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Preparation and Diagnostics of Schiff Base Complexes and Thermodynamic Study for Adsorption of Cobalt Complex on Iraqi Attapulgite Clay Surface

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Abstract

Three new complexes of Co(II), Ni(II), and Zn(II), containing ligand of Schiff base (DHMA) derived from methyldopa (mdop) with 3-hydroxybenzaldehyde have been prepared. The synthesized ligand and its complexes were diagnostics by using different physical techniques, The results showed that the complexes have an octahedral shape. In addition it has been studied the adsorption behavior, Uv-Vis technique that applied to survery the isotherm of adsorption. The results showed the possibility of applying the langmair equation. The effect of temperature on the adsorption of Co-complex on the surface of Iraqi Attapulgite clay was studied. The thermodynamic functions ΔGo, ΔHo and ΔSo of Co- complex have been studied and she was ΔGo =(-10.7766, -11.5205, -12.3537)KJ/ mol, this is evidence that the adsorption process is a spontaneous while ΔSo=(63.6461)J/ mole.K which means an increase in the randomness. The value of ΔHo was (8544.29)J/mole indicate the endothermic natural of the process.

Keywords : Methyldopa , Adsorption, Co complex, Attapulgite Surface.

Introduction

The chemistry of coordination that is associated with claw or complexes has got great attention[1,2] . Schiff bases are stable with some transitional metal ions, and they play an important role in public life with industries such as chemistry[3-5]. Aldomet (L-methylldoba) is an antihypertensive drug, a carboxylic-inhibiting aromatic amino acid in the animals and man[6] . Methyldopa(M-dop) α-methyl-3,4-dihydroxyphenyl alanine is one of the catecholic molecules which are liable to interact with Fe (II)[7]. Heavy metals have a significant impact on plants, animals and public health it has more toxic than metals and when excessive , are dangerous for living organism[8,9]. Removing toxic metals such as cobalt from waste water is necessary and good for maintining human health and preserving the environment, the effect of cobalt on a persons life can lead to damge to the heart, liver and thyroid gland[10]. In the presence of a high concentrtion of Co(II) it may cause genetic mutations in living cells, emphasis should be placed on increasing a wareness of the problems related to the toxicty of cobalt [11]. As for the methods of removing havey elements , the adsorption process is considered one of the most impotant methods, as it is a simple and cost-effective process, and more efficient than other technlogyies such as solvent extraction, electrolytic processes, ion-exchange, chemical precipitation---etc[12]. In this paper we prepared and synthesized the new complexes Co(II), Ni(II), and Zn(II), with schiff base ligand (DHMA), The study of effect of temperature on the adsorption of Co-complex on the surface of Iraqi attapulgite clay. The thermodynamic functions ΔG, ΔH and ΔS of Co- complex have been studied

Experimental materials and devices :

all the metal salts used are from Fluka, and a ligand schiff base is previously set up and crystallized, The structure of Attapugite clay it was obtained from (The General Company for Geological Survey and Mining), Baghdad, Iraq

Melting point were carrid out on Stuart Melting Point Apparatus. FTIR in rang 4000-400cm^{-1} were recorded by Shimadzu as KBr discs. Electronic transfers spctra were measured using Shimdzu UV-160A and Shimdzu UV-1800. Atomic absoption M% carrid out on Shimadzu AA620G. The ^{1}HNMR was recorded by Brucker 400 MHz . The magnetic measurements values for complexes were carrid out a

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BRUKER BM6 at room temperature . CHNS was measured on Euro EA 3000. Shaking water bath, Centrifuge 6000 rpm, Hettich (EBA-20) .

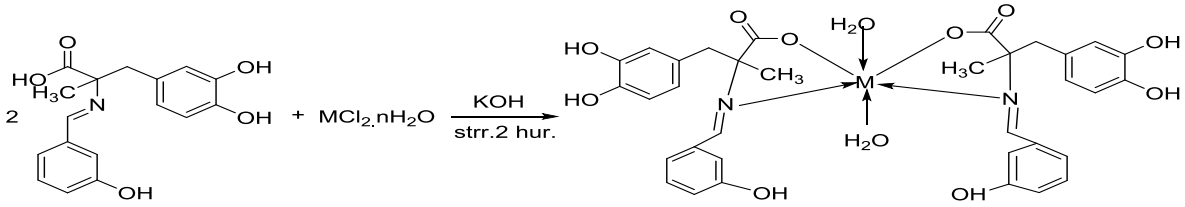
Synthesis of ligand (E)-3-(3,4-dihydroxyphenyl)-2-((3-hydroxybenzylidene) amino)-2-methylpropanoic acid (DHMA)

