0.7522	0.15	-1.9
70	0.633	0.069	-2.674
75	0.598	0.0451	-3.1
80	0.532	---------	----------

Table 8: Show the values of initial rates for photo-degradation at(0.5x10^{-4}) for Co- complex:

$C\infty =$0.532		$Co - C\infty = 1.468$	
Time (min).	[react.] (Ct)	Ct-Cα /Co-Cα	lnCt-Cα /Co-Cα
35	0.811	0.795	-0.229
40	0.581	0.534	-0.628
45	0.484	0.427	-0.85
50	0.3511	0.279	-1.273
55	0.307	0.2299	-1.47
60	0.248	0.164	-1.81
65	0.1997	0.1108	-2.2
70	0.162	0.069	-2.674
75	0.137	0.0408	-3.2
80	0.1	---------	----------

Table 9: Show the values of initial rates for photo-degradation at (1x10^{-5}) for Co -complex:

$C\infty =$0.13		$Co - C\infty = 0.516$	
Time (min).	Conc. of reactant(Ct)	$Ct - C\infty / Co - C\infty$	ln$Ct - C\infty / Co - C\infty$
35	0.592	0.895	-0.11
40	0.4337	0.5886	-0.53
45	0.376.	0.477	-0.74
50	0.292	0.313	-1.162
55	0.265	0.262	-1.34
60	0.238	0.2093	-1.564
65	0.197	0.129	-2.05
70	0.173	0.083	-2.494
75	0.151	0.0416	-3.18
80	0.13	---------	----------

Table 10: Show the values of initial rates for photo-degradation at (1x10^{-4}) for Ni complex.

$C\infty =$0.27	$Co - C\infty = 1.58$, K=٠,٠١٣	$Co = 1.85$	
Time (min).	Conc. of reactant(Ct)	$Ct - C\infty / Co - C\infty$	ln$Ct - C\infty / Co - C\infty$
35	1.299	0.651	-0.43
40	1.267	0.631	-0.46
45	1.218	0.600	-0.51
50	1.1548	0.56	-0.58
55	1.112	0.533	-0.63
60	1.071	0.507	-0.68
65	1.0395	0.487	-0.72
70	0.987	0.454	-0.79
75	0.945	0.427	-0.85
80	0.888	0.391	-0.94
85	0.759	0.310	-1.17

Table 11: Show the values of initial rates for photo-degradation at (0.5x10^{-4}) for Ni complex:

$C\infty =$0.26	K=0.0131,$Co - C\infty =$1.02		$Co = 1.28$
Time (min).	[react.] (Ct)	Ct-Cα /Co-Cα	lnCt-Cα/ Co-Cα
35	0.597	0.33	-1.11
40	0.593	0.3263	-1.12
45	0.5068	0.242	-1.42
50	0.495	0.23	-1.471

55	0.481	0.217	-1.526
60	0.480	0.216	-1.532
65	0.470	0.206	-1.58
70	0.454	0.190	-1.66
75	0.449	0.185	-1.69
80	0.447	0.183	-1.7
85	0.422	0.1589	-1.84

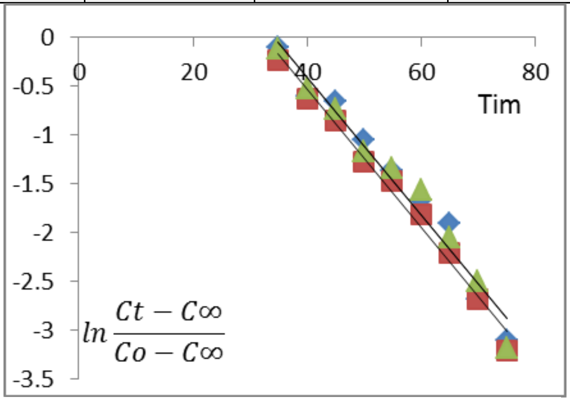


Fig.5: Referred to rate constant calculation for three conc. of Co-Schiff base complex.

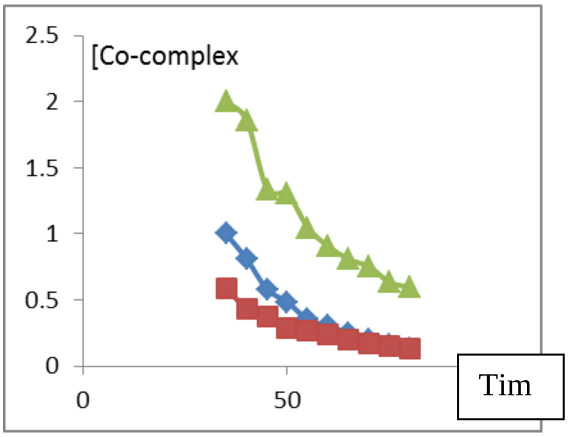


Fig.6: Referred to relationship between Time and Conc. of Co complex

Nickle-Schiff base complex: For Nickle-Schiff base photo study, It is clear to us that Nickle complex was active and sensitive for Uv-light. Reaction Order of Photo-degradation was from first order by significance of Nickle concentration and Rat constant was calculated by the same way for Manganese complex. Values of rate constant was (٠,٠١٣)min^{-1} for(1×10^{-4})M , (0.0131) min^{-1} for (0.5×10^{-4})M and (0.0133)min^{-1} for (0.1×10^{-4}) M. The values of rate constant (K), for the three radiated concentration, directed us that the reaction order was from the first order. Also, other order reactions law was achieved and gave non identical values of (K) which enhanced that reaction was from the first order. Concentration reduced with the radiation time and this was represented by plot of Concentration at Y-axis and time at X-axis[*Omprakash Sharma,2017, Adil Ahmed A.Al-Dulimia etal 2017*]. Fig.(7) showed the relation to calculated order reaction when Fig.(8) referred to decreasing of complex concentration against radiation time.

Table11: Show the values of initial rates for photo-degradation at ($0.5x10^{-4}$) for Ni complex:

$C\infty =$0.26	K=0.0131,$Co - C\infty =$1.02		$Co = 1.28$
Time(min).	[react.](Ct)	$Ct - C\infty / Co - C\infty$	ln$Ct - C\infty / Co - C\infty$
35	0.597	0.33	-1.11
40	0.593	0.3263	-1.12
45	0.5068	0.242	-1.42
50	0.495	0.23	-1.471
55	0.481	0.217	-1.526
60	0.480	0.216	-1.532
65	0.470	0.206	-1.58
70	0.454	0.190	-1.66
75	0.449	0.185	-1.69
80	0.447	0.183	-1.7
85	0.422	0.1589	-1.84

Table 12: Show the values of initial rates for photo-degradation at ($0.1x10^{-4}$) for Ni-Complex:

$C\infty =$0.07	K=0.0133,$Co - C\infty = 0$.62		$Co = 0.69$
Time (min).	[react.] (Ct)	$Ct - C\infty / Co - C\infty$	ln$Ct - C\infty / Co - C\infty$
35	0.303	0.375	-0.98
40	0.257	0.301	-1.2
45	0.241	0.275	-1.29
50	0.232	0.262	-1.34
55	0.226	0.252	-1.38
60	0.124	0.237	-1.44
65	0.298	0.228	-1.48
70	0.2	0.21	-1.56
75	0.192	0.196	-1.63
80	0.182	0.18	-1.717
85	0.169	0.159	-1.84

Table 13: Show the values of initial rates for photo-degradation at ($1x10^{-4}$) of Cu-complex:

$C\infty =$0.87	K=0.0207,$Co - C\infty$=1.02		Co=1.89
Time(min)	[react](Ct)	$Ct - C\infty / Co - C\infty$	ln$Ct - C\infty / Co - C\infty$
35	1.79	0.909	-0.096
40	1.775	0.887	-0.12
45	1.604	0.719	-0.33
50	1.553	0.67	-0.4
55	1.508	0.625	-0.47
60	1.49	0.604	-0.505
65	1.447	0.566	-0.57
70	1.43	0.549	-0.6
75	1.47	0.526	-0.642
80	1.29	0.411	-0.89
85	1.16	0.284	-1.26
90	1.134	0.259	-1.35

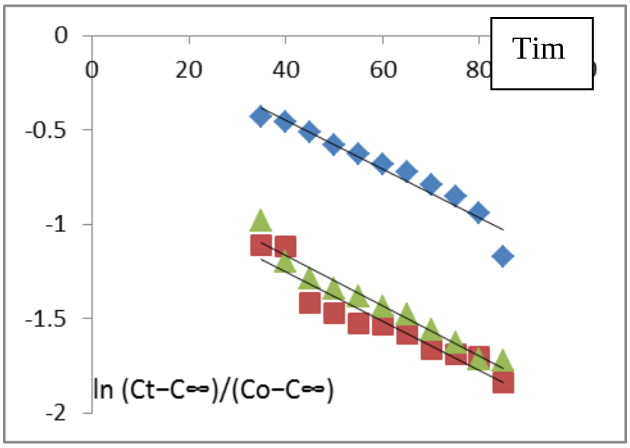


Fig.7: Referred to rate constant calculation for three conc. of Ni-Schiff base complex.

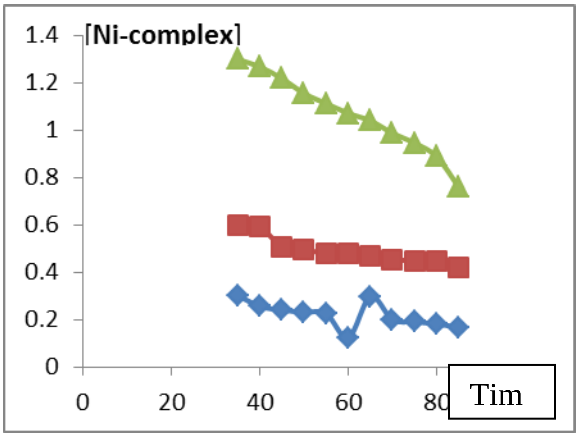


Fig.8: Referred to relationship between Time and Conc. of Ni complex.

Copper –Schiff base complex: Copper complex gave the same results which gained for Nickle complex with respect to the order of reaction. It was from the first order. The data that gained for rate constant was (0.0207)min^{-1}for (1x10^{-4})M,(0.0206)min^{-1}for(0.5x10^{-4}) M and (0.0206)min^{-1}for (0.1x10^{-4})M. This data referred to first order reaction by the terms of Copper-Schiff base complex. Like the other complexes. The relation between radiation time and concentration was achieved and showed that complex concentration lessened [A.J.AL-Lami etal 2009] and Fig.(9) clarifies the relation of gained order reaction and fig.(10) showed the decreasing of Copper complex concentration via radiation time.

Table 14: Show the values of initial rates for photo-degradation at (0.5x10^{-4}) of Cu-complex:

$C\infty$ =0.43	K=0.0206, $Co - C\infty$=0.77		Co=1.2
Time(min).	[react.](Ct)	$Ct - C\infty / Co - C\infty$	ln$Ct - C\infty / Co - C\infty$
35	0.679	0.323	-1.13
40	0.606	0.228	-1.48
45	0.592	0.21	-1.561
50	0.581	0.196	-1.63
55	0.571	0.183	-1.69
60	0.559	0.167	-1.79
65	0.550	0.156	-1.86
70	0.544	0.148	-1.91
75	0.529	0.128	-2.06
80	0.524	0.122	-2.104
85	0.507	0.1	-2.3
90	0.492	0.08	-2.53

Table 15: Show the values of initial rates for photo-degradation at(0.1x10^{-4}) of Cu complex:

