



## Study of Isothermal, Kinetic and Thermodynamic Parameters of Adsorption of Glycolic Acid by a Mixture of Adsorbent Substance with ab- Initio Calculations

Rana T. Ali<sup>1</sup>; Noor H. M. Saeed<sup>2</sup>; Khaleel Ibrahim Al-Niemi<sup>2</sup>

<sup>1</sup>Chemistry Department, College of Education for girls, University of Mosul, Mosul, Iraq

<sup>2</sup>Chemistry Department, College of Education for pure sciences, University of Mosul, Mosul, Iraq



### Abstract

The present study deals with the adsorption of glycolic acid (GA) from aqueous solutions by using a mixture of adsorbents of clay and charcoal. Recovery process depends on contaminated water obtained from scientific research laboratories and drug manufacturing plants, with adsorption technology via using activated carbon adsorbent with a new natural adsorbent that collected from dust storms. Thermodynamic parameters ( $-\Delta G$ ,  $-\Delta H$  and  $-\Delta S$ ) and the isotherms were correlated with a model based on the principle of phase equilibrium.

**Keywords:** Adsorption; Glycolic acid, Theoretical study; Adsorption kinetic, isotherms.

### 1. Introduction

Glycolic acid, is known as hydroxyl-acetate acid (GA,  $\alpha$ -hydroxy acid), is the most used acid in treatment in chemical peels, facial treatment, as key ingredients in skin care products; creams, cleansers, toners, peels and exfoliates. Also, it reduces acne scarring, wrinkles, and hyper-pigmentations.[1-3] It can be prepared, example by reaction of carbon monoxide with formaldehyde, preferably in the presence of water.[4, 5]

GA is good intermediate in organic reactions such as esterification, oxidation-reductions, in dental field, is used as a monomer in the preparation of poly-glycolic acid, and long chain polymerization.[6-8] GA is used in the textile industry as a dyeing and tanning agent, in food processing as a flavoring agent and as a preservative.[9, 10] GA is as additives for ink and paint in order to improve flow properties, is often

included into emulsion, solvents, polymers, and impart gloss. Natural sources of GA include sugar beets, sugar cane, cantaloupe, pine apple, and unripe grapes.[11]

Recovery process of GA is mandatory and essential from its source of production and there are many technologies that used for recovery such as reactive extraction, adsorption, reverse osmosis, electro-dialysis etc.[10, 12, 13] Among these technologies, there is adsorption technology that employed in waste water treatment for recovery certain vital products such as GA. [14] Also, adsorption of glycolic acid from aqueous solutions has been studied using many materials such as fly ash residues [15], adsorption resins (HPD 950, HPD 450 [16], and AB-8), and metallic surfaces [17].

There are three types of Adsorbents

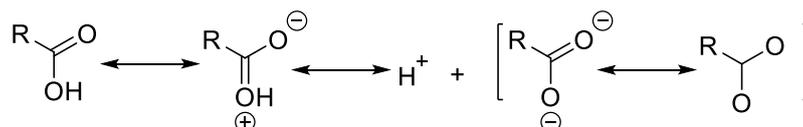
- a. Oxygen containing compounds (zeolite and silica gel)
- b. Carbon based compounds (activated carbon and graphite)

c. Polymer based compounds (porous polymer matrix)

Although synthetic polymeric and silica based adsorbents are used for waste water adsorption but since they are costly, cheap adsorbents such as activated charcoal, bagasse fly ash (BFA), tea waste etc. are gaining attractiveness in advanced wastewater treatment.

Glycolic acid has acidic and alcoholic properties, the hydroxyl group has strong electronegativity

which leads to electronic interference from the hydrogen of the carboxyl group, GA is polar that forms hydrogen bonding with other molecules. The losing of hydrogen ion by ionization leads to stability for acidic molecules by anion resonance, the alcoholic (OH) as electron-donating group decrease acidity of carboxylic group, the carboxylic acid can donate hydrogen ion more easily than hydrogen in alcohol (Figure 1).[18, 19]



**The stability of anion by resonance is more than the stability of acid by resonance**

**Figure 1: Resonance stability of GA**

The aim of our work is to study glycolic acid adsorption from contaminated water obtained from scientific research laboratories and drug manufacturing plants, with adsorption technology via using activated carbon adsorbent with a new natural adsorbent that collected from dust storms, and study influencing factors and identifying adsorption type on the sand surface.

## 2. Experimental

### 2.1. Materials And Method

#### 2.1.1. Chemicals,

All chemicals were obtained from international companies (Fluka and BDH).and they were used without further purification (Glycolic acid, Sodium hydroxide, Potassium hydrogen phthalate, Ph.Ph. indicator, Activated carbon).

#### 2.1.2. Instruments

Electrical conductivity meter (Company HANA), pH-meter (Company DENVER), Electrical shaker, water path (Company nüve) and thermometer.

#### 2.1.3. Solutions Preparations

- 0.1M glycolic acid was prepared.
- Sodium hydroxide solution (0.1, 0.01 and 0.001 M)
- NaOH was titrated with potassium hydrogen phthalate in presence of PhPh. indicator to

get NaOH concentration before using to determine glycolic acid residues in adsorption solution.

#### 2.1.4. The adsorbent material

- Adsorbent material is a new clay that was collected from the sand storm that arrived in Mosul city using plastic utensils with 60 cm.
- The new clay contains several metal oxides considered the active side because being have negative charges facilitated the adsorption of positive ions on it.
- The metal oxides are present in different percentages in the clay as shown in the table (1).
- The surface area of clay was calculated which arrive in 3434cm<sup>2</sup>/g by using instruments (Plaine) in a technical institute of Mosul.
- A sieving process was performed for clay using a sieve 75 μm and the components of clay was calculated by using X-ray appearance type (PAN analytical 7602 EA, Almelo) in the Padush cement factory.
- Activated carbon was used as the adsorbent material in this study.

**TABLE 1.**The Components of a New Clay with Oxides %.

The oxide	Percentage
SO <sub>3</sub>	0.48 %
FeO <sub>3</sub>	1.89 %
MgO	3.47 %
Al <sub>2</sub> O <sub>3</sub>	5.91 %
SiO <sub>2</sub>	19.71 %
CaO	37.36 %

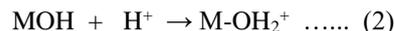
### 3. Results and iscusson

We used an adsorbent mixture of clay and activated carbon (clay contains some metal oxides as active sites), the liquid phase is water which contains acid ions of positive and negative charges in the adsorption system.

Adsorption process occurs in two steps,

- The adsorption begins by transferring positive ions or water to clay surface to be a positive surface

$MO^- + H_2O \rightarrow M-OH \dots\dots (1)$   $MO^-$  (Metal oxide surface)

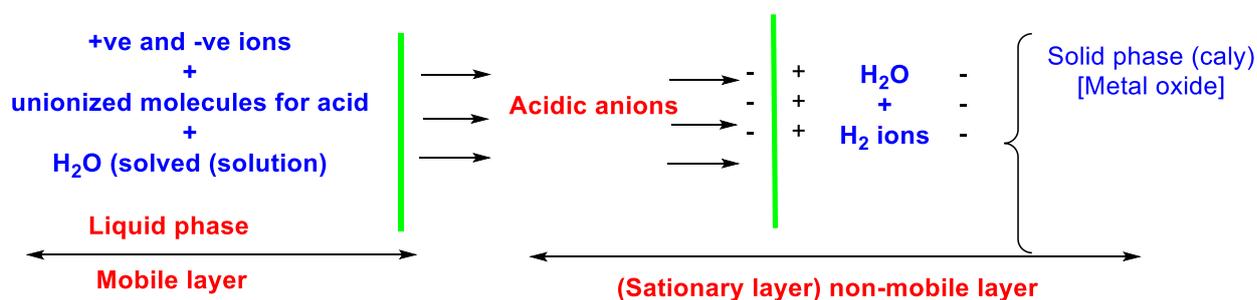


- Acid anions had been adsorbed on clay surface

Carboxylic acid anions ( $RL^-$ ) reacts with metallic oxides on the surface of the clay by chemical or physical adsorption.[20, 21]



The solvent water interacts and interferes with acid anions by forming hydrogen bonds, especially in concentrated solutions. The ions in the solution move towards the adsorbent surface with arrangement (Figure 2).[22-24]



**Figure 2: The stages of occurrence of absorption within the solution**

On the other hand, the adsorption of acid molecules and ions of activated carbon is through the presence of pores in it which are non-polar, which makes the adsorption process to a large extent dependent on the nature of the pore structures in it.[25]

The titration method is used in our study calculate GA residual concentration the adsorption process. The favour concentration range is 0.01-0.05 M (i.e. we didn't use spectrophotometric methods to get residual concentration because to higher absorbance value and it is outside the scale of absorbance in this technique).

