Egypt. J. Chem. **Vol. 64**, No. 8. pp. 4569 - 4581 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

A practical and theoretical study of the mechanical kinetics of ascorbic acid adsorption on a new clay surface

Rana Tahseen Ali[1], Khaleel Ibrahim Al-Niemi[2], Noor Hazim Mohammed Thalji[2*]
[1]*Chemistry Department, College of Education for girls, University of Mosul, Mosul, Iraq*
[2]*Chemistry Department, College of Education for pure sciences, University of Mosul, Mosul, Iraq*

Abstract

Ascorbic acid is considered one of the weak phenolic acids, as practical experiments have shown that it can adhere to the adsorbent clay particles by forming electrostatic forces, hydrogen bonds, and the loss of positive protons if the adsorbent material contains electron density on the surface because it contains more than one hydroxyl alcohol and phenolic group. Phenolic hydroxyl groups act as weak acids that can lose a proton and convert to the phenoxide ion since ascorbic acid contains two contiguous phenolic hydroxyl groups. We note that the loss of hydrogen protonation gives a more stable product, which is 1,2 di-ketones. Therefore, the dissociation of ascorbic acid increases as the base medium increases. In this research we have studied the effect of adding sand (a natural substance) on the presence (activity) of ascorbic acid in the aqueous medium, adsorption technology was used in this study through which the most important factors affecting the adsorption process of ascorbic acid molecules were identified. The kinetic models were applied such as pseudo-first and second-order on the adsorption process, which is considered as a complex process that passes through several steps. In this study, the adsorption of ascorbic acid is in agreement with the pseudo-first and second-order models by obtaining a linear relationship with a high correlation coefficient as well as the experimental and theoretical capacity values of the adsorption process are equal. The Langmuir and Freundlich isotherms were used to describe the relationship between the adsorbent and adsorbate substance through the capacity of adsorption, the energy bonding, and favorite of adsorption, the results of adsorption are in agreement with Langmuir isotherm. The thermodynamic parameters (ΔG, ΔH, ΔS) for the adsorption process were calculated. To obtain more information about the adsorption process, this study confirms some conclusions, the modified Arrhenius equation was applied to the results of the adsorption process, by studying the potential sticking of ions on the surface of the clay. This study comprehensively highlights the nature of the adsorption of ascorbic acid ions on the surface of the clay .The theoretical side of the ascorbic acid adsorption process for the oxides present on the adsorbent surfaces was studied using the (DFT) theory, and it was found that the theoretical results corresponded with the practical results. Ascorbic acid is transformed by negative charges and double bonds to a more stable di-ketone compound. The adsorption mechanism has been proposed, which corresponds to the practical results reached, Finally, to prove the adsorption mechanism, the resulting compound was diagnosed using an infrared spectrum.

Keywords: Adsorption, Adsorption kinetic, Ascorbic acid, probability of sticking, The isotherms.

1. Introduction

The human body needs vitamin (C) (ascorbic acid) to create blood vessels, cartilage, and muscles, this compound presents naturally in fruits and vegetables. It is widely used as a medicine to fight infections as well as for other medicinal purposes. It is an organic compound used as a drug for scurvy disease. There are many analytical methods present in the literature that are used to estimate the percentage of ascorbic acid present in juices and fruits, because of the lack of studies that revolve around the adsorption of ascorbic acid from its aqueous solutions using sand as adsorbent, this research has been done. Ascorbic acid contains multiple hydroxyl groups as well as the carboxylic group in its composition that contributes to facilitating its adsorption on the surface of the clay as a polarizing adsorbent because it contains a group of metallic oxides, especially in its dilute aqueous solutions [1-2]. The adsorption process in solution means the transition of adsorbate substance (molecules and ions) from a liquid phase to a solid surface (clay) which consists of several metal oxides [3-4]. In this study, it was used a new clay collected from the sand storm which reached Mosul city containing metal oxides. There are some isotherms valuable in literature where these isotherms represent the relation between the adsorbate and adsorbent substance at equilibrium, each isotherm describes the

*Corresponding author e-mail: noorsaeed@uomosul.edu.iq
Received date 8 April 2021; revised date 4 May 2021; accepted date 9 May 2021
DOI: 10.21608/ejchem.2021.71632.3572

nature of this relation by applying the experimental results of the adsorption process on both models Langmuir and Freundlich isotherms [5-9]. This relation gives constants to describe the nature of the adsorption system. Calculating the capacity of adsorption at different times is useful to study the kinetics of the adsorption process by using the pseudo-first and second-order models[10-11]. Several factors are affecting on adsorption process such as contact time, temperature, solvent, acidity function, etc., all these factors were studied also. Several theoretical studies have given an accurate description of the dissociation of amino acids in the acidic medium, and their results were very accurate compared with the practical results [12] also the mechanism of reactions has been proposed based on the oxidation kinetics of some organic compounds [13-14]. Adsorption reactions often depend on the pigment present, which the clays remove [15]. The kinetic study of adsorption is carried out under optimal conditions in terms of the concentration of the adsorbent and adsorbent material with certain temperature degrees similar to conditions for kinetic reactions of oxidation [16-17].

2. Materials and Methods

2.1. –Chemicals All chemicals supplied from Fluka and BDH companies.

1- Ascorbic acid (M.Wt =176.1 gm / mole).
2- Sodium hydroxide.
3- Potassium hydrogen phthalate.
4- ph. ph as an indicator.

2.2. Preparation of solutions

Preparation of a stock solution of ascorbic acid (0.1) M and from this solution different concentrations were prepared.

Sodium hydroxide solutions prepared with (0.1), (0.01), (0.001) M and titrated with potassium hydrogen phthalate using ph. ph. as an indicator to determine the exact concentration of sodium hydroxide solution before using it to determine the residual concentration of ascorbic acid after the adsorption process.

3-The adsorbent substance (clay) was collected from the sand storm which reached Mosul city, the components of clay listed as following:-

TABLE 1. Percentage of metal oxides in the adsorbent material (clay).

Metal Oxide	Percentage
SiO_2	19.71 %
FeO_3	1.89 %
MgO	3.47 %
CaO	37.36 %
Al_2O_3	5.91 %
SO_3	0.48 %

A sieving process was performed for clay using a sieve (75) micrometer and the components of clay were calculated by using X-ray appearance type (PAN analytical 7602 EA, Almelo) in the Padush cement factory.

The surface area of clay was calculated by (3434) cm2/gm by using instruments (plaine) in a technical institute of Mosul.

2.3.Instruments

1-Electrical conductivity meter type HANA Instrument.
2 - pH-meter type DENVER Instrument.
3- A water path with an Electric vibrator was used type NUVE and using a thermometer to approximate temperature until arriving at equilibrium.

Study the Factors Affecting on Adsorption Process

1-Effect of Concentration of Adsorbate Substance:-

The ascorbic acid was prepared with different concentrations (0.005, 0.009, 0.01 , 0.013 , 0.015 , 0.02, 0.05, 0.09) M by using distilled water as solvent. Then, a constant amount of clay(0.1) g was added to all samples by using one batch method at 30C° for 30 min., the efficiency of adsorption was calculated as follows .

$$\% \text{ Adsorption} