# *Adsorption Study of Symmetrical Schiff Base Ligand 4,4'-[hydrazine-1,2-diylidenebis(methan-1-yl-1-ylidene) bis (2-methoxyphenol)] on Granulated Initiated Calcined Iraqi Montmorillonite via Columnar Method.*

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Abstract

The adsorption ability of Iraqi initiated calcined granulated montmorillonite to adsorb Symmetrical Schiff Base Ligand 4,4'-[hydrazine-1, 2-diylidenebis (methan-1-yl-1-ylidene)) bis (2-methoxyphenol)] derived from condensation reaction of hydrazine hydrate and 4-hydroxy-3-methoxybenzaldehyde, from aqueous solutions has been investigated through columnar method.The ligand ($H_2L$) adsorption found to be dependent on adsorbent dosage, initial concentration and contact time.All columnar experiments were carried out at three different pH values (5.5, 7and 8) using buffer solutions at flow rate of (3 drops/ min.),at room temperature ($25 \pm 2$) ℃. The experimental isotherm data were analyzed using Langmuir, Freundlich and Temkin equations. The monolayer adsorption capacity is 5.7347 mg ligand (L) per 1g calcined Montmorillonite. The experiments showed that highest removal rate 75.70 % for ligand (L) at pH 7.The kinetic data for the adsorption process obeyed pseudo-second-order rate equations.

Key words: Adsorption Study, Schiff base Ligand, Iraqi Montmorillonite,Columnar Method., Calcined.

1.   Introduction

  Schiff bases are most widely used as chelating ligands in coordination chemistry [1]. They are also useful in catalysis and in medicine as antibiotics, analytical applications and antitumor agents [2-3].Tetra, dentate Schiff bases are well known for their coordination with various metal ions, forming stable compounds [4].Generally the organic compounds containing hetero atoms like O, N, S and P are found to work as very effective corrosion inhibitors [5] .The efficiency of these compounds depends upon electron density present around the hetero atoms [6] .The number of adsorption active centers in the molecule and their charge density, molecular size, mode of adsorption and formation of metallic complexes [7]. They are also used as catalysts in polymer and dyes industry, beside some uses as antifertility and enzymatic agents [8].Macrocyclic Schiff bases containing either thiophene or phenol subunits were synthesized and the effect of ligand atoms on the liquid—liquid extraction of bivalent transition metal ions was studied. The phenol groups in the macrocycle led to a large increase in the extraction of transition metal ions. The least stable manganese (II) complex was extracted quantitatively into nitrobenzene as an ion pair with tetraphenylborate ion at (pH = 9) [9]. Clay minerals are the most important inorganic components in soil due to their excellent adsorption properties [10]. Natural mineral clays possess specific surface chemical properties, e.g., cation exchange capacity, and adsorptive affinity for some organic and inorganic compounds. bentonite is  absorbent aluminum phyllosilicate, essentially impure clay consist in mostly of montmorillonite. There are different types of Montmorillonite, each named after the respective dominant element, such as potassium (K), sodium (Na), calcium (Ca), and aluminum (Al) [11]. Montmorillonite clay deposits are mostly composed of clay minerals, a subtype of phyllosilicate minerals, which imparts plasticity and harden when fired or dried [12]. Montmorillonite possess adsorption properties mainly because of their colloidal nature which stems from their very small particle size. The structure of

montmorillonite is an octahedral alumina sandwiched between two tetrahedral silica sheets to form the structural unit. Variations in interstitial water and exchangeable cations in the interlayer space affect the properties of Montmorillonite [13]. Vermiculite and Montmorillonite are clay minerals with high CEC.The CEC for vermiculite, for instance, is approximately 100 – 150 meq per 100 g. The surface area for west Iraqi (Traifawi) bentonite was estimated using methylene blue (MB) adsorption method and it was (123 m$^2$ /g) [14]. West Iraqi (Traifawi) bentonite consists mostly of calcium – montmorillonite. The percent of montmorillonite is between (60 – 65 %) of crude bentonite, (Table 1) show the chemical analysis of West Iraqi (Traifawi) Montmorillonite. Therefore it is necessary to remove the impurities before the bentonite is ready to use [15].

Table 1 : Chemical analysis of West Iraqi (Traifawi) bentonite.

| Compound | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | Na$_2$O | K$_2$O | LiO$_2$ | SO$_3$ | L.I.O. | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Weight % | 55.81 | 14.91 | 5.78 | 5.72 | 3.5 | 1.29 | 0.41 | 0.67 | ---- | 10.86 | 99.67 |

In this study we investigate the adsorption of Symmetrical Schiff Base Ligand (H$_2$L) derived by reaction between hydrazine hydrate and 4-hydroxy-3-methoxybenzaldehyde in ethanol to form tetradentate dibasic ligand of the ONNO type, on the surface of calcined initiated Iraqi Montmorillonite clay packed in glass columns, and calculate the effect of factors like pH, ionic strength contact time and weight of clay on percentage of removal of the drug, also calculate the isothermic factors of adsorption process.

2. Materials and methods

2.1. Materials

All the chemicals and solvents were of analytical grade (supplied by either Merck or Fluka) received. CdCl$_2$. H$_2$O (BDH), without further purification. Distilled and deionized water with conductivity value of 1.5 x 10$^{-5}$ S cm$^{-1}$ was used in all experiments. Montmorillonite clay mineral obtained from the General Company for Geological Survey and Mining in Baghdad, Iraq. The samples were sieved to produce the desired particle size fractions. The samples with a particle size 45 μm was then dried for 24 h at 110 ℃ in an electric oven and stored in a desiccator until use.

2.2. General procedure for the Preparation of the Schiff base 4, 4'-(hydrazine-1, 2-diylidenebis (methan-1-yl-1-ylidene)) bis (2-methoxyphenol) C$_{16}$H$_{12}$N$_2$O$_4$ [H2L] ligand[16].