A solution of M-dopa 0.211 gm,1mmol in methanol (20 ml) and 0.056 gm,1mmol, KOH was added to a solution of 3-hydroxybenzaldehyde 0.136 gm, 1mmol in methanol 10 ml. The mixture was refluxed for 5 hr. with stirring. The resulting was a deep orange solution allowed to cool and dried at room temperature, then re-crystallized with ethanol. The brown colored solid mass formed during refluxing was cooled to room temperature, filtered and washed completely with hot ethanol, and recrystallized from acetone to get a pure sample C17H17NO5. Yield:65%, melting point 175ºC, M. Wt=315.33.gm/mol.

Cal.(found)%; C: 66.65(64.95), H:5.87(6,08), N: 11.66(11.86), O: 13.32.

Synthesis of [M(DHMA)$_2$] complexes :

A solution of ligand (DHMA) (0.631g , 2mmol and KOH 0.116g,2mmol) in 20ml ethanol were add to a solution of metal chlorid (1mmol) . The mixture was stirred for 2h. The result was filtered, washed with acetone and dried at room temperature.



Scheme 1 : The synthesis of Co(II), Ni(II), and Zn(II) complexes.

Preparaion of Clay Powder:

Attapulgite consists mainly of magnesium – aluminium silicates in addition to amounts of iron and magnesium in different proportion. Attapulgite is called another name (palyg or skite). It was used as an adsorbent. It is expressed in the following chemical formula $[(OH_2)_4(Mg, Al, Fe)_5(OH)_2Si_8O_{20}]. 4H_2O$. Attapulgite dried in an oven for 7 hours at 100ºC. The clay was ground and sieved by using sieve (200 mesh) (≤75µm). Table (1) shows the chemical analysis of Attapulgite clay.

Com.	MgO	Fe_2O_3	CaO	Al_2O_3	SiO_2	SO_3	Loss on ignition	Total
Wt%	3.93	4.08	17.93	10.68	41.08	1.3	20.96	99.96

Table 1: The chemical analysis of Attapulgite

Synthesis of solutions:

Standard stock solution of cobalt (II) complex solution (100ppm)

Standard stock solution of cobalt (II) complex solution (100ppm) was prepared by dissolving (0.01gm) of $[Co(DHMA)_2(H_2O)_2]$ in (3ml) of ethanol. The volumetric flask (250ml) was completed to the mark with an ethanol solvent. Cobalt (II)complex solution of different concentration was prepared by serial dilution absorbance values of these solution was measured at specified (λ= 470nm).

Results and discussion

Part One:

The physical and analytical data for **ligand** and **[Co(DHMA)$_2$ (H$_2$O)$_2$]**, **[Ni(DHMA)$_2$(H$_2$O)$_2$] and [Zn(DHMA)$_2$(H$_2$O)$_2$]** were agreement with suggest structures of studied comounds[12] .

The physical and analytical data for **(E)-3-(3,4-dihydroxyphenyl)-2-((3-hydroxybenzylidene)amino)-2-methylpropanoic acid (DHAM)**

Yield: 65% (yellow);176-178 °c; FTIR(KBr cm^{-1}): 3360(OH), 1635 (HC=N schiff base band), Anal.:chemical formula:$C_{17}H_{17}NO_5$; Mwt. 315.32gm/mol; Elemental Analysis: 64.75; H, 5.43; N, 4.44; O, 25.37.