Also, dilute GA leads to unacceptable adsorption efficiency (very low adsorption percentage). So, we use standard sodium hydroxide solution to determine the concentration of GA solution after adsorption by titration method.

#### 3.1. Factors Affecting on Adsorption Process

##### a) Adsorbent Weight

The relation between adsorbent weights and adsorption process is proportional due to increasing inactive sites on the surface, two adsorbents had been used (clay and activated carbon).The use of similar and different weights of them gives a high percentage of adsorption (Table

2). Using clay alone leads to 96% adsorption efficiency due to presence of metal oxides while using activated carbon alone gives 68% adsorption

efficiency. So, clay is better adsorbent than the mixture of clay and activated carbon with the best weight of 0.4g (Table 2).

**TABLE 2.** The Relation Between The Weight of Adsorbent Substance and Percentage Adsorption at (0.01) M of Glycolic Acid, Contact Time (30) min. , at a Natural Acidity Function and 25 C°.

Weight of Adsorbent Substance (g)	Adsorption efficiency (%)
0.4 g clay	96
0.4 g activated carbon	68
(0.2 g clay+ 0.2 g activated carbon)	76
<b>(0.4 g clay+ 0.4 g activated carbon)</b>	<b>76 (Favour weight %)</b>
(0.5 g clay+ 0.5 g activated carbon)	84
(0.8 g clay+ 0.8 g activated carbon)	76
(0.5 g clay+ 1 g activated carbon)	80
(1 g clay+ 0.5 g activated carbon)	84

### b) Glycolic Acid initial Concentration

Initial concentration of glycolic acid increased at a favourite adsorbent weight and a natural acidity cause increasing the efficiency adsorption because of increasing GA ions which have the ability to adsorption on the surface of a mixture adsorbent which contains enough active sites (Table 3).

**TABLE 3.** Effect of Initial Concentration on Percentage of Adsorption of Glycolic Acid, Use (0.4g Clay +0.4g activated Carbon), Contact time (30) min as a Natural Acidity Function, at 25 C°.

Conc. (M)	K <sub>ads.</sub>	Adsorp.%
0.01	5.25	76
0.02	9.00	90
0.03	9.71	91
0.04	10.1	91
0.05	10.4	91

### c) Contact Time Effect

**TABLE 4.** Effect of Contact Time on Adsorption Efficiency at 0.01M Glycolic Acid, (0.4+0.4) gm Charcoal and Clay, at a Natural Acidity Function and 25 C°.

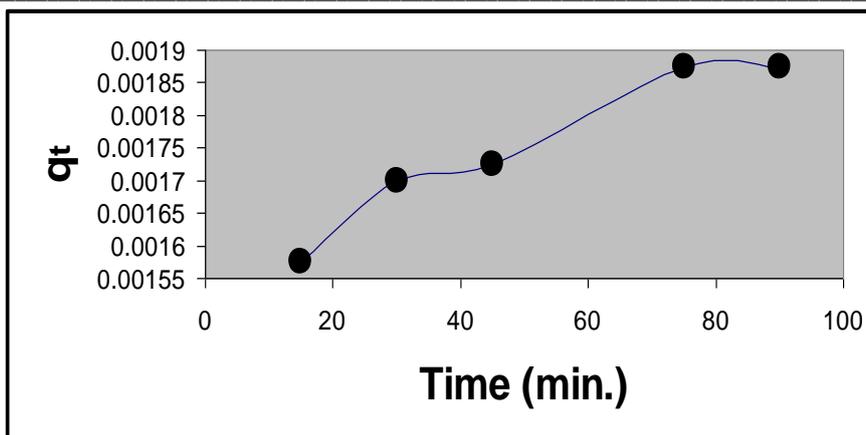
Time (min.)	C <sub>ads</sub> (mg/L)	q <sub>t</sub> (mg g <sup>-1</sup> )	Adsorp.%
15	0.0252	0.001575	84
30	0.0272	0.001700	90
45	0.0276	0.001725	92
75	0.030	0.001875	100
90	0.030	0.001875	100

The contact time means the presence of glycolic acid ions in solution contacting with adsorbent substance to get equilibrium state and facilitate the kinetic study of the adsorption process.

At 15 min as initial time, we got a high adsorption rate (84%) (Table 4). After that, the rate of adsorption begins to slow down at a contact time (30-90) min as the adsorption efficiency increase by only compared to the initial contact time (1-15) min.

Due to presence of availability of active sites on the surface, the ions transition easily from solution and adsorb quickly on the surface with increasing time. These active sites decreased with time and competition between ions to adsorb on the surface will start.

At 75 min we get 100 % of adsorption which means complete adoption glycolic acid ions. The capacity of adsorption (q<sub>t</sub>) increases with time (Figure 3) at equilibrium state.



**FIGURE 3.** Effect The Contact Time on The Adsorption Capacity of Glycolic Acid on The Adsorbent Substance.

#### d) Temperature Effect

There is a proportional between temperature and adsorption process due to increasing ions collisions in solution to facilitate its movement with removal of interactions and association and electrical attraction between ions and solvent as well as an increase of dissociation of GA.[22, 23, 26]

A high percentage of adsorption obtained at 298K° this indicate that the adsorption process is spontaneous and the efficiency of adsorption increase with increasing of temperature which arrived in (86%) at 318K°. Studying the adsorption process at different temperatures helps to determine the thermodynamic parameters which describe the nature of the adsorption system, the results listed in Table (5).

**TABLE 5.** Effect of Temperature on Adsorption

Percentage, at (0.01)M of Glycolic Acid, Use (0.4+0.4) gm Clay and Activated Carbon, Contact Time (30) min. and at a Natural Acidity Function.

Temp.(K°)	Adsorb. %
298	76
303	78
308	81
313	84
318	86

#### e) Acidity Function Effect

Acidity function changes nature of surface charges of the clay and the solution [23, 27] and it affects the adsorption efficiency. At different acidity functions, changing of charges affecting the adsorption process of ions and molecules from solution to surface by a mean decrease or increase in the efficiency of adsorption.

Adsorption process conducted at different acidity functions, pH = 2.5, 3.006, 7, and 11. At pH = 2.5 that has a large number of (H<sup>+</sup>) ions in solution with getting adsorption efficiency of 73% (Table 6).

At natural acidity function (pH=3.006) the efficiency increased to (82%) because the acidity function increased ( $\Delta$ pH=0.5), this means the (H<sup>+</sup>) ions in solution decreased continuously, when arrived to (pH<sub>11</sub>) the efficiency equal (89%), because at (pH<sub>2.5</sub>) there is a further (H<sup>+</sup>) ions in solution leads to decreasing the dissociation of glycolic acid and for these reasons the glycolic acid anions decreased in the solution because it converted to glycolic acid molecules by presence of (H<sup>+</sup>) ions in solution leads to decreasing the number of anions to adsorb on the surface of clay and for this reason decreasing the efficiency of adsorption with increasing of positive ions (H<sup>+</sup>) in solution, at the basic medium these is ions decrease in solution by conversion to water molecules, and the number of anions increase in solution. The presence of different metal oxides in clay which carry negative charges contribute to adsorption of (H<sup>+</sup>) ions and water molecules, converting the surface of the clay to carrying positive charges [23-24], helps to adsorption of anions of glycolic acid which carries negative charges, as well as the presence of pores in activated carbon which can be occupied by positive and negative ions which adsorbed but by a small percentage compared with clay (Table 2). From all results obtained we can conclude that using a natural acidity function is more favourite in the adsorption process than others. The results listed in Table (6), which showed that the acidity function

after adsorption increased because the (H<sup>+</sup>) ions contribute to the adsorption process at all acidity

functions, all these results are in good agreement with the literature[28, 29]

**TABLE 6.** Values of Percentage Adsorption of Different Acidity Functions, at (0.01)M of Glycolic Acid, Use (0.4+0.4) gm Clay and Activated Carbon, Contact Time (30) min., and at 25 C°.

pH (before adsorption)	pH (after adsorption)	Adsorp.%
2.500	4.10	73
3.006 ( natural acidity function)	6.33	76
7.000	9.02	87
11.000	12.51	89

### 3.2. Thermodynamic Study

The thermodynamic parameters ( $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ ) were calculated.