A solution of hydrazine hydrate(0.833gm,0.5mol) in ethanol 10ml was added drop wise to a stirred solution of 4-hydroxy-3-methoxybenzaldehyde(5gm,1mol)and the mixture was refluxed for 4h the reaction mixture was distilled under reduced pressure .The solid obtained was recrystallized from ethanol. , M .wt. = 300.30, m .p =158 ℃.The color of the product is orange, yield 85.10 %, Anal. Calcd (H2L),C = 63.99 %, H = 5.37%,N = 9.33%.= Found: C = 61.59 %,H=6.2%, N = 9.78%. ; Infrared (KBr, cm$^{-1}$): υ(OH), 3132,υ (CH) cyclic 2939, υ (C=N) 1625 vs. υ (N =N). 1266 υ (C–O). UV-visible in DMF (λ max, nm): two bands at 342 nm (29230 cm$^{-1}$) and 357 nm (28011 cm$^{-1}$)) attributed to π → π* and n → π* transitions respectively [16].
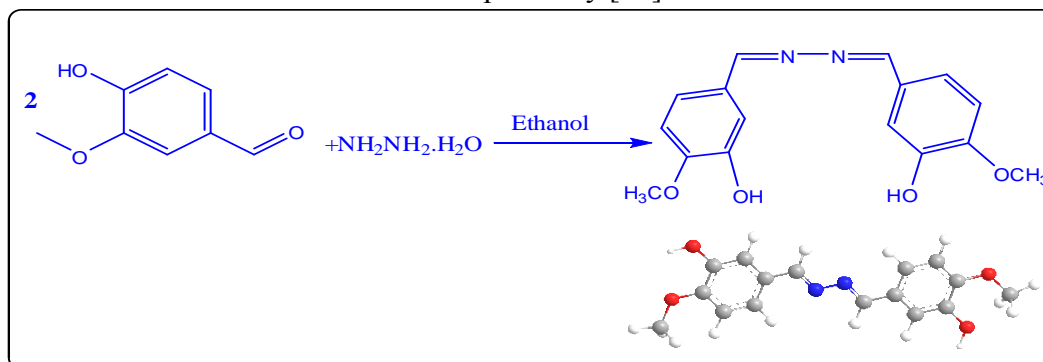


Scheme (1): Schematic representation of synthesis of the ligand (H2L). [16].

### 2.3. Preparation of buffer and stock solutions.

Three phthalate and phosphate buffer solutions of pH values (5.5, 7, and 8) were prepared respectively [17], also a three stock solutions of the prepared ligand (H$_2$L) of 2000 mg /L concentration were prepared in 100 ml volumetric flask using the above buffer solutions.

### 2.4.Procedure for synthesis of granulated Iraqi calcined Initiated Na– montmorillonite clay.

In this study the bentonite was beneficiated to improve its Smectite (Montmorillonite) content by attrition – scrubbing at high solid concentration (50%) and at high impeller speed (2500 r.p.m.) for 1 h, using flotation cell. In order to convert calcium - montmorillonite to sodium - montmorillonite the process performed by mixing the bentonite preconcentrate with Na – form activated amberlight orange ion exchanger followed by agitation for 1 h, at 150 r.p.m. The clay was separated from the mixture by filtration, washed five times with distilled water. Each washing step involved stirring the slurry in distilled water, followed by centrifugation and removal of the supernant, the obtained Na – monmorillonite finally treated with 0.5 M NaCl to ensure complete transformation to the Na – form, then the treated clay was washed with distilled water to remove excess NaCl, turned to a granules of (2mm) diameter using granulating machine ( GK Dry Granulating Machine ) and dried at 110 ℃ for 3h, until constant mass, and then burned at 650$^o$C to make an ion – exchange column ready to use

### 2.5. Columnar adsorption procedure.

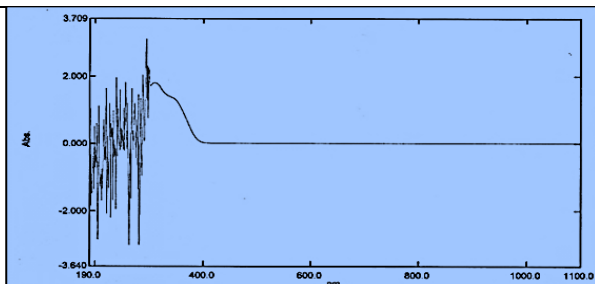Three standard solutions of ligand (H$_2$L)30 mg /L concentration were prepared from stock solutions



**Fig. 1. Scanning graph of Ligand (H$_2$L), Buffer soln.**
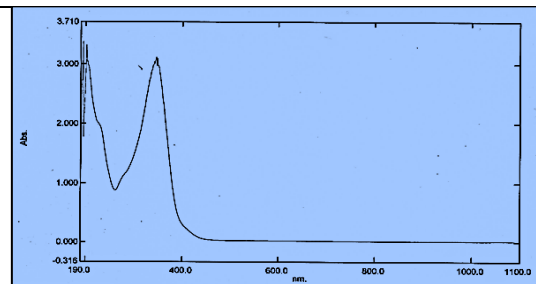**pH = 5.5, Conc. = 30 ppm., at λ max. = 311 nm.**



**Fig.** 2. Scanning graph of Ligand (H$_2$L), Buffer soln.
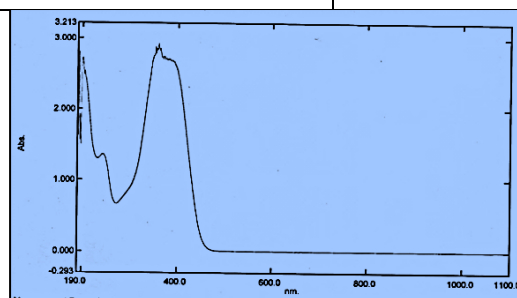pH =7, Conc.= 30 ppm., at λ $_{max}$. = 347 nm.