The physical and analytical data for **[Co(DHMA)$_2$(H$_2$O)$_2$] complex**:(light pink); d.p235-237°c; M%(8.57); Mwt.(687.56gm/mol);FTIR(cm^{-1}):3090(C-H),1620 (azomethine), 459(M-O), 568(M-N), UV-vis. Ɛmax(cm^{-1}DMSO): 15290; B.M.(5.62 µeff); molar conductance µScm-1(3.5); **[Ni(DHMA)$_2$ (H$_2$O)$_2$] complex**:(green); d.p(224-226°c); M%(8.54);Mwt.(687.32gm/mol); FTIR(cm^{-1}): 3092(C-H),1622 (azomethine), 415(M-O), 567(M-N), UV-vis. Ɛmax: 17391; B.M.(2.73µeff); molar cond. µScm^{-1}(8.9); **[Zn(DHMA)$_2$ (H$_2$O)$_2$] complex**:(white); d.p(236-238°c);M%(9.42); Mwt (694.02gm/mol); FTIR(cm^{-1}):3090(C-H), 1625(HC=N), 425(M-O), 567(M-N); molar cond. µScm^{-1}(7.8).

Spectroscopic techniques:

FTIR spectra: The data FTIR spectra of ligand and their complexes were listed in Table-2 , and the spectrum of Ligand was shown in Figure 1. The FTIR spectrum of (**DHMA**) shown a sharp band at 1635 cm^{-1} due to υ(HC=N) , this band was shifted to lower frequency for three complexes in the range (1625-1620) cm^{-1} reference to coordination the azomethine(C=N) with the metal ion[14]. The carboxylate group at (1593,1365)cm^{-1} due to asymmetric and symmetrical stretching vibrations respectively on complexation these bands were shifted to a lower frequency in their complexes in rang (1583-1580)cm^{-1} and (1372-1364)cm^{-1} [15],this indicates the coordination the oxygen atom with the metal ion. New bands were found in spectra of complexes in regions (567-568) cm^{-1}, (415,459) cm^{-1} and (825,830,832) cm^{-1}, that were attributed to the ν (M-N), (M-O) and M-OH_2 mode respectively[16,17]. So from the FTIR spectra ,it concluded that the ligand behaves as bidentate uni negative charge.

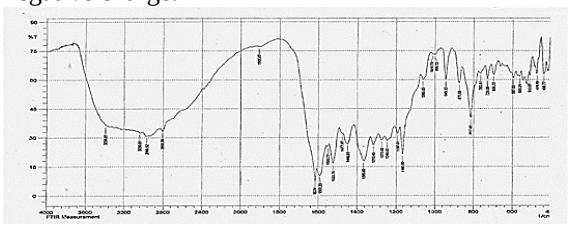


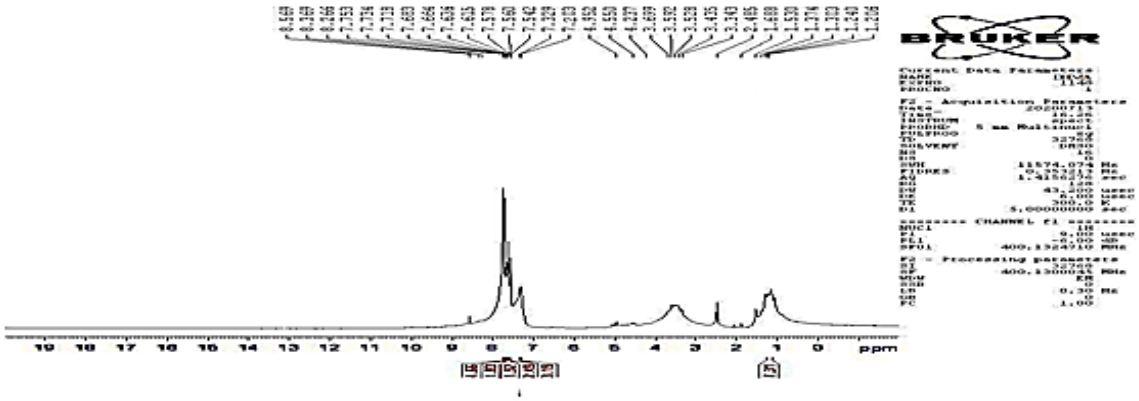
Figure 1: the FTIR spectrum of ligand DHMA

Table 2: FTIR spectra of ligand and three complexes

Comp.	$(O-H)_{acid}$ $(O-H)$.	$(C-H)_{arom.}$ $(C-H)_{alph.}$	$(COO)_{asy}$ $(COO)_{sy}$	HC=N	C=C	M-N	M-O M-OH_2
DHMA	3473 3360	3039 2966	1593 1364	1635	1490	-----	------
C1	---- 3480	3370 3090	1583 1362	1620	1536	568	459 825
C2	---- 3482	3306 3092	1580 1372	1622	1535	567	415 830
C3	----- 3480	3297 3090	1582 1372	1625	1535	567	425 823