$C\infty$ =0.16	K=0.0206, $Co - C\infty$=0.793		Co=0.953
Time(min).	[react.]Ct)	$Ct - C\infty / Co - C\infty$	ln$Ct - C\infty / Co - C\infty$
35	0.947	0.992	-0.0083
40	1.071	0.956	-0.045
45	0.886	0.916	-0.088
50	0.885	0.914	-0.09
55	0.879	0.906	-0.099
60	0.778	0.779	-0.25
65	0.613	0.571	-0.56
70	0.558	0.502	-0.689
75	0.542	0.482	-0.729
80	0.499	0.428	-0.848
85	0.473	0.395	-0.928
90	0.452	0.368	-1

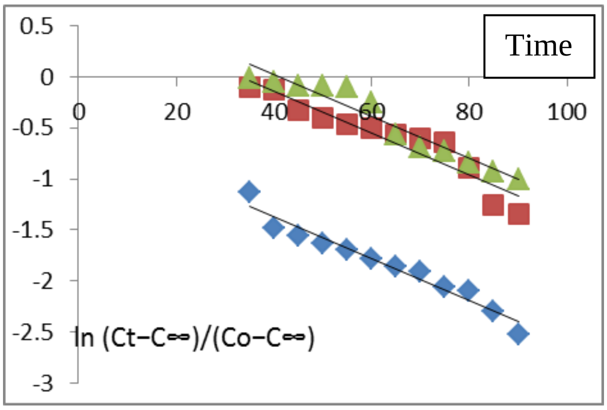


Fig.9: Referred to rate constant calculation for three conc. of Cu-Schiff base complex.

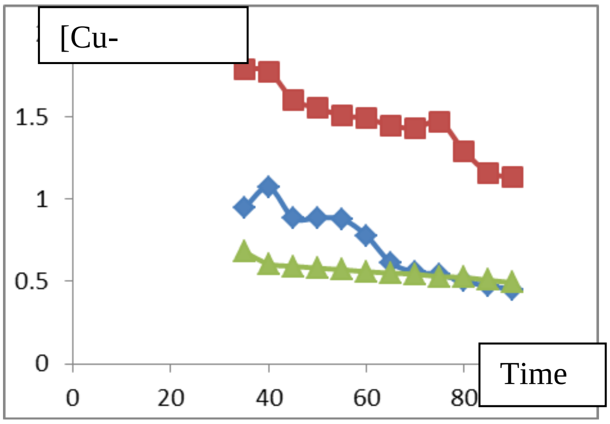


Fig.10: Referred to relationship between Tim and Conc. of Cu complex.

Enzymatic Study of Prepared Complexes: The enzyme MAO has the ability to oxidase the primary alveolar amines as well as the oxidation of aromatic amines, in addition to its ability to oxidize some secondary and tertiary amines. This in the body of the organism and its different body tissues and the interaction of the enzyme with the amines can be summarized by the following chemical formula:

$RCH_2NR`R``+O_2+H_2O$ $RCHO +NR`R``+H_2O_2$[Keith F. Tipton etal 2004].

These activities were studied by using the five complexes:

Chromium – Schiff base complex enzymatic activity: The results obtained showed that this complex has high proportion inhibitory effect on MAO as demonstrated in table(16). Type of inhibition and kinetic parameters for MAO with complex has been studies and the results showed that competitive Inhibition for complex with MAO and as in table(16) and figure(11). This competitive inhibition can be due to the competitive between the substrate and the complex to link with the active site for the enzyme which disable the enzyme action and it was less active. This can be treated by increasing the concentration of substrate. Values of Km and Vmax were (0.045) and (50.0) respectively. Its values referred to competitive inhibition [*Agents Betül Kaya Çavu etal 2018, B Rita Meleddua etal 2017, Samantha Mostert etal 2012*]. Data of Vmax and Km gained by drawing the relationship between the Inverted concentration of substrate on x-axis and the overturned of enzymatic reaction rate on Y-axis. The intercept on Y-Axis referred to the value of Maximum value of enzymatic reaction rate while the intercept on x-axis represented the value of (-Km). these data drew and gained according to linear Lineweaver-Burk graphics[*Nafiz Öncü Can etal 2017, Charles M. Mcewen etal 1965*]. Table 16 showed the enzymatic activity data of prepared complexes.