**Fig. 3.Scanning graph of Ligand (H$_2$L), Buffer soln.**
**pH = 8, Conc. = 30 ppm., at λ $_{max}$. = 360 nm.**

of ligand (H$_2$L)in different pH values (5.5, 7and 8) using buffer solutions. UV-Visible scanning spectrum has been recorded and wavelength value corresponding to the maximum absorption found to be at (311 nm for pH = 5.5),(347 nm for pH =7),and (360 nm for pH = 8), as shown in (Fig.1), (Fig.2), and (Fig. 3) Respectively, these values choose for measurements of estimation throughout this research.

Seven standard solutions of ligand ($H_2L$) in the range of (5 - 17 ppm or mg /L) concentration were prepared from stock solutions of ligand ($H_2L$) at different pH values (5.5, 7and 8) using buffer solutions. The absorbance of each solution was measured at λ max. (311 nm for pH = 5.5),(347 nm for pH =7), and (360 nm for pH = 8) respectively against blank (buffer solution Corresponding to pH value).A calibration curves were drown between absorbance and concentration of ligand ($H_2L$) standard solutions, as shown in (Fig. 4),(Fig. 5), and (Fig. 6) Respectively.
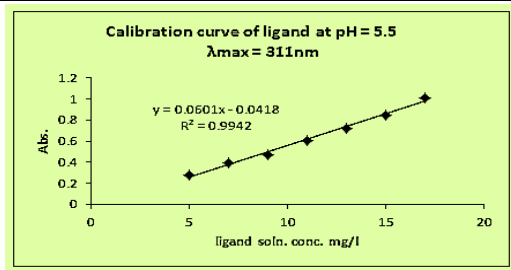


**Fig. 4. Calibration curve of ($H_2L$) dissolved in buffer soln. pH = 5.5 at λ max. = 311 nm.**
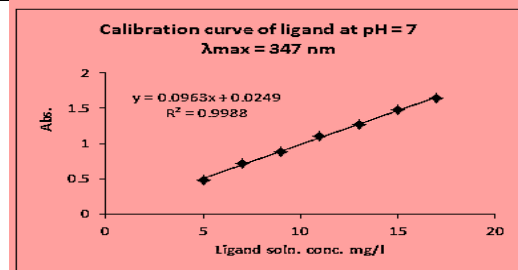


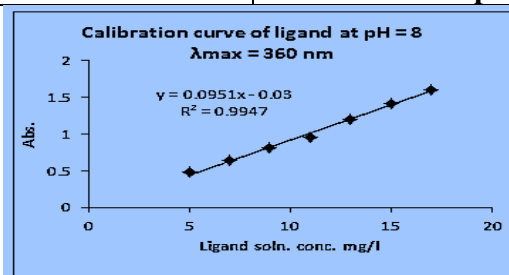**Fig. 5.Calibration curve of ($H_2L$) dissolved in buffer soln. pH = 7 at λ max. = 347 nm.**



**Fig. 6.Calibration curve of ($H_2L$) dissolved in buffer soln .. pH = 8 at λ max.= 360 nm**

A six glass columns (50 cm X 10 mm i.d.) filled with known mass (1gm) of natural mineral clay adsorption bed (Initiated Burned Na - montmorillonite) corresponding to bed heights of (17 mm) (the surface area of 1 gm. mass of natural clay adsorption bed was calculated physically and its found to be 23.904 c m$^2$ ) have been prepared to run (10 ml) of each of (5 – 25 mg/L) ligand ($H_2L$) solutions adjusted to different pH values (5.5, 7and 8) using buffer solutions at flow rate of
(3 drops/ min.),at room temperature (25±2) ℃. Then we examine the percolated solutions by measuring the absorbance of each solution at fixed λ max., that have been identified for each pH value, using (UV-Vis – 1800 Shimadzu Spectrophotometer ).The equilibrium adsorption uptake and percent removal of ligand ($H_2L$) from the aqueous solution $q_e$ (mg/g) was calculated using the relationship noted at the bottom of the (Table 2).

**Table 2:Adsorption parameters of adsorption of ($H_2L$)on initiated burned Iraqi bentonite clay mineral.**

| Adsorb ate ($H_2L$) concentration C∘ | pH 5.5 | | | pH 7 | | | pH 8 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $C_e$ | Removal % | $q_e$ | $C_e$ | Removal % | $q_e$ | $C_e$ | Removal % | $q_e$ |
| 5 | 2.792 | 44.16 | 0.0220 | 1.215 | 75.70 | 0.0378 | 2.397 | 52.06 | 0.0260 |
| 10 | 5.603 | 43.47 | 0.0439 | 3.635 | 63.65 | 0.0636 | 6.067 | 39.33 | 0.0393 |
| 15 | 8.881 | 40.79 | 0.0611 | 6.273 | 58.18 | 0.0872 | 9.369 | 37.54 | 0.0563 |
| 20 | 11.060 | 44.70 | 0.0894 | 7.571 | 62.15 | 0.1242 | 11.272 | 43.64 | 0.0872 |
| 25 | 11.810 | 52.76 | 0.1319 | 8.723 | 65.11 | 0.1627 | 12.103 | 51.58 | 0.1289 |

Amount adsorbed $q_e = (C_0 - C_e)V/W$ (mg of adsorbate / g of adsorbent), removal $\% = 100$ $(C_0 - C_e)/C_e$, Where $C_0$ is the initial sorbate concentration (mg/L), $C_e$ the equilibrium adsorbate concentration (mg/L),V is the volume of solution in L and w is the mass of the adsorbent in (g) [18].