The ^{1}HNMR spectrum of ligand (Figure 2), multiple chemical shifts around δ (7.203-7.753) ppm was appointed for doublet due one proton of aromatic ring of phenyl, The single signal at position δ (3.343 ppm) it refers to the proton of the phenolic (OH) group, the formation of Schiff base is supported by the presence of a singlet at (δ 8.569) ppm corresponding to the azomethine proton (–N=CH). The signals observed at δ (1.688) ppm ascribed to methyl protons (-CH3)[18-21] .

Figure 2: The ^{1}HNMR spectrum of ligand DHMA



The Electronic spectra of the ligand shows two peaks at 301nm and 344nm due to (π→ π) and (n→ π*) transition respectively[22] Table 3 . The UV-Vis specta of C1, and C2 and C3 complexes showed the absorption peaks at 363 nm, 296 nm and 350 nm respectively due to charge transfer transition respectively[23]. The spectrum of C1 and C2 showed peaks at 654nm and 575 nm which were assigned to (d-d) transition type $^4T_1g(F)$ $^4A_2g(F)$ and $^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$[24-26]. These compounds which are agree with C1, C2 and C3 complexes having octahydral structures.

Table 3: Electronic spectra data for Ligand and its complexes

Comp.	Band position nm	Band position cm^{-1}	Molar Conductivity $Mol^{-1}.cm^{-1}$	μeff BM	Aissignment
DHMA	301 344	33222 29069	1650 1712	----	($\pi \rightarrow \pi$) ($n \rightarrow \pi^*$)
C1	363 654	27548 15290	6.2	5.62	Charge transfer $^4T_1g(F)$ $^4A_2g(F)$
C2	296 575	33783 17391	33.8	2.73	Charge transfer $^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$
C3	350	28571	35.3	----	Charge transfer

Effect of shaking time on equilibrium adsorption system

The time that is sufficient for the adsorption to reach equilibrium at 30 ºC, C_o=50ppm and particle size (75 μm) has been studied and found 75 minute as shown in the following Figure3.

Adsorption Isotherm:

The adsorption $[Co(DHMA)_2(H_2O)_2]$ from ethanol solution on Attapulgite clay has been studied at different temperature (30,40,50 ºC). Figure 4 shows adsorption isotherm of Co (II) complex on Attapulgite clay at different temperature.

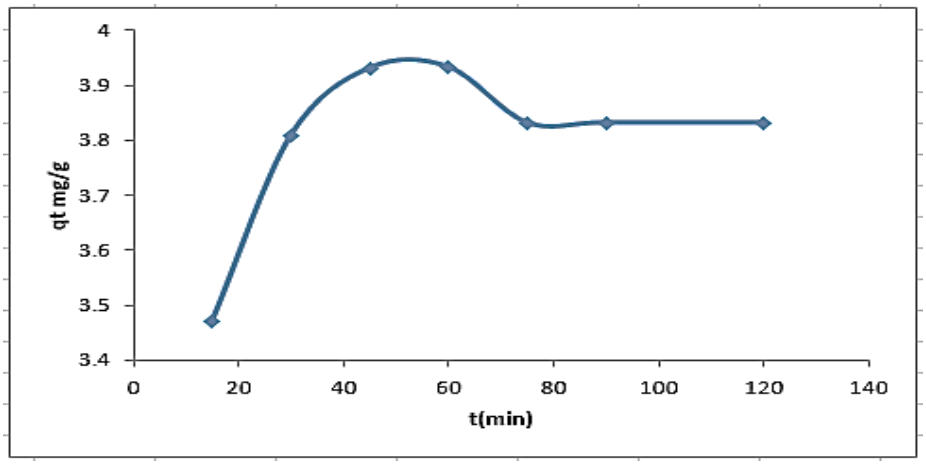


Figure 3: equilibrium time for each adsorbent- adsorbate.