- $\Delta G$  has low negative values with an increase of temperature, which confirms that the adsorption process is spontaneous.
- $\Delta H$  has low positive value refers to endothermic process happened, ( $\Delta H$ ) value refers to that a physical adsorption predominant in this adsorption system

which depends on formation weak physical bonds between the adsorbate substance and adsorbent.

- The ( $\Delta S$ ) has a low positive value indicate that the ions in solution are more systematic than ions on the surface because of using a mixture from the adsorbent substance (clay+ activated carbon) which have different reactivity toward the adsorbate acid (Table 7).[30]

**TABLE 7.** Thermodynamic Functions for Adsorption Process, at (0.01) M of Glycolic Acid, Use (0.4+0.4) g Clay and Activated Carbon, Contact Time (30) min., and at a Natural Acidity Function.

Temp. (K°)	$\Delta G$ (KJ/mole)	$\Delta H$ (KJ/mole)	$\Delta S$ (KJ/mole)
298	-2.854		+ 0.081
303	-3.284		+ 0.081
308	-3.766	+ 21.498	+ 0.082
313	-4.314		+ 0.082
318	-4.383		+ 0.081

### 3.3. Kinetic Study

Kinetic adsorption is a complex process different than kinetic ordinary chemical reactions [31]because the adsorption process passes through several steps with different activation energies. Several kinetic models are used to study the adsorption process such as pseudo-first and second-order as well as the Elovich kinetic model, which depends on the capacity of adsorption at equilibrium state and at times (t) the equation for a pseudo-first-order model written as follows [32].

$$\ln(q_e - q_t) - \ln q_e = K_1 t$$

The equation for the pseudo-second-order model is.

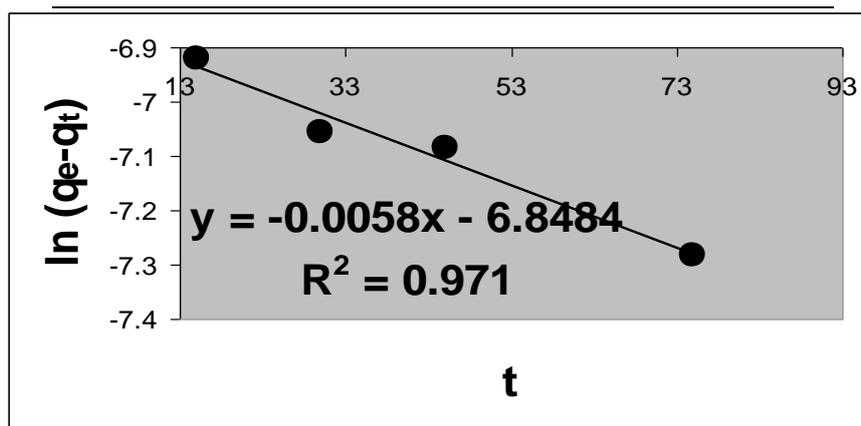
$$t / q_t = 1 / K_2 q_e^2 + 1 / q_e \cdot t$$

Where  $K_1$ ,  $K_2$  rate constant, t = time.

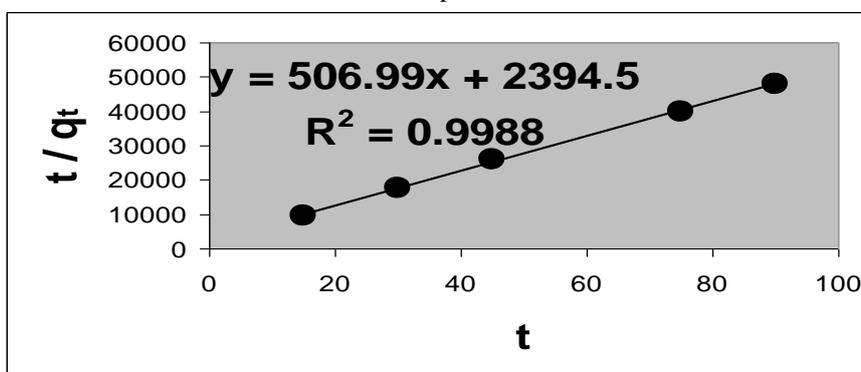
When applying the results of adsorption on each model gives a linear relationship with a high correlation coefficient, this indicates that these results are in good agreement with this model. The applying pseudo-first-order model with the results gave a theoretical adsorption capacity value lower than on the experimental adsorption capacity value ( $q_e$ ) with a high correlation coefficient ( $R^2= 0.971$ ), Fig. (3) explains the application of pseudo-first-order model on experimental results, while the pseudo-second-order model gave a theoretical adsorption capacity value ( $q_e$ ) close to the experimental adsorption capacity value ( $q_e$ ) with a high correlation coefficient, see Fig.(4), the results listed in Table (8).

**TABLE 8.** The Values of Rate Constant, Experimental and Theoretical ( $q_e$ ) for Purdue First and Second-Order Models, at (0.01) M of Glycolic Acid, Use (0.4+0.4) gm Clay and Activated Carbon, Contact Time (30) min., at a Natural Acidity Function and 25 C°.

Order	Experimental ( $q_e$ ) mg. g <sup>-1</sup>	Theoretical ( $q_e$ ) mg. g <sup>-1</sup>	K	R <sup>2</sup>
Pseudo first order	0.00187	0.00106	0.0058 (min <sup>-1</sup> )	0.971
pseudo second order	0.00187	0.00197	107.6 (L. mol <sup>-1</sup> . min <sup>-1</sup> )	0.9988



**FIGURE 3.** The Pseudo First Order Kinetic Model for The Adsorption of Glycolic Acid on The Adsorbent Substance at The Optimum Conditions.



**FIGURE 4.** The Pseudo-Second Order Kinetic Model for The Adsorption of Glycolic Acid on Adsorbent Substance, at Optimum Conditions.

### 1.1. Elovich Kinetic Model

The adsorption kinetics equation for the Elovich is suitable for heterogeneous systems [29] and that the adsorption process is limited in rate in the adsorption step [33], the value of the initial rate of adsorption ( $\alpha$ ), and the adsorption constant ( $\beta$ ) are calculated from the following equation.

$$q_t = 1 / \beta * \ln(\alpha\beta) + 1 / \beta * \ln(t)$$

That both ( $\alpha$ ) and ( $\beta$ ) changes as a function of the initial concentrations of the absorbing substance, this equation is called (mass

transfer equation) in addition to the change ( $\alpha$ ) and ( $\beta$ ) as a function of the temperature of the solution, Fig. (5) show the relationship between ( $q_t$ ) versus  $\ln(t)$ , ( $t$ ) represents the time.

### 1.2. Intra Particle Diffusion Model

The adsorption process in a (liquid/solid) system includes intraparticle diffusion and mass action of physical adsorption. Therefore diffusion adsorption models are mainly

developed to describe the intraparticle diffusion process.