### 2.6.Characterization of bentonite clay mineral.

Natural Iraqi bentonite was characterized by FT –IR spectroscopic analysis (Shimadzu FTIR Spectrometer – 30 000:1/ IRAff ). FT- IR spectrum (Fig. 7. A) showed absorption band at 3628.10 cm-1(Al-Al-OH) (Mg-OH-Al) corresponding to vibration of structural OH starching groups coordinating to Al-Al pair or Mg-OH-Al. Adsorbed water gives a broad bands from 4306.29 cm-1 to 3533.59cm-1 corresponding to H2O- stretching vibration . Al, Mg bound water molecules gives H-O-H stretching vibration bond at 1643cm-1. Also three bands at 1546.91, 1427.32 and 1384.89 cm-1corresponding to H..O..H weak .The complex broad band around 1033 cm-1 belongs to Si-O stretching vibration. Two bands at 914.26 cm-1 and 837.11 cm-1 are most characteristic for quartz. Finally the bands from 420.00 cm-1to 516.93 cm-1 are related to Al-O-Si , Si-O-Si deformations. Initiated bentonite FT- IR spectrum (Fig.7.B) Showed the same bands of (Fig.7.A) but with higher transmittance percent and sharper than bands of FT- IR spectrum of natural bentonite.Nevertheless H..O..H weak disappear in this spectrum. Adsorbed water band appear at 4321.72 cm-1, two bands belong to Al, and Mg bound water molecules observed at 1654.92 cm-1 and 1641.42 cm-1. The broad complex band becomes single band at 1039 cm-1 belongs to Si-O stretching vibration. Also we observe two bands belongs to Al…OH stretching vibration at 937.04 cm-1 and 916.19 cm-1 with higher transmittance percent .the quartz characteristics band from 694.37 cm-1 to 839.03 cm-1 become broader. Finally Al-O-Si, Si-O-Si and Si-O stretching vibration bands from 426.27 cm-1 to 522.71 cm-1 become sharper and triplet bond [19]. calcined initiated Iraqi Montmorillonite FT- IR spectrum (Fig. 7. C) Showed the same bands of that in (Fig.7. B) but sharper and with higher transmittance percent , also the band of adsorbed water become a single band at 3421.7 cm-1 mostly due to burning process and the same thing happen with band Al, Mg around water molecule stretching vibration also H…O...H weak bands disappear in this spectrum.
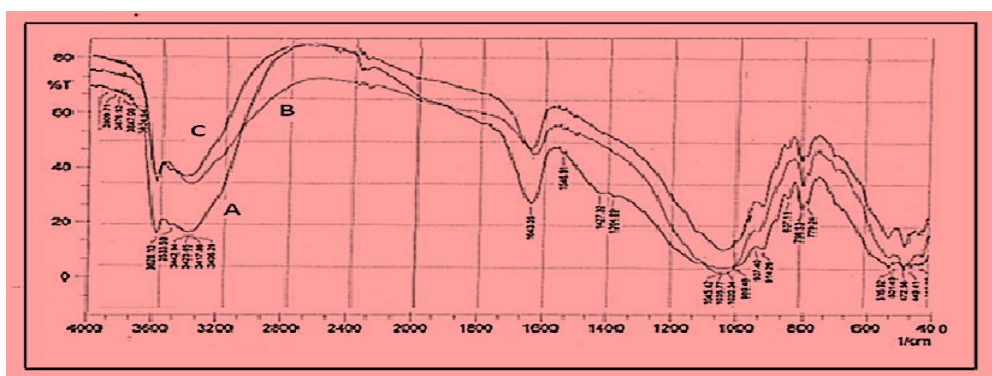


Fig. 7. **A**- FT-IR spectrum for crude Iraqi bentonite (Trifawi) ,**B** -FT- IR spectrum for initiated bentonite, **C**- FT- IR spectrum for burned initiated bentonite

### 2.7.Calibration graphs.

Three linear calibration curves for ligand (H2L)were obtained at different pH values (5.5, 7and 8) (Figs.4,5, and 6), which show that Beer's law was obeyed in the concentration range of (5 − 17) mg L-1, Coefficient of determination R², Limit of detection (sensitivity) LOD, in addition to other parameters are given in (Table 3).

**Table 3-Spectral characterization and statistical data of the regression equation for Ligand (H$_2$L) adsorption on calcined Iraqi Montmorillonite**.

| Parameter | Ligand (H$_2$L) | | |
|---|---|---|---|
| | pH 5.5 | pH 7 | pH 8 |
| **Linearity range (ppm)** | 5 -17 | 5 -17 | 5 -17 |
| **Regression equation** | | | |
| **Intercept** | - 0.04179 | 0.024911 | - 0.03000 |
| **Standard deviation of intercept** | 0.023995 | 0.017367 | 0.036257 |
| **slope** | 0.060071 | 0.096268 | 0.095143 |
| **Standard deviation of slope** | 0.00205 | 0.001484 | 0.003098 |
| **Coefficient of determination  R $^2$** | 0.994211 | 0.998814 | 0.994728 |
| **Standard error of Y & X axis STEYX** | 0.021695 | 0.015702 | 0.032782 |
| **Limit of detection (sensitivity) LOD** | 1.191814 | 0.538253 | 1.137031 |
| **Limit of quantitation LOQ** | 3.611559 | 1.630563 | 3.445550 |