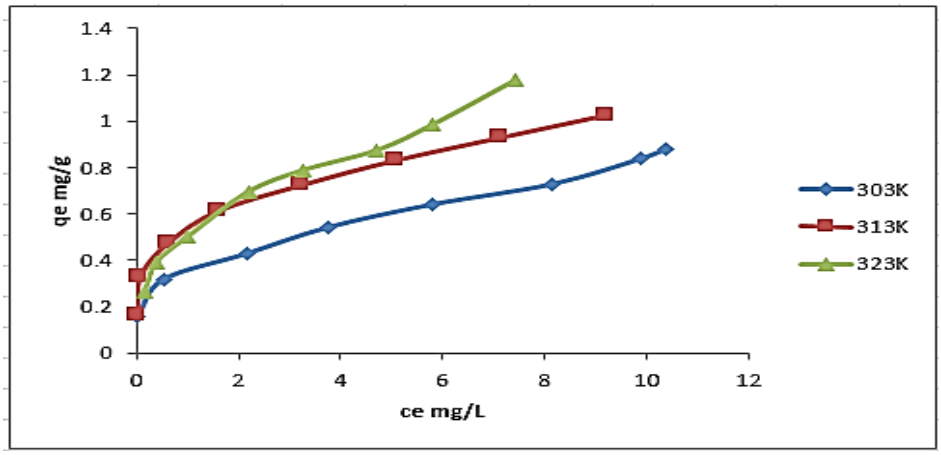


Figure 4: adsorption isotherm of Co (II) complex on Attapulgite clay at various temperature

Three isotherm equilibrium models, Langmuir, Freundlich and Temkin were used to describe the equilibrium data. Langmuir shape is determined from the equation [27].

$$\frac{Ce}{qe} = \frac{1}{KLqemax} + \frac{Ce}{qemax} \quad \text{.....(1)}$$

Were C_e and q_e are the concentration at equilibrium (mg/L), and amount adsorbent (mg/gm), K_L Langmuir constant in (kg/mg), and

$q_{e\ max}$ is the maximum amount in (mg/g)

The Freundlich isotherm which used to describe the adsorption of heterogeneous system [28].

The equation is below:

$$\log qe = \log Kf + \frac{1}{n}\log Ce \quad \text{..... (2)}$$

Where Kf and n are Freundlich constant, Kf (intercept, mg/g) and n (slop, without unite).

The Kf and n, have calculated by drawing log q_e against log C_e. The Temkin isotherm can be calculated by using the equation [29].

$$qe = BT\ lnKT + BTlnCe \quad \text{.....(3)}$$

When drawing q_e Vs ln C_e can be determination the Temkin constant (K_T, B_T). the data for the three isotherms are graphed and recorded in Figure 5 and Table 4.

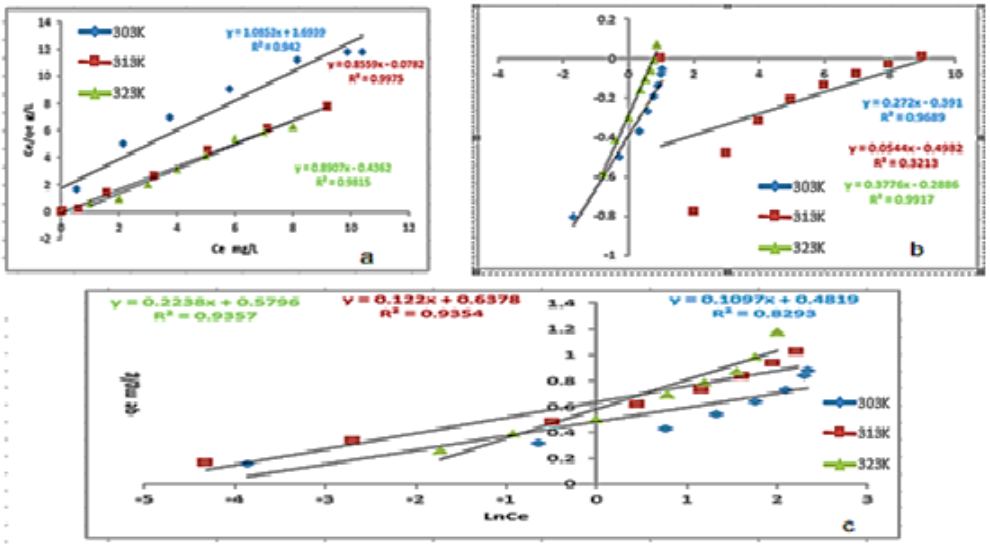


Figure 5: Langmuir (a), Freundlich (b) and Temkin (c) isotherm of cobalt (II) complex on Attapulgite Iraq clay at different temperatures.