The initial rate of intraparticle diffusion can be calculated according to the following equation:-

$$q_t = K_i t^{1/2} + C$$

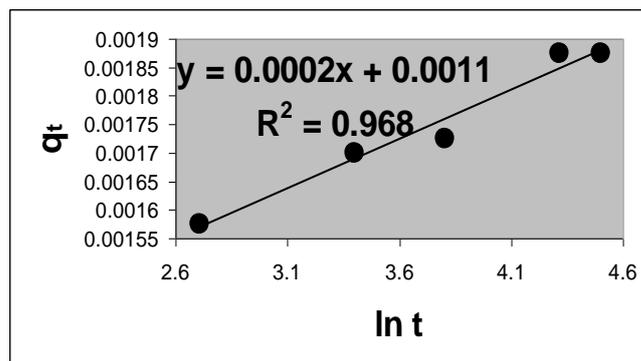
where  $K_i$  = rate constant of intraparticle diffusion ( $\text{mg/g} \cdot \text{min}^{1/2}$ ),  $C$  = intercept.

The rate of adsorption is controlled by several factors [34-36]. This model is used to analyze the practical results, the high values of ( $K_i$ ) explain that there is an enhancement in the rate of adsorption and that the adsorption process is a controlled diffusion process and that the specified step for the adsorption is intraparticle mass transfer resistance. Applying this model to the practical data for glycolic acid adsorption was obtained. The results listed in Table (9) show that the value of the initial adsorption rate is good and fast indicating the availability of many empty adsorption sites capable of adsorbing the adsorbed ions from the solution to the surface until reaching the equilibrium state, then the competition process begins between the ions for adsorption on the surface which leads to an increase in the departure of the ions adsorbed on the surface and this is evident from the high value of ( $\beta$ ). The total rate of adsorption is determined by the slowest step and then the intraparticle diffusion is the only step affecting the rate of the adsorption. The relationship of ( $q_t$ ) versus ( $t^{1/2}$ ) gives a straight line close to the point of origin with a small value of the intercept (0.0014) and with a high correlation coefficient as shown in Fig.(6) and obtaining a single straight line which indicates that the only influencing mechanism in the adsorption process is the intraparticle diffusion mechanism, and that the value of the intercept ( $C$ ) is an indication of the thickness of the outer layer of the solution boundary, and that the small value of ( $C$ ) indicates a lower effect of this layer, finally, all the results obtained are in agreement with the literature [37-39].

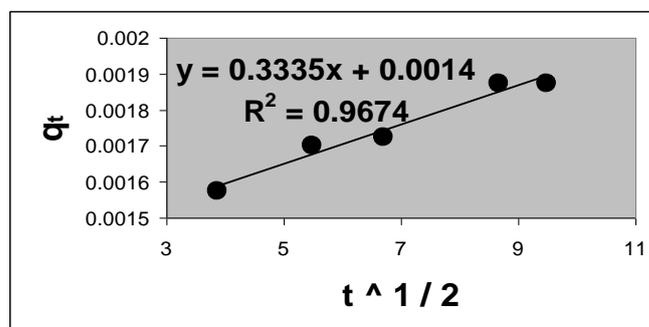
**TABLE 9.** The Values According to The Elovich Kinetic Model and The Intra Particle Diffusion Model at Optimum Condition.

Values of the Elovich Kinetic Model			
$R^2$	$\alpha$ ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$ )	$\beta$ ( $\text{g} \cdot \text{mg}^{-1}$ )	$1/\beta$
0.968	0.048	5000	0.0002
Values of the Intra Particle Diffusion Model			
$R^2$	$K_i$ ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{1/2}$ )	$C$ ( $\text{mg/g}$ )	

0.9674	0.3335	0.0014
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**FIGURE 5.** The Relationship Between  $q_t$  vs.  $\ln(t)$  According to The Adsorption Kinetics Model for The Elovich.



**FIGURE 6.** The Relationship Between  $q_t$  vs.  $t^{1/2}$  According to The Intra Particle Diffusion Model.

### 1.3. Study of Isotherms

Tow types of isotherms were applied on results of adsorption, the first is Langmuir isotherm which gives constants describe the shape of isotherm ( $b$  constant) and application success of this isotherm on the results of adsorption process shown through separation factor ( $R_L$ ) which refer to acceptance of this isotherm, this values favorite when ( $0 < R_L < 1$ ), the value (1) indicates the present a linearity relationship of adsorption process and refer to the agreement of isotherm, the zero value refer to a none reversible equilibrium, the value of ( $R_L$ ) un favorite at a value more than once, the results listed in Table (10)(11) [40-43].

$C_e / q_e = 1 / b * q_{\max} + C_e / q_{\max}$  (Langmuir equation).

$b$  represent Langmuir constant ( $\text{L/mg}$ ),  $q_{\max}$  = a maximum capacity of adsorption process ( $\text{mg} \cdot \text{g}^{-1}$ ).

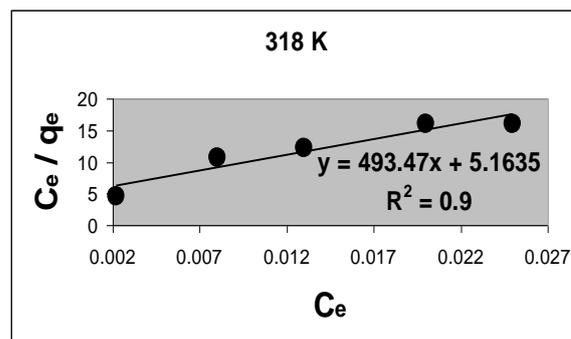
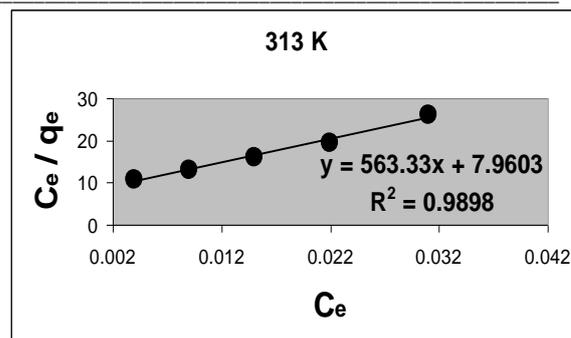
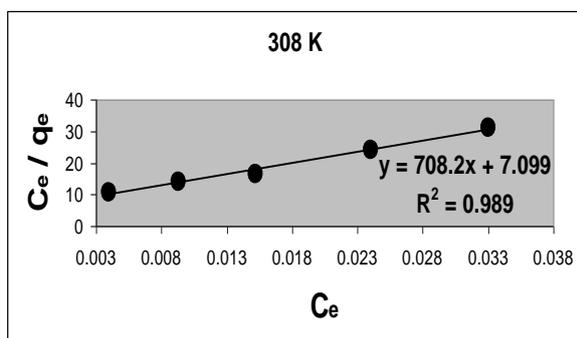
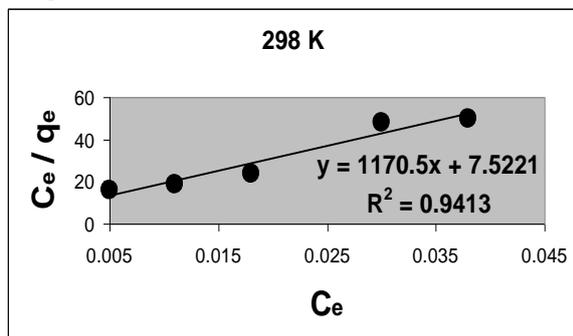
$R_L = 1 / (1 + B * C_i)$ .

**TABLE 10.** Values of Langmuir Constants at Different Temperature and Constant Concentration, at (0.01) M of Glycolic Acid, Use (0.4+0.4) gm

Clay and Activated Carbon, Contact Time (30) min. and at a Natural Acidity Function.

Temp.(K°)	q <sub>max</sub> (mg.g <sup>-1</sup> )	b (L / mg)	K <sub>L</sub> (L / mg)	R <sup>2</sup>
298	0.00085	156	0.1326	0.9413
303	0.00118	128	0.1411	0.9834
308	0.00141	100	0.1510	0.9890
313	0.00177	142	0.2513	0.9898
318	0.0020	96	0.1920	0.9000

The Langmuir constant (b) decreases with increasing temperature, which has a relation with adsorption energy this refers to a weak bonding for ions with the surface. The max capacity of adsorption increase with temperature, the (K<sub>L</sub>) value which produced from (q<sub>max</sub> \* b) increase with temperatures, the separation factor (R<sub>L</sub>) at different temperatures and constant concentration increase with temperature, but this value decrease with the increasing of concentration at a constant temperature, the results listed in Table (11) which gives a good (R<sup>2</sup>) value at all temperature this refers to the agreement of the results with Langmuir isotherm.