### 2.8.Effect of adsorbate initial concentration (C∘) of ligand (H$_2$L).

To study the adsorbate concentration on a fixed weight surface of adsorption1g clay bed at different PH values (5.5, 7and 8) using buffer solutions, and at room temperature (25$\pm$2) ℃. Plotting (C$_o$) values from (Table 2) against removal % of ligand (H$_2$L), as shown in (Fig.  8).
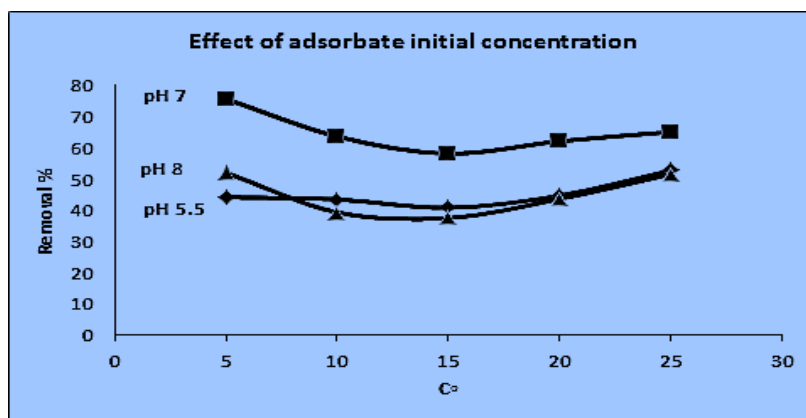


Fig, 8. Effect of adsorbate initial concentration of ligand (H$_2$L).

When we notice the graph we find that the highest adsorption of ligand occurs at PH = 7, and the increase in the initial concentration of ligand decrease the amount of ligand removed.to the extent that we get maximum adsorption capacity of the clay surface.

### 2.9.Effect of pH.

pH were studied and their impact on the adsorption of ligand (L) On the surface of Calcined initiated Montmorillonite clay by preparing three ligand (H$_2$L) solutions of constant concentration (20) ppm adjusted to different pH values (5.5, 7and 8) using buffer solutions. Then passage (10 ml) of each solution through a three columns of 1g clay bed with constant flow rate (3 drops min^{-1}) at room temperature (25$\pm$2) ℃, then by measuring the absorbance of these solutions after passing through the adsorption column, calculation of removal % of ligand (H$_2$L) by the clay bed, and plotting removal % against the pH values as shown in (Fig.  9) it's found that the best pH value of adsorption of ligand (H$_2$L) on clay bed was (pH = 7), and that is due to the neutral character of ligand (H$_2$L).
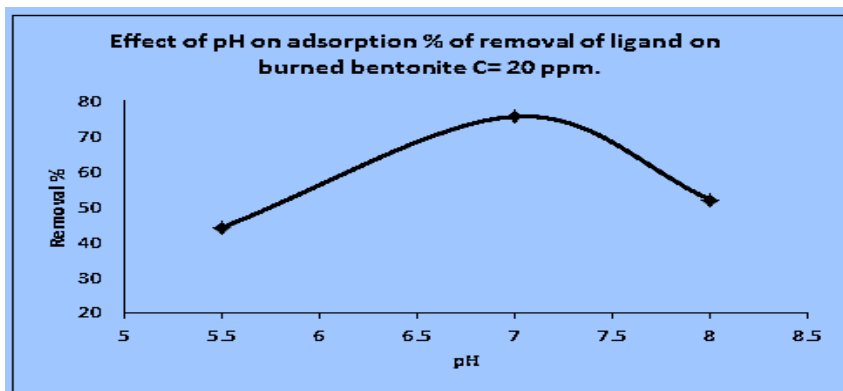
Fig. 9. Effect of pH on adsorption % of removal of (H₂L) on Calcined Montmorillonite, C = 20 ppm.

### 2.10.Effect of clay weight.

Seven different clay weight columns ranged from (1 – 2.2 g) clay bed were prepared for the passage (10 ml) of ligand (H₂L) solution at pH = 7 and concentration of (5) ppm with constant flow rate of (3 drops/ min.) at room temperature (25±2) ℃, then by measuring the absorbance of these solutions after passing through the adsorption column, calculation of removal % of ligand (H₂L) by the clay bed, and plotting removal % against the clay weight as shown in (Fig. 10) it's found that the highest adsorption of ligand (H₂L) occurs on clay bed of 2.0 g weight. This means increasing absorption with increasing weight of clay to the upper limit of clay capacity, and adsorption surface area.
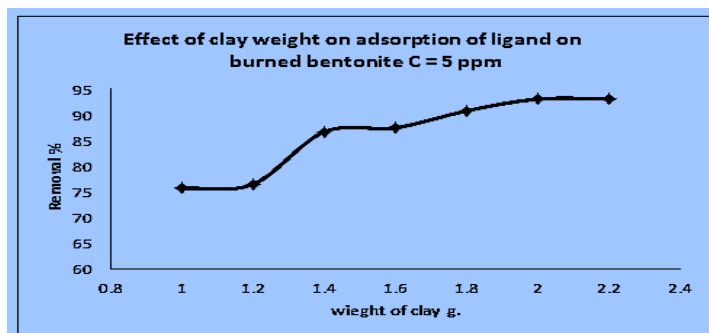


Fig.10. Effect of clay weight on adsorption removal% of (H₂L) n Calcined Montmorillonite,C= 5 ppm.