Manganese – Schiff base complex enzymatic activity: As same to Cr-complex, Manganese–Schiff base complex data clearify high ratio of inhibitory effect toward MAO as showed in Table(16). Type of Inhibition was competitive and values of Km and Vmax for enz -ymatic reaction the complex against the MAO enzyme which were be (50) and (0.015) for Vmax and Km respectively. The cause of enzyme inhibition was the existence complex which was competing with amine group of substrate to link with bending site of the enzyme. By rising the amount of tsubstrate, Toxicity with Mn-Schiff base complex was treated because the high amount take place ahe nd more chance to make linkage with active site of the MAO enzyme. Tocixity kinetic of Mn was illustrated in many research and its` ability to inhibited MAO differ from male compare to female and from pregrant female from not[Amit S. Kalgutkar etal 1995, Nadia Abdelouahab etal 2010, Yuanliang Gu etal 2016].

Cobalt – Schiff base complex enzymatic activity: From gained data, the Cobalt-Schiff base complex showed inhibition for the Mao enzyme action from kind uncompetitive inhibition. This referred that the complex link to the complex of Enzyme-substrate or it was link to the MAO enzyme from different side of the bending enzyme site. Vmax and Km data were (40) and (0.011) sequent.

Nickle and Copper– Schiff base complexes enzymatic activity: Like Co complex, Ni and Cu–Schiff Base complexes gave the same behavior toward MAO enzyme. The two complexes didn`t compete with the substrate but its showed uncompetitive inhibition by make linkage with other side of enzyme non to its active site or the two, Cu, Ni –Schiff base complexes link to the complex Substrate–Enzyme[*Eric M. Shepard etal 2015, H.O.Borbe etal 1990*].

Table 16: Kinetics parameters V_m, K_m and Inhibition type for the five complexes with Monoaminooxidase (MAO) enzyme activity.

Complex	K_m	V_{max}	Inhibition type
Cr-complex	0.045	50.0	Competitive
Mn-complex	0.015	50.0	Competitive
Co-complex	0.011	40.0	Un- Competitive
Ni-complex	0.015	28.5	Un- Competitive
Cu-complex	0.019	33.3	Un- Competitive

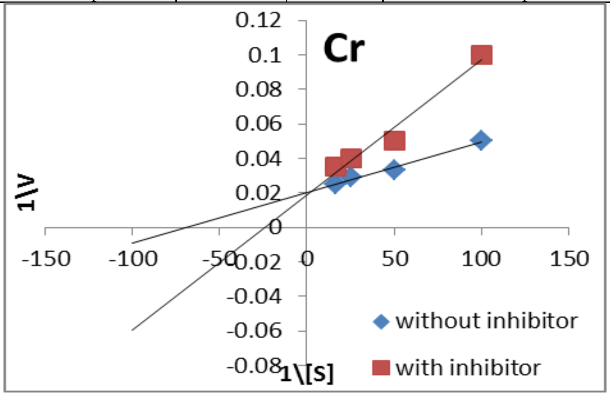


Fig11: Enzymatic activity for Cr complex.