Table 4: Langmuir, Freundlich and Temkin isotherm constants for the adsorption of Nickel complex by Attapulgite Iraqi clay

	30^{O}C			40^{O}C			50^{O}C		
Isotherm	**KL (L/mg)**	**$q_{e\ max}$ (mg/g)**	**R^2**	**KL (L/mg)**	**$q_{e\ max}$ (mg/g)**	**R^2**	**KL (L/mg)**	**$q_{e\ max}$ (mg/g)**	**R^2**
Langmuir	0.6407	0.9214	0.942	-10.9529	1.1683	0.9975	-2.0420	1.1227	0.9815
Freundlich	**K_F (mg/g)**	**n**	**R^2**	**K_F (mg/g)**	**n**	**R^2**	**K_F (mg/g)**	**n**	**R^2**
	0.4064	3.6764	0.9689	0.3175	18.3823	0.3213	0.5145	2.6483	0.9917
Temkin	**K_T**	**B_T**	**R^2**	**K_T**	**B_T**	**R^2**	**K_T**	**B_T**	**R^2**
	80.8665	0.1097	0.8293	186.3823	0.122	0.9354	13.3271	0.2238	0.9357

This table summarizes the values of the correlation coefficients as well as the isothermal constants. Where we note the applicability of the isotherm Temkin, also B_T values increased with increasing temperature.

Thermodynamic parameters

Thermodynamic parameters such as Δ^0G, Δ^0H, and Δ^0S were calculated by using the following relationship[30]:

$\Delta^0G = -RT \ln K_{eq}$ ……(4)

$\Delta^0G = \Delta^0H - T\Delta^0S$……..……(5)

$$Keq = \frac{qe}{Ce} \times \frac{w}{v} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where T the absolute temperature, R is gas constant, Keq is the equilibrium constant, qe is the amount of adsorbent (mg/g), and Ce is the concentration of the remaining substance in the solution (mg/L), V is the volume of cobalt complex(L), and m is the mass of clay used (g)[31,32].

When plotting the values of L_nK_{eq} against 1/T, we get a straight line, and from the slope and the intercept we can calculate the values of Δ^0H and Δ^0S respectively as shown in Table 5,6 and Figure 6.

Table 5: The values of the thermodynamic equilibrium constants for the adsorption of the cobalt complex at different temperatures.

T	1/T	$\ln K_{eq}$
303	0.0033	4.2779
313	0.0031	4.4271
323	0.0030	4.6003

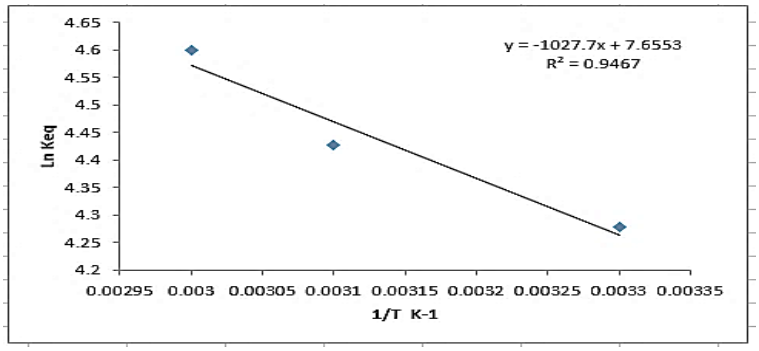


Figure 6: drawings of the Vanderhoff equation for adsorption of the cobalt complex on the surface of the Attapulgite.

Table 6: values of the thermodynamic functions for the adsorption of the complex on the surface of the Attapulgite at different temperatures.

T (K)	Δ^0G (KJ/mol)	Δ^0H (J/mol)	Δ^0S (J/mol)
303	-10.7766	8544.2978	63.6461
313	-11.5205	----	---
323	-12.3537	----	---

From the above table, we note that the values of Δ^0G are negative at all temperatures. This is evidence that the adsorption process is a spontaneous process, the positive value of Δ^0H indicate the endothermic natural of the process. We note also that the value of Δ^0S is positive, which means an increase in the randomness during the adsorption process.