### 2.11.Effect of ionic strength.

Ionic strength factor was studied by adding different concentrations of sodium chloride (0.1, 0.3, and 0.5M) to three (10) ml solutions of ligand (H₂L) of constant concentration (5) ppm. Then measuring the absorbance of these solutions run through four adsorption columns of clay bed weight of 2.0 g,calculation of (q$_e$), and plotting (qe) against the molar concentration of NaCl as shown in (Fig.11).The graph shows that the adsorption decreases with the increasing of Na$^+$ and Cl$^-$ ions concentration on the clay bed surface, which is due to high electrostatic interaction of these ions with the clay surface and that hinders ligand (H₂L) adsorption on the clay surface.
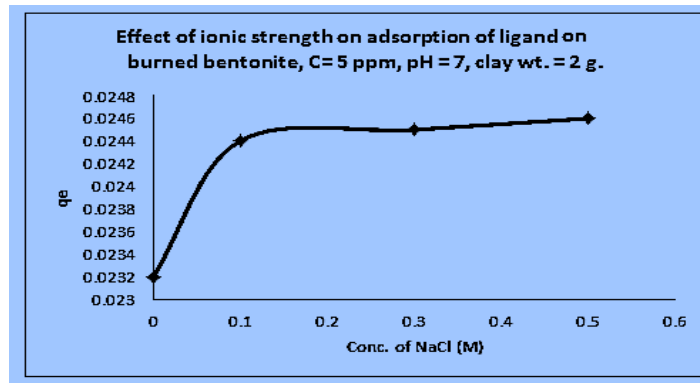
Fig. 11. Effect of ionic strength on adsorption removal % of Ligand (H₂L) on Calcined Montmorillonite,  C = 5 ppm.

## 2.12. Adsorption Isotherms.

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich, and Temkin isotherms [18].The set of experimental results as presented in (Fig. 12) at room temperature $(25 \pm 2)$ were fitted with the Langmuir, Freundlich, and Temkin models. Adsorption isotherms were obtained and the adsorptive capacity interpreted using both models.
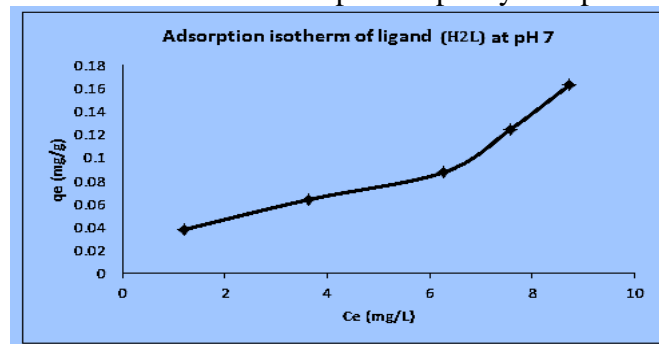


Fig. 12. Adsorption isotherm of Ligand (H₂L) at pH = 7

## 2.12.1. The Langmuir isotherm.

The Langmuir model [20, 21] is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{———— (1)}$$

The constants in the Langmuir isotherm can be determined by plotting $(1/qe)$ versus $(1/Ce)$ and making use of above equation rewritten as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} \quad \text{———— (2)}$$

Where $q_m$ (mg/g) and $K_L$ (L/mg) are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. The values of $q_m$ and $K_L$ can be evaluated from the intercept and the slope of the linear plot of experimental data (Table 4) of $(1/q_e)$ versus $(1/C_e)$ (Fig.  13), and were found to be 5.7347 mg / g and 26.0420 L / mg, respectively. Also the isotherm data fits the Langmuir equation well where the coefficient of determination ($R^2 = 0.9276$).
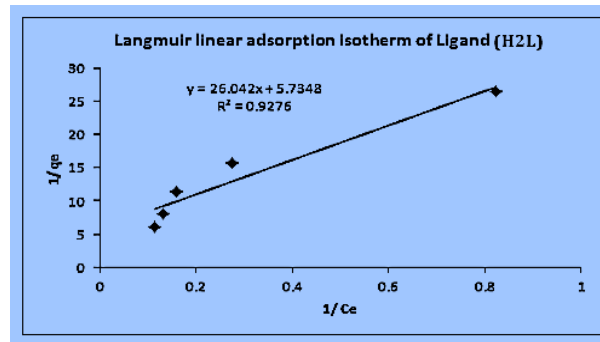
Fig 13. Langmuir linear adsorption isotherm of Ligand (H$_2$L).

Table 4  -Experimental data of the Adsorption Isotherms.

| Langmuir | | Freundlich | | Temkin | |
|---|---|---|---|---|---|
| 1 / C$_e$ | 1 / q$_e$ | Log q$_e$ | Log C$_e$ | q$_e$ | Ln C$_e$ |
| 0.8230 | 26.4550 | - 1.4225 | 0.0845 | 0.0378 | 0.1947 |
| 0.2751 | 15.7232 | - 1.1965 | 0.5605 | 0.0636 | 1.2906 |
| 0.1594 | 11.4678 | - 1.0594 | 0.7974 | 0.0872 | 1.8362 |
| 0.1320 | 8.0515 | - 0.9058 | 0.8791 | 0.1242 | 2.0243 |

### 2.12.2. The Freundlich isotherm.

  The Freundlich isotherm model [22, 23] is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of ligand adsorbed per unit mass of adsorbent,$q_e$, and the concentration of the nickel at equilibrium, $C_e$.

$$q_e = K_f \; c_e^{1/n} \qquad \text{———— (3)}$$

The logarithmic form of the equation becomes,

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \qquad \text{———— (4)}$$

  Where $K_f$ & $n$ are the Freundlich constants, the characteristics of the system. $K_f$ and $n$ are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log $C_e$ vs. log $q_e$ was employed to generate the intercept value of $K_f$ and the slope of $n$. from (Fig.  14) The Freundlich constants $K_f$ and $n$ were found to be -1.5194 and 0.6818 respectively. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. Freundlich isotherm fitted well with the coefficient of determination ($R^2$ = 0.9178).
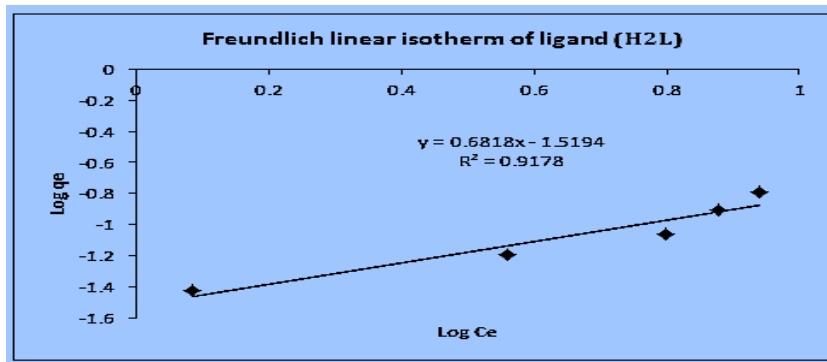
Fig. 14. Freundlich linear adsorption isotherm of Ligand (H$_2$L).