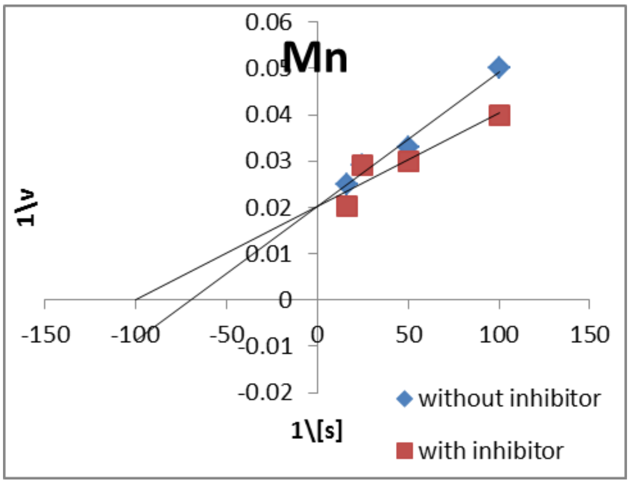


Fig.12: Enzymatic activity of Mn complex.

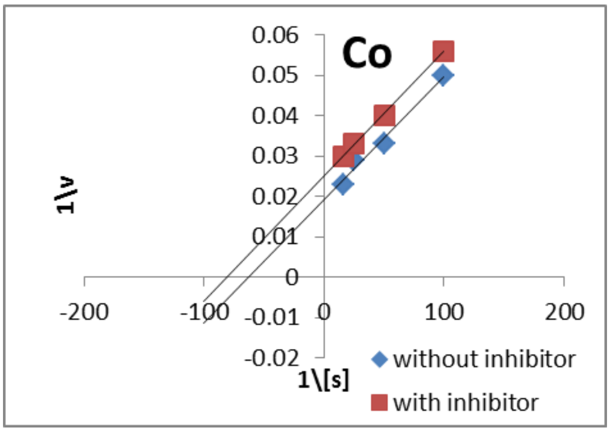


Fig.13: Enzymatic activity of Co complex

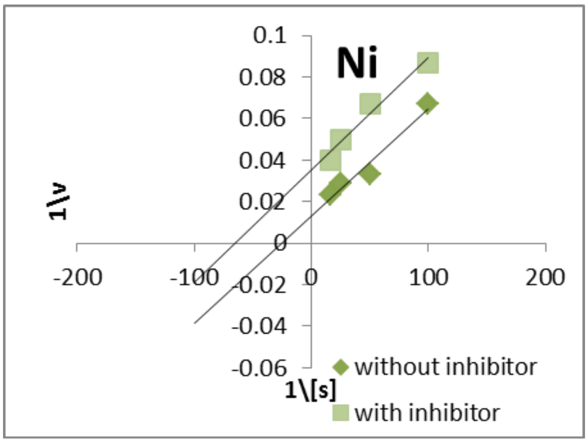


Fig.14: Enzymatic activity of Ni complex.

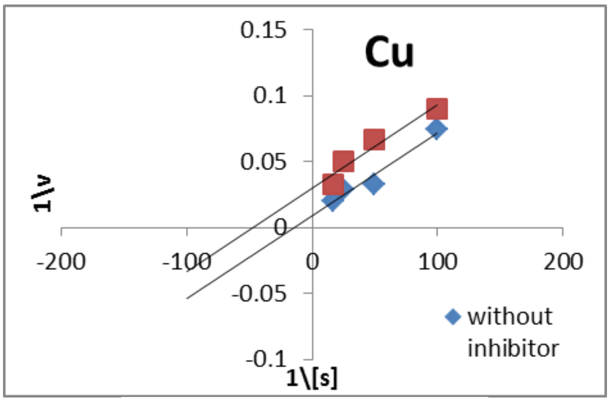


Fig.15: Enzymatic activity of Cu complex.

4. Conclusions

The five prepared complexes have photo-activity against Uv-light. Photo-reaction for all prepared complexes was from first order which refer to reaction depending on metal complexes concentration. From the enzymatic activity reaction for the prepared complexes, it`s observed that the five complexes have enzymatic activity by inhibition the enzyme MAO work. The reaction of complexes –enzyme showed that the reaction was com -petitive for Cr and Mn metal complexes and uncompetitive to Co, Ni and Cu complexes.

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