**FIGURE 7.** Langmuir Isotherms Linear Adsorption for Glycolic Acid at Different Temperatures and The Optimum Conditions.

**TABLE 11.** The Values of (R<sub>L</sub>) at Different Concentrations and Temperatures, Use (0.4+0.4) gm Clay and Activated Carbon, Contact Time (30) min. , and at a Natural Acidity Function.

Conc.(M)	R <sub>L</sub>				
	Temp.(K°)				
	298	303	308	313	318
0.01	0.390	0.438	0.500	0.413	0.510
0.02	0.242	0.280	0.333	0.260	0.342
0.03	0.176	0.206	0.250	0.190	0.257
0.04	0.138	0.163	0.200	0.149	0.206
0.05	0.113	0.135	0.166	0.123	0.172

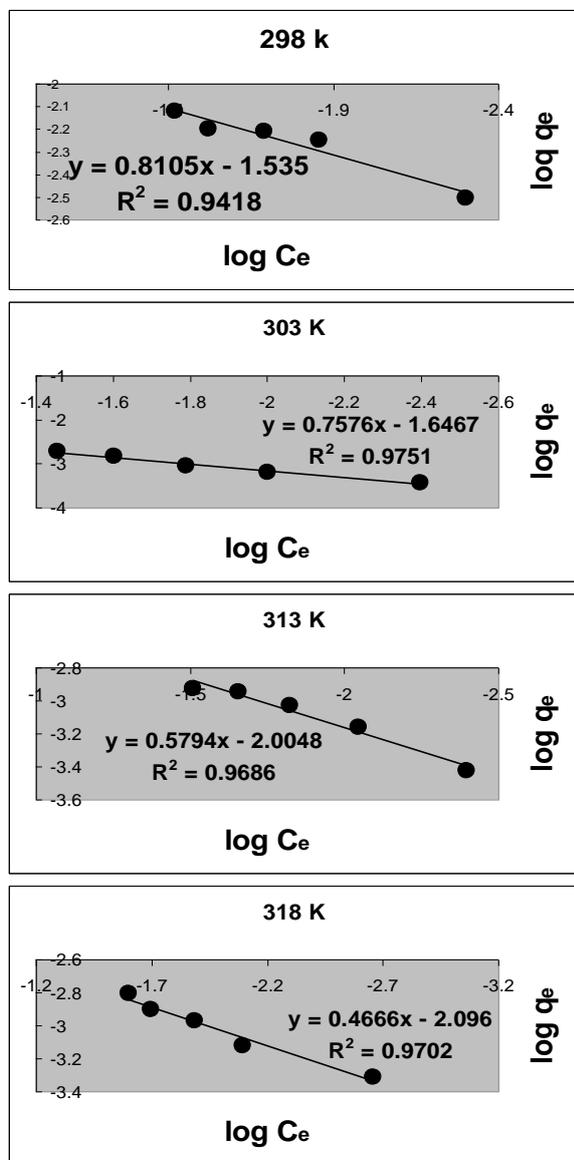
All (R<sub>L</sub>) values are less than one which is favored in the adsorption process. The second important isotherm is the Freundlich isotherm, this model is different from than Langmuir isotherm, which has two constant, (K<sub>F</sub>) which represent the relation with a capacity of adsorption and (n) constant represent the intensity of adsorption, this value favorite between (1-10) and not favorite at a value less than one.

$\log q_e = \log K_F + 1/n \log C$  (Freundlich equation).

K<sub>F</sub> represent the adsorption capacity (L/mg), (1/n) = the adsorption intensity.

Table (12) explains K<sub>F</sub> and (n) values at different temperatures, which (K<sub>F</sub>) have different values at

each temperature, the (n) values of adsorption process at different temperatures give value more than one and obtains high ( $R^2$ ) values at all temperatures.



**FIGURE 8.** Freundlich Isotherms Linear Adsorption for Glycolic Acid at Different Temperature and The Optimum Conditions.

**TABLE 12.** Values of Freundlich Constant at Different Temperatures, Use (0.01) M of Glycolic Acid, (0.4+0.4) gm Clay and Activated Carbon, Contact Time (30) min. , and at a Natural Acidity Function.

Freundlich Isotherm Constant			
Temp. (K°)	$K_F$	n	$R^2$
298	34	1.23	0.9418
303	44	1.31	0.9751

308	53	1.41	0.9756
313	101	1.72	0.9686
318	124	2.14	0.9702

#### 1.4. Study Potential of Probability of Sticking on The Surface ( $S^*$ )

Another support confirms that the physical adsorption is predominant for adsorption of glycolic acid, from the experimental data of adsorption the value of ( $S^*$ ) and apparent activation energy (AAE) was estimated. This study is depending on the coverage of ions or molecules ( $\Theta$ ) on the surface of adsorbent substances at different temperatures and constant concentrations using a modified Arrhenius equation[44].

$$\ln(1-\Theta) = \ln S^* - E_a / RT$$

$E_a$  = apparent activation energy (AAE)

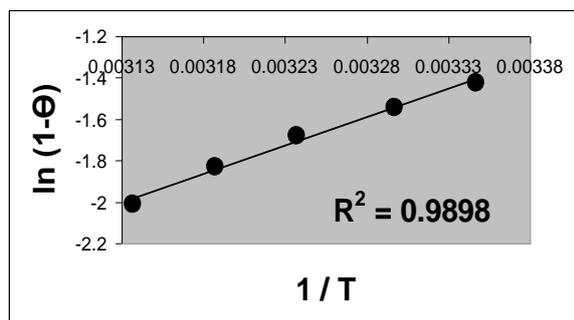
The probability of stickiness ( $S^*$ ) indicates the measurement of the potential of an adsorbate substance to stay on the surface of an adsorbent substance for indefinite.

The value of ( $S^*$ ) is estimated from plotting the values of  $\ln(1-\Theta)$  views ( $1/T$ ) which gives a linear relationship with, intercept ( $\ln S^*$ ), the slope of a linear plot ( $E_a/R$ ) gives a value of AAE. The value of ( $S^*$ ) for glycolic acid on the surface of a mixture adsorbent substance is(0.135), the results indicate that the probability of sticking for glycolic acid ions to the adsorbent substance surface is very high because the ( $S^*$ ) value is ( $S^* \ll 1$ ), this value indicates the occurrence of physical adsorption. While the value of AAE is equal to(-22.752) j/mole, the negative value of AAE indicates that the adsorption of glycolic acid ions favors a lower solution temperature to removal by a mixture adsorbent. The low value of AAE suggests that the adsorption of glycolic acid ions is a diffusion-controlled process, Fig. (9) Explain the relationship between  $\ln(1-\Theta)$  views.  $1/T$ , All results of this study are in good agreement with the literature [12][13][21].

**TABLE 13.** The Values of  $\ln(1-\Theta)$  ves.  $1/T$  at Different Temperatures, Use (0.01) M of Glycolic Acid, (0.4+0.4) gm Clay and Activated Carbon Contact Time (30) min. , and at a Natural Acidity Function.