Conclusion :

The work consists of two parts: the first part is the preparation and characterization of the Schiff base ligand, which is derived from the methyl-dopa drug with three ions of the elements cobalt, nickel and zinc. The results indicated that the ligand Schiff base behaves as bidentate ligand and coordinated with the metal ions, the second part, the study surface of iraq attapulgite was tested for adsoption of the Co complex, the results indicate the high susceptility of the surface to adsorption of the complex under study. The Temkin model was the most appropriate of the others modes. The values of the thermodynamic functions indicate that the adsorption process is spontaneous, endothermic and more random.

References:

1. S. Annapoorani and C. Krishnan ,"Synthesis and spectroscopic studies of trinuclear N4 Schiff base complexes international", ***International Journal of ChemTech Research***., 5 (1): 180–185(2013).

2. Chen, D. and Martell, A.E. Dioxygen affinities of synthetic cobalt Schiff base complexes. ***Inorganic Chemistry***, 26, 1026-1987(1987)..
3. A. B.Patil and T. H. Mhaske. , "Potentiometric Studies on Binary and Ternary Complexes of Transition Metal Ions with Some Pharmaceutical Compounds" ***Asian Journal of Chemistry***., 13(4): 1544-1548(2001).
4. Atmaram. K. Mapari and Kiran. V. Mangaonkar. ***International Journal of ChemTech Research***, 3(1):477-482(2011).
5. Khaleel, A. M. N., & Jaafar, M. I. Synthesis and characterization of boron and 2-aminophenol Schiff base ligands with their Cu (II) and Pt (IV) complexes and evaluation as antimicrobial agents. ***Oriental Journal of Chemistry***, 33(5), 2394-2404(2017).
6. M. Q. Al-Abachi, Raghad Sinan and Hind Haddi.," Spectrophotometric determination of methyldopa and dopamine hydrochloride in pharmaceutical preparations using flow injection analysis", ***National Journal of Chemistry***, 36: 597-604. (2009).
7. "WHO Model List of Essential Medicines",World Health Organization. October,Retrieved 22 April (2014).
8. Saravanan, A.; Brindha, V.; Manimekalai, R.; Krishnan,S.; "An evaluation of chromium and zinc biosorption by a sea weed (Sargassum sp.) under optimized conditios"; ***Indian journal of science and technology***., 2(1), 53-56, (2009).
9. Ong, S.; Seng, C.; Lim,P.; " kinticsof adsorption of Cu(II) and Cd(II) from aqueous solution on rice husk and modified husk"; ***Electronic Journal of Environmental, Agricultural and Food***.,6(2),1764-1774, (2007).
10. Sharmaa S.P ,Sharma b.S.***Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*** ; 92(15), 212-224(June 2012) .
11. Ottavio G., Jochanan B. .***Inorganica Chimica Acta*** , 80, 103-106(1983) .
12. Geary, W. ***Coordination Chemistry Reviews***, 7, 81-122(1971).
13. British pharmacopoeia, (1993),30th edition 1 london, 43,47,58,370.
14. Nakamoto K., (1996) "Infrared Spectra Of Inorganic And Coordination Compounds "4 th ED ;John. Wiley and Sons, New York.
15. Sahib, S. K., & Karem, L. K. A. "Some Metal Ions Complexes Derived From Schiff Base Ligand with Anthranillic Acid: Preparation, Spectroscopic and Biological Studies". ***Baghdad Science Journal***, 17(1)2020.
16. Al-Noor, T. H., Mohapatra, R. K., Azam, M., Karim, L. K. A., Mohapatra, P. K., Ibrahim, A. A., ... & Pintilie, L. "Mixed-ligand complexes of ampicillin derived Schiff base ligand and Nicotinamide: Synthesis, physico-chemical studies, DFT calculation, antibacterial study and molecular docking analysis". ***Journal of Molecular Structure***, 1229, 129832(2021).
17. MAHDI, S. H., & KAREM, L. K. A. Synthesis, Physicochemical Studies and biological estimation of new mixed ligand complexes from hetrocyclic compounds. ***International Journal of Pharmaceutical Research***, Supplementary 1(Jan - Jun 2020).
18. Vogel AIA .1978"Text Book of Quantitative Inorganic Analysis " 2 th Ed (Longman, London). 694.
19. Simons WW..1978 "The Sadtler Handbook of Proton NMR Spectra, Sadtler Re-search Laboratories", Philadelphia, Sadtlerk,.
20. Rehab K. al shemary, Lekaa K. Abdul Karim , Wurood A. Jaafar., ***Baghdad Science Journal***, 14(2), 390-402(2017).
21. Al-Noor T. H.; Abdul Karim L. K." Synthetic, Spectroscopic and Antibacterial Studies of Co(II),Ni(II),Cu(II),Zn(II),Cd(II)and Hg (II),Mixed Ligand Complexes of Trimethoprime Antibiotic And Anthranilic Acid" ***TOFIQ Journal of Medical Sciences***,3(2):64-75(2016).
22. Lever A.B.P..1984 "Inorganic spectroscopy" Elsevier publishing company, 3th Edit; Wiley; New York.
23. El-Gammal, O. A., Mohamed, F. S., Rezk, G. N., & El-Bindary, A. A. (" Synthesis, characterization, catalytic, DNA binding and antibacterial activities of Co (II), Ni (II) and Cu (II) complexes with new Schiff base ligand". ***Journal of Molecular Liquids***, 326, 115223(2021).
24. Al-Obidi, L. K., & Al-Noor, T. H. "Synthesis, Spectral and Bacterial Studies of Mixed Ligand Complexes of Schiff Base Derived from Methyldopa and Anthranilic Acid with Some Metal Ions". ***Ibn AL-Haitham Journal for Pure and Applied Science***, 235-247(2018).
25. Fomina, I. G., Dolgushin, F. M., Koroteev, P. S., Mantrova, Y. V., Korshunov, V. M., Taydakov, I. V., & Eremenko, I. L. "Binuclear Gadolinium (III) Pivalates with 4, 7-Diphenyl-1, 10-Phenanthroline: Synthesis, Structure, Thermal Behavior, Magnetic and Photoluminescence Properties". ***European Journal of Inorganic Chemistry***, (5), 464-472(2021).
26. Sarhan, B. M., Mohammad, M. Y., & Salman, T. M. " Synthesis and Characterization of Some New MixedLigand Complexes Containing Schiff Base and 3-Picoline with Some Metal Salts". ***Ibn AL-Haitham Journal For Pure and Applied Science***, *29*(1)2017.