### 2.12.3. The Temkin isotherm.

The Temkin isotherm [24] has been used in the following form:

$$q_e = \frac{RT}{b} \ln(A C_e) \qquad\qquad (5)$$

A linear form of the Temkin isotherm can be expressed as:

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \qquad\qquad (6)$$

$$q_e = B \ln A + B \ln C_e \qquad\qquad (7)$$

Where $B = \frac{RT}{b}$, R is gas constant (8.314 J/mol/K), T is Temperature (K)

The sorption data can be analyzed according to Eq. (7). Therefore a plot of $q_e$ versus lnCe enables one to determine the constants $A$ and $B$. The values of the Temkin constants $A$ and $B$ are listed in Table 1 and the plot of this isotherm is shown in (Fig. 15). The coefficient of determination ($R^2 = 0.7681$) obtained showed that adsorption of ligand (H$_2$L) also followed Temkin model.
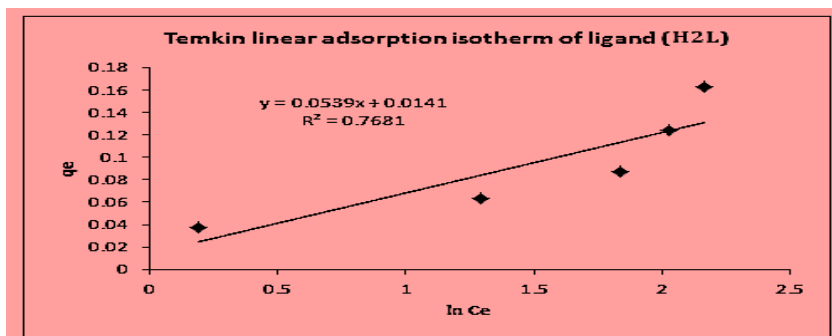


Fig. 15. Temkin adsorption isotherm of Ligand (H$_2$L).

The Langmuir, Freundlich, and Temkin adsorption constants calculated from the corresponding isotherms with the coefficient of determination ($R^2$) are presented in (Table 5).

Table 5. Isotherm Models Constants and the coefficient of determination ($R^2$) of ligand (H$_2$L) from Aqueous Solution.

| Adsorbent | Langmuir isotherm | | | Freundlich isotherm | | | Temkin | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_m$ (mg/g) | $K_L$ L/mg | $R^2$ | $K_f$ | $n$ | $R^2$ | $A$ (L/g) | $B$ | $R^2$ |
| Initiated burned Iraqi bentonite clay | 5.7347 | 26.0420 | 0.9276 | -1.5194 | 0.6818 | 0.9178 | 1.2990 | 0.0539 | 0.7681 |

## 2.13. Effect of flow rate (contact time).

Adsorption of ligand ($H_2L$) was measured at five different flow rates for a solution of ligand ($H_2L$) (5) ppm, concentration. From (Fig. 16), the plot reveals that removal percent of ligand ($H_2L$) is higher at low flow rates. This is probably due to higher contact time at these low flow rates. (Table 6) show the calculated parameters that illustrate the importance of flow rate and contact time.
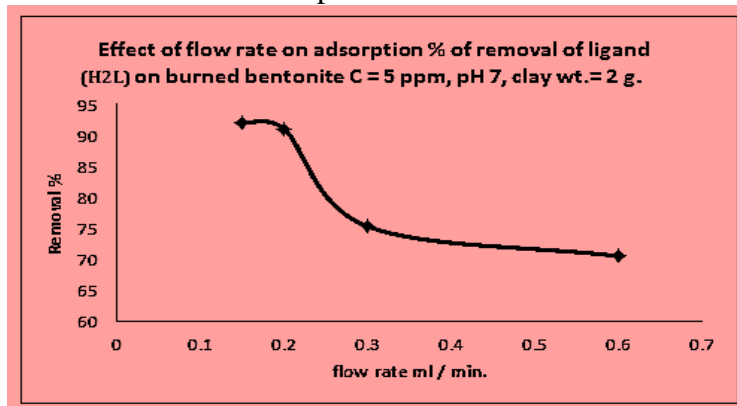


Fig. 16. Effect of flow rate on adsorption removal % of Ligand ($H_2L$) on burned bentonite, C = 5 ppm.

**Table 6 :Effect of contact time on the adsorption of (5 mg/mL),($H_2L$) from aqueous solution.**

| itial Conc. (mg/L) | Flow rate drop / min | Flow rate ml / min. | Time (min) | Equilibrium Conc.$C_t$ (mg/L) | Removal % | $q_t$ (mg/g) | Ln $(q_e - q_t)$ | $t/q_t$ | Equilibrium Time (min) |
|---|---|---|---|---|---|---|---|---|---|
| 5.00 | 3 | 0.15 | 66.666 | 0.395 | 92.1 | 0.0230 | | 2898.521 | 66.666 |
| | 4 | 0.2 | 50.000 | 0.447 | 91.06 | 0.0227 | - 8.1117 | 2936.828 | |
| | 6 | 0.3 | 33.333 | 1.236 | 75.28 | 0.0188 | - 5.4726 | 3546.063 | |
| | 12 | 0.6 | 16.666 | 1.475 | 70.5 | 0.0176 | - 5.2213 | 3787.840 | |