T	1/T	$\ln(1-\Theta)$
298	0.00335	-1.426
303	0.00330	-1.544
308	0.00324	-1.678

313	0.00319	- 1.832
318	0.00314	-2.009



**FIGURE 9.** The Relation Between  $\ln(1-\theta)$  vs.  $1/T$  at Different Temperatures and Optimum Conditions.

### 1.5. Study The Mechanism of Adsorption by Changing Acidity Function and Electrical Parameters.

The adsorption system in this study consists of a solution of glycolic acid, which is ionized to give  $(H^+)$  ions and glycolic acid anion as well as a mixture of clay and activated carbon as an adsorbent substance. The presence of  $(H^+)$  ions in the solution gives a value of the acidity function at a certain concentration and increases the electrical conductivity in a solution. The positive and negative ions of glycolic acid give value for the potential difference in solution, the presence of an adsorbent substance in this solution which has polarization sites carrying an electrical charge (clay surface) violating the charges of ions in the solution, these ions help to move from the solution to these sites at the surface of clay by adsorption process in several steps, whether positive or negative ions there will be clear changes in the value of the acidity function and electrical conductivity as well as voltage difference of this solution after the transition of the ions to surface and adsorb on it. These changes can be useful in describing the adsorption mechanism, for example

**TABLE 14.** The Physical Properties of Glycolic Acid Solution (at Different Values Concentrations) Before and After Adsorption, Use (0.4+0.4) gm Clay and Activated Carbon, Contact Time (30) min. , at a Natural Acidity Function, and at 25°C.

Conc. (M)	pH*	pH**	Cond* (ohm <sup>-1</sup> )	Cond.** (ohm <sup>-1</sup> )	MV*	MV**	Adsorp. %
0.01	3.00	6.20	0.3	0.6	222	33	76.0
0.02	2.78	6.01	0.4	1.1	234	45	90.0
0.03	2.70	5.63	0.5	1.4	242	69	90.6
0.04	2.61	5.25	0.7	1.7	245	89	91.0
0.05	2.59	4.61	0.7	1.9	248	128	91.0

The symbol (\*) means before adsorption, (\*\*) means after adsorption.

when reviewing the results in Table (14) we note that the value of the acidity function after adsorption has increased at all concentrations used. This increase in the value of acidity function indicates that several hydrogen ions have been adsorbed on the clay surface mainly. It is the first step in the adsorption process causing an increase in the acidity function, at the same time there was an increase in the electrical conductivity because of the variability of  $(H^+)$  ions in solution and this indicates that the number of negative ions in the solution was reduced due to its adsorption on the surface of the clay after converting it at the first step of adsorption from a negatively polarized surface to a positively polarized surface that helped adsorb the glycolic acid anions as a second step in the adsorption process. This is causing dilution of glycolic acid anions in solution and led to greater freedom of movement of ions in solution due to the removal of the ionic interaction in the solution after adsorption and the occurrence of the dilution process on other hand, this led to an increase in the ionization of the glycolic acid molecules and all this led to an increase in the number  $(H^+)$  ions present in solution and more freedom of movement, which led to an increase in conductivity and confirms for negative ions adsorption. The potential difference is affected by the number of charges in solution, the adsorption process is including of transition of positive and negative ions from solution as a liquid phase to clay surface as a solid phase in this case the number of charges in solution decrease after adsorption this cause different of several charges between solution and surface this results in a voltage difference. This mechanism of adsorption on how the ions are arranged from the solution to the solid surface is described in the introduction to this paper, the results listed in Table (14).

### 3.4. Study Effect of Temperature on Acidity Function, Electrical Conductivity and Potential Difference Before and After Adsorption

This study was conducted at a constant concentration (0.01)M and an ideal weight of the mixture of adsorbent substances and different temperatures. In general, the temperature increase has positive aspects of the adsorption process, especially in removing ionic and molecular interactions, which facilitate the movement of ions and increase the ionization of the acid. The results in Table (15) show that there is a small decrease in the values of the acidity function before adsorption with increasing temperature. This indicates a slight increase in the number of hydrogen ions in the solution. After the adsorption process, the values of the acidity function at all temperatures have increased, and this confirms a decrease in the number of hydrogen ions in the solution as a result of their participation with the solvent molecules in the adsorption process. The difference in the values of acidity function before and after adsorption decreases ( $\Delta\text{pH}$ ) with an increase in temperature, this indicates that the number of hydrogen ions remains in the solution after the adsorption process leading to an increase in the specific electrical

conductivity of the acidic solution, and this is clear from the electrical conductivity values in Table (15) compared with this values before adsorption and this also happened because the adsorption process leads to a dilution of negative ions of the acid in solution and turn led to the removal of ionic molecular associations, which facilitates the movement of ions and conversion of bound ions to free, noting that the adsorption of water molecules as solvent leads to an increase the concentration of the remaining hydrogen ions with an increase in the dissociation of the remaining acid molecules. Regarding the voltage difference values, these values have decreased after adsorption, and this confirms the adsorption of ions with their charges to the surface or in pores of activated carbon. These values generally increase before adsorption by small values with an increase in the temperature accordingly. The adsorption efficiency increases slightly with an increase in temperature. It seems clear from this study that the effect of temperature in the glycolic acid adsorption system is little compared to the effect of increasing the concentration of acidic solution whose effect is clear on all the studied values and the temperature effect is limited because the adsorption process is spontaneous.

**TABLE 15.** The Physical Properties of Glycolic Acid Solution (at Different Temperatures) Before and After Adsorption, Use (0.01) M of Glycolic Acid, (0.4+0.4) gm Clay and Activated Carbon, Contact time (30) min. , at a Natural Acidity Function, and at 25°C.

Temp.(K°)	Cond.* (ohm <sup>-1</sup> )	Cond.** (ohm <sup>-1</sup> )	pH*	pH**	$\Delta$ pH	MV*	MV**	Adsorp. %
298	0.3	0.6	3.006	6.335	3.329	210	33	76
303	0.3	0.8	2.831	5.910	3.079	214	112	78
308	0.5	0.8	2.752	5.381	2.629	216	115	81
313	0.5	0.9	2.660	4.709	2.049	219	121	84
318	0.5	1.0	2.592	4.252	1.660	220	126	86

The symbol (\*) means before adsorption, (\*\*) means after adsorption.

### 3.5. Theoretical study

We adopt the density function theory (DFT) method of becks three parameters exchange and gradient corrected correlation function of Lee Yang and Par (B<sub>3</sub>LYP) for optimization of the reactants, transition state (TS). All computational studies were carried out using the density functional theory (DFT) methods implemented in the Gaussian 09 suit of the program[45-48]. The molecular properties of the compound have been computed by DFT using a standard 6-311G basis set.

The chemical reaction descriptor calculated using DFT is Homo, Lumo energy, chemical hardness ( $\eta$ ), electronic chemical potential ( $\mu$ ), and electrophilicity (W).

The chemical hardness measures the resistance to change in the electron distribution or charge transfer and it is associated with the stability and reactivity of a chemical system.

Based on the frontier molecular orbitals, chemical hardness corresponds to the gap between the HOMO and LUMO, chemical hardness is approximated using equation (1).

$$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}}) / 2 \dots\dots\dots (1)$$

where the LUMO and HOMO energies electronic chemical potential to potential is defined as the negative of electronegativity of a molecule and calculated using equation (2)

$$\mu = (E_{\text{LUMO}} + E_{\text{HOMO}}) / 2 \dots\dots\dots (2)$$

Global electrophilicity index ( $w$ ) is calculated using the electronic chemical potential is shown in equation (3)

$$w = \mu^2 / 2\eta \dots\dots\dots(3)$$

table (16): extracted the values of Homo, Lumo, hardness, chemical electronic potential, global electrophilicity index.

Comp. no.	Homo	Lumo	$\eta$	$\mu$	W
I	-19.11637	0.5009	9.808	19.0662	18.966
II	-19.00811	0.07836	9.541	18.929	18.777

A theoretical study was conducted for glycolic acid and extracted the values of Homo, Lumo, hardness, chemical electronic potential, global electrophilicity index as the table (16).

### 3.6. Infrared spectrum

When identifying the complex produced after adsorption using infrared spectroscopy and comparing it with glycolic acid (the adsorbent substance), we notice the disappearance of the carboxylic acid OH stretch band, which was appearing in the region ( $2558 \text{ cm}^{-1}$ ) compared to the product collected after adsorption, which did not show this band. On the loss of the acid proton and the formation of the terminal complex (III) as shown in Figure 11.