27. Mohammed, S. S., & Al-Heetimi, D. T. " Adsorption of Methyl Violet Dye from Aqueous Solution by Iraqi Bentonite and Surfactant–Modified Iraqi Bentonite". ***Ibn AL-Haitham Journal For Pure and Applied Science***, *32*(3), 28-42(2019).
28. Abbas, A. M. ; Abd, S. S. ; Himdan, T. A. Kinetic Study of Methyl Green Dye Adsorption from Aqueous Solution by Bauxite Clay at Different Temperatures, ***Ibn AL-Haitham Journal For Pure and Applied Science***, 31(1),58-66(2018).
29. Amari , A.; Gannouni , H.; Khan , M. I. ; Almesfer , M. K. ; Elkhaleef , A. M. ; Gannoun, A. "Effect of Structure and Chemical Activation on the Adsorption Properties of Green Clay Minerals for the Removal of Cationic Dye" , ***Applied Science***. , 8,1-18(2018).
30. CHEN, L., ZUO, L., JIANG, Z., JIANG, S., LIU, K., TAN, J. & ZHANG, L. " Mechanisms of shale gas adsorption: Evidence from thermodynamics and kinetics study of methane adsorption on shale". ***Chemical Engineering Journal***, 361, 559-570(2019).
31. Esmaielzadeh, S., & Zarenezhad, E. " Copper (II) schiff base complexes with catalyst property: Experimental, theoretical, thermodynamic and biological studies". ***Acta Chimica Slovenica***, 65(2), 416-428(2018).
32. Zhao, J. Y., Ren, N., & Zhang, J. J. "Crystal structures and thermodynamic properties of lanthanide complexes with 2, 6-dimethylbenzoic acid and 2, 2′: 6′, 2″-terpyridine". ***The Journal of Chemical Thermodynamics***, 152, 106293(2021).