### 2.14. Adsorption kinetics.

Kinetic models are used to examine the rate of the adsorption process in the present work; the kinetic data obtained from the studies have been analyzed by using pseudo-first-order and pseudo-second-order models.The first order equation of Lagergren is generally expressed as follows.
$dq/dt=k_1(q_e-q_t)$ ,
where $q_e$ is the amount of Ligand ($H_2L$) adsorbed at equilibrium (mg/g), qt is the amount of Ligand ($H_2L$) adsorbed at time t ($min^{-1}$), and $k_1$ is the rate constant of pseudo-first-order adsorption. If it supposed that q=0 at t=0, then: $\ln(q_e-q_t)= \ln q_e- k_1t$
The pseudo-second-order kinetic rate equation is expressed as follows. $dq_t/dt=k_2(q_e-q_t)^2$
Where $k_2$ is the rate constant of pseudo-second-order sorption (g/mg/min). The integrated form of Equation when (t=0 →t and qt=0→ 0$q_e$) the following expression is obtained:
$t/qt=1/k_2q_e^2+t/q_e$

The rate constant $k_1$, $k_2$ and qe calculated from the slopes and intercepts of the linear plot of $\ln(q_e-q_t)$ or ($t/qt$) against t respectively (Figs. 17, and 18). It is seen that Ligand ($H_2L$) adsorption is well described by the pseudo second order reaction kinetic. Moreover, the correlation coefficient ($R^2$), of second order reaction kinetic (0.9081) is higher than that of the first order reaction kinetic (0.8147) and greater value of rate constant for the adsorption data. (Table 7) shows the rate constants, qe (experimental and calculated) and correlation coefficient ($R^2$) for pseudo first and second order reaction kinetic.
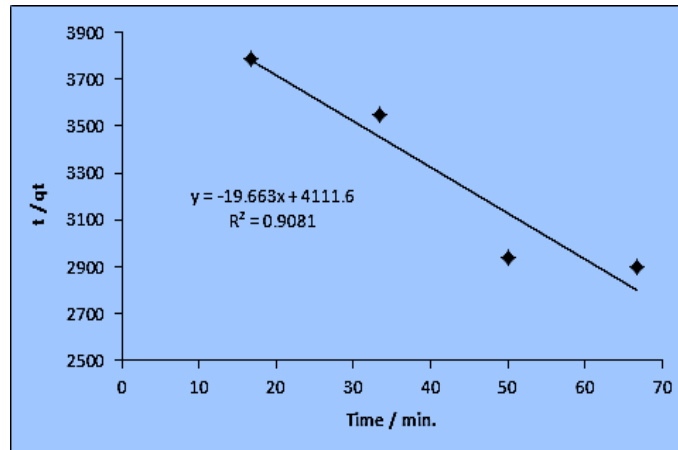
Figure 17.The pseudo-second-order kinetic models for the adsorption of 5 ppm. of Ligand ($H_2L$) at $(25 \pm 2)$ $°C$ under optimum conditions.
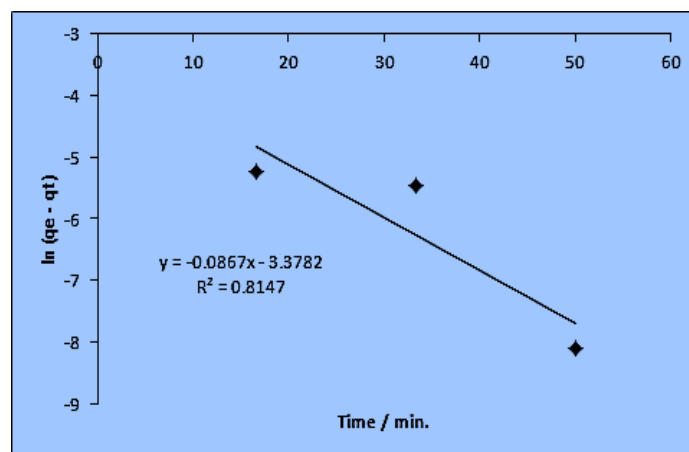


Figure18, The pseudo-first-order kinetic models for the adsorption of 5 ppm. of Ligand ($H_2L$) at $(25 \pm 2)$ $°C$ under optimum conditions.

**Table 7 :The pseudo - first and second- kinetic order parameters for the adsorption of 5 ppm. of Ligand ($H_2L$) at $(25 \pm 2)$ $°C$ under optimum conditions.**

| qe Experimental (mg/g) | The pseudo-first-order kinetic models | | | The pseudo-second-order kinetic models | | |
|---|---|---|---|---|---|---|
| | $q_e$ calculated (mg/g) | $K_1$ ($min^{-1}$) | $R^2$ | $q_e$ calculated (mg/g) | $K_2$ (g/mg/min) | $R^2$ |
| **0.0230** | **0.0341** | **0.0867** | **0.8147** | **0.0508** | **0.000627** | **0.9081** |

## 3-Conclusions

The present investigation shows that Iraqi initiated burned bentonite clay mineral is an effective adsorbent for the removal of ligand ($H_2L$) from aqueous solutions. From the kinetic studies, it is observed that adsorption of ligand ($H_2L$) is very rapid in the initial stage and decreases while approaching equilibrium. The equilibrium time increases with initial ligand ($H_2L$) concentration. The percentage removal of ligand ($H_2L$) increases with the increase in adsorbent dosage and decreases with increase in initial ligand ($H_2L$) concentration. Experimental results are in good agreement with Langmuir, Freundlich and Temkin adsorption isotherm models, and have shown a good fitting to the experimental data. Adsorption of ligand ($H_2L$) obeys pseudo-second order equation with good correlation

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