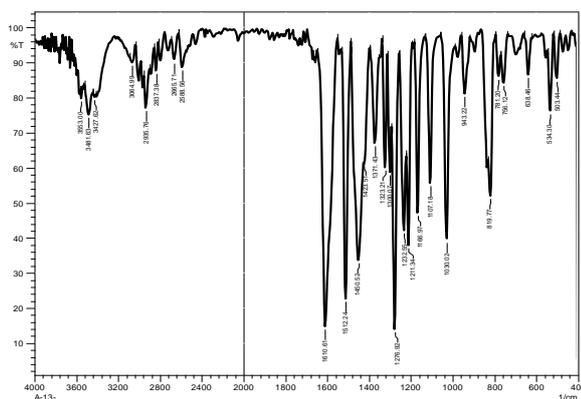


Fig (10): IR spectra for glycolic acid before adsorption

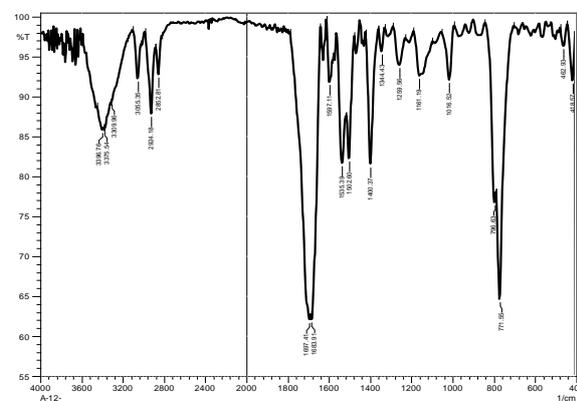
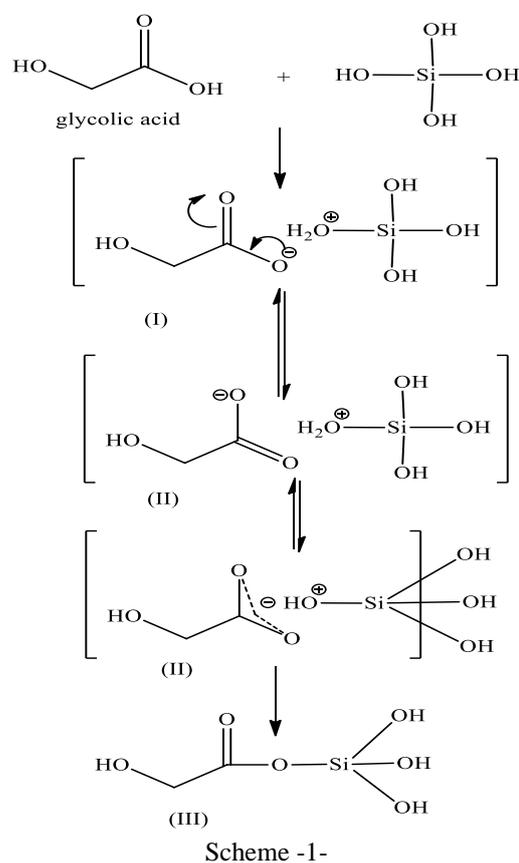


Fig (11): IR spectra for glycolic acid after adsorption



#### 4. CONCLUSION

It was noted from the result that the values of the energy functions of glycolic acid found that the value of HOMO energy was calculated by the DFT method is equal to (-19.11637) and the value of LOMO is equal to (0.05009), then the HOMO and LOMO energy value of glycolic acid begins to change to become (-19.00811) (0.07836) respectively, this change in energy was accompanied by a decreased capacity of the compounds in electronic payment capacity of the compounds in the resonant state (loss of proton) and have charged with the negative shipment. (the increase in the value of the HOMO and the decrease in the value of the LUMO) it means the difference in energy between the two partial levels decreases, and thus decreases in the energy required for electronic transmission (excitation energy), and this, in turn, increases the ability of the compound to give electrons.

As the basic oxides work to pull the proton and be more stable for the intermediate compound. The three variables, chemical hardness ( $\eta$ ), chemical electronic potential, global, and electrophilicity index ( $w$ ) are decreased schemes (I, II, III) consecutive. This confirms that glycolic acid in the resonant state is a nucleophilic factor.

#### 5. References

- R.C. Tung, W.F. Bergfeld, A.T. Vidimos, B.K. Remzi,  $\alpha$ -Hydroxy acid-based cosmetic procedures, *American journal of clinical dermatology* 1(2) (2000) 81-88.
- I. Eroglu, These are The Worst Skincare Ingredients For People with Rosacea.
- J. Sharad, Glycolic acid peel therapy—a current review, *Clinical, cosmetic and investigational dermatology* 6 (2013) 281.
- A. Panova, L.J. Mersinger, Q. Liu, T. Foo, D.C. Roe, W.L. Spillan, A.E. Sigmund, A. Ben-Bassat, L.W. Wagner, D.P. O'Keefe, Chemoenzymatic synthesis of glycolic acid, *Advanced Synthesis & Catalysis* 349(8-9) (2007) 1462-1474.
- N. Wang, X.S. Wu, C. Li, M.F. Feng, Synthesis, characterization, biodegradation, and drug delivery application of biodegradable lactic/glycolic acid polymers: I. Synthesis and characterization, *Journal of Biomaterials Science, Polymer Edition* 11(3) (2000) 301-318.
- S.J. Yoon, S.H. Kim, H.J. Ha, Y.K. Ko, J.W. So, M.S. Kim, Y.I. Yang, G. Khang, J.M. Rhee, H.B. Lee, Reduction of inflammatory reaction of poly (D, L-lactic-co-glycolic acid) using demineralized bone particles, *Tissue Engineering Part A* 14(4) (2008) 539-547.
- M.J.R. Virlan, D. Miricescu, A. Totan, M. Greabu, C. Tanase, C.M. Sabliov, C. Caruntu, B. Calenic, Current uses of poly (lactic-co-glycolic acid) in the dental field: a comprehensive review, *Journal of Chemistry* 2015 (2015).
- X. Deng, M. Qasim, A. Ali, Engineering and polymeric composition of drug-eluting suture: A review, *Journal of Biomedical Materials Research Part A* (2021).
- K. GLYKOLOVA, K. HYDROXYOCTOVA, E.G. NUMBER, Glycolic Acid, (2020).
- D. Datta, S. Kumar, Modeling and optimization of recovery process of glycolic acid using reactive extraction, *International journal of chemical engineering and applications* 3(2) (2012) 141.
- C.R. Noll Jr, R. Burris, Nature and Distribution of Glycolic Acid Oxidase in Plants, *Plant physiology* 29(3) (1954) 261.
- S. Tschirner, E. Weingart, L. Teevs, U. Prüße, Oxidation of Monoethylene Glycol to Glycolic Acid with Gold-Based Catalyst and Glycolic Acid Isolation by Electrodialysis, *Reactions* 3(1) (2022) 47-58.
- L. Reyes, C. Nikitine, L. Vilcoq, P. Fongarland, Green is the new Black—A review of technologies for carboxylic acids recovery from black liquor, *Green Chemistry* (2020).
- J. Zhang, C. Zhu, H. Sun, Q. Peng, Separation of glycolic acid from glycolonitrile hydrolysate using adsorption technology, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 520 (2017) 391-398.
- A. Soni, A. Keshav, V. Verma, S. Suresh, Removal of glycolic acid from aqueous solution using bagasse flyash, (2012).
- G. Wei, X. Yang, W. Zhou, J. Lin, D. Wei, Adsorptive bioconversion of ethylene glycol to glycolic acid by *Gluconobacter oxydans* DSM 2003, *Biochemical engineering journal* 47(1-3) (2009) 127-131.
- M. Müller, J. Vörös, G. Csucs, E. Walter, G. Danuser, H. Merkle, N. Spencer, M. Textor, Surface modification of PLGA microspheres,

- Journal of Biomedical Materials Research Part A: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials 66(1) (2003) 55-61.
18. R.P.F. Lanao, A.M. Jonker, J.G. Wolke, J.A. Jansen, J.C. van Hest, S.C. Leeuwenburgh, Physicochemical properties and applications of poly (lactic-co-glycolic acid) for use in bone regeneration, *Tissue Engineering Part B: Reviews* 19(4) (2013) 380-390.
  19. K.J. Jem, B. Tan, The development and challenges of poly (lactic acid) and poly (glycolic acid), *Advanced Industrial and Engineering Polymer Research* 3(2) (2020) 60-70.
  20. M. Migahed, A.N. Abdu, H. Elfeky, M. EL-Rabiei, Electrochemical behavior of Cu-10Al-10Zn alloy in seawater in the presence of cationic surfactants benzotriazole derivatives, *Egyptian Journal of Chemistry* 63(2) (2020) 703-719.
  21. M.E.S. Hassan, J. Bai, D.-Q. Dou, Biopolymers; definition, classification and applications, *Egyptian Journal of Chemistry* 62(9) (2019) 1725-1737.
  22. K.I. Al-Niemi, Application of kinetic model of adsorption for Elovich and the intraparticles diffusion, the Sticking probability ( $S^*$ ), Tempkin isotherm on some different aromatic and aliphatic acids, *JOURNAL OF EDUCATION AND SCIENCE* 28(1) (2019) 246-272.
  23. A.A. Alghamdi, A.-B. Al-Odayni, W.S. Saeed, A. Al-Kahtani, F.A. Alharthi, T. Aouak, Efficient adsorption of lead (II) from aqueous phase solutions using polypyrrole-based activated carbon, *Materials* 12(12) (2019) 2020.
  24. S. Abd Alhalim, M. Mabrouk, S. Kanawy Ibrahim, N. H Hamdy, A. Ramadan, Synthesis and Physicomechanical Studies of Nano ZnO Coated Textile fabrics, *Egyptian Journal of Chemistry* 63(2) (2020) 625-631.
  25. G.F. El Fawal, Polymer nanofibers electrospinning: A review, *Egyptian Journal of Chemistry* 63(4) (2020) 1279-1303.
  26. X. Jiang, W. Zhang, S. Zhao, S. Zhou, Y. Shi, Z. Xin, Effect of benzoic acid surface modified alumina nanoparticles on the mechanical properties and crystallization behavior of isotactic polypropylene nanocomposites, *RSC advances* 8(37) (2018) 20790-20800.
  27. L. Khenniche, F. Aissani, Characterization and utilization of activated carbons prepared from coffee residue for adsorptive removal of salicylic acid and phenol: Kinetic and isotherm study, *Desalination and Water Treatment* 11(1-3) (2009) 192-203.
  28. K.I. Alniemi, Calculation Values of potential Stickiness ( $S^*$ ) and Apparent Activation Energy (AAE) from Adsorption of Some Aromatic Carboxylic Acids on the Surface of a New Adsorbent Substance, *JOURNAL OF EDUCATION AND SCIENCE* 29(4) (2020) 76-89.
  29. K.I. AL-NIEMI, S.A. AL-DBOONE, T. ABD-ALGANE, Effect Of Using MnO<sub>2</sub> As Adsorbant On The Ionization Constant And Electrical Conductivity For Some Aliphatic Carboxylic Acid Containing By Hydroxyl Group On A-Position, *Journal of University of Anbar for Pure science* 5(3) (2011).
  30. S.M. Al-Mahmoud, Kinetic and Thermodynamic Studies for the Efficient Removal of Methylene Blue Using Hordeum Murinum as a New Biosorbent, *Egyptian Journal of Chemistry* 63(9) (2020) 8-9.
  31. K.I. Al-Neimi, A.G. Ahmed, Isothermic Adsorption and Applications of Kinetics Models, Thermodynamics Functions, Probability Sticking for Benzoic Acid and Some Substituted by Using Anew Adsorbent Substance, *JOURNAL OF EDUCATION AND SCIENCE* 28(2) (2019) 23-39.
  32. A. Masoud, M. Saeed, M. Taha, M. El-Maadawy, Uranium adsorption from Bahariya Oasis leach liquor via TOPO impregnated bentonite material; Isothermal, kinetic and thermodynamic studies, *Egyptian Journal of Chemistry* 63(2) (2020) 721-741.
  33. G. Sharaf, E. Abdel-Galil, Y. El-eryan, Modeling studies for adsorption of phenol and co-pollutants onto granular activated carbon prepared from olive oil industrial waste, *Advances in environmental technology* 4(1) (2018) 23-40.
  34. S.-Y. Yoon, C.-G. Lee, J.-A. Park, J.-H. Kim, S.-B. Kim, S.-H. Lee, J.-W. Choi, Kinetic, equilibrium and thermodynamic studies for phosphate adsorption to magnetic iron oxide nanoparticles, *Chemical engineering journal* 236 (2014) 341-347.
  35. M. Pan, X. Lin, J. Xie, X. Huang, Kinetic, equilibrium and thermodynamic studies for

- phosphate adsorption on aluminum hydroxide modified palygorskite nano-composites, *RSC advances* 7(8) (2017) 4492-4500.
36. S. Yakout, E. Elsherif, Carbon—science and technology. Applied Science Innovations Pvt. Ltd, India 1 (2010) 144-153.
  37. Y.-S. Ho, G. McKay, Application of kinetic models to the sorption of copper (II) on to peat, *Adsorption Science & Technology* 20(8) (2002) 797-815.
  38. F.-C. Wu, R.-L. Tseng, R.-S. Juang, Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems, *Chemical Engineering Journal* 150(2-3) (2009) 366-373.
  39. Sdeek, G. T., Mauf, R. M., & Saleh, M. Y. (2021). Synthesis and Identification of some new Derivatives Oxazole, Thiazole and Imidazol from Acetyl Cysteine. *Egyptian Journal of Chemistry*, 64(12), 7565-7571.
  40. U.A. Edet, A.O. Ifelebuegu, Kinetics, isotherms, and thermodynamic modeling of the adsorption of phosphates from model wastewater using recycled brick waste, *Processes* 8(6) (2020) 665.
  41. G. Mahmoud, M. Abdel Khalek, E. Shoukry, M. Amin, A. Abdulghany, Removal of Phosphate Ions from Wastewater by Treated Hydrogel Based on Chitosan, *Egyptian Journal of Chemistry* 62(8) (2019) 1537-1549.
  42. Saeed, N. H. M., & Abbas, A. M. (2020). Kinetics and mechanism of tetrahydrofuran oxidation by chloraminet in acidic media. *Periodico Tche Quimica* 17:449-461.  
DOI: 10.52571/PTQ.v17.n35.2020.39.
  43. Ayoob, A., Sadeek, G., Saleh, M. (2022). Synthesis and Biologically Activity of Novel 2-Chloro -3-Formyl -1,5-Naphthyridine Chalcone Derivatives. *Journal of Chemical Health Risks*, 12(1), 73-79. doi: 10.22034/jchr.2022.688560
  44. M. Peleg, M.D. Normand, M.G. Corradini, The Arrhenius equation revisited, *Critical reviews in food science and nutrition* 52(9) (2012) 830-851.
  45. G. Mohamed, O. El-Shafey, N.A. Fathy, Preparation of carbonaceous hydrochar adsorbents from cellulose and lignin derived from rice straw, *Egyptian Journal of Chemistry* 60(5) (2017) 793-804.
  46. Karam, F. F., Saeed, N. H., Al Yasarri, A., Ahmed, L., & Saleh, H. (2020). Kinetic study for reduced the toxicity of textile dyes (reactive yellow 14 dye and reactive green dye) using UV-A Light/ZnO system. *Egyptian Journal of Chemistry*, 63(8), 2987-2998.
  47. S. Abd El Wanees, M. Alahmdi, M. Alsharif, Y. Atef, Mitigation of hydrogen evolution during zinc corrosion in aqueous acidic media using 5-Amino-4-imidazolecarboxamide, *Egyptian Journal of Chemistry* 62(5) (2019) 811-825.
  48. Ali, R. T., Al-Niemi, K. I., & Mohammedthalji, N. H. (2021). A practical and theoretical study of the mechanical kinetics of ascorbic acid adsorption on a new clay surface. *Egyptian Journal of Chemistry*, 64(8), 4569-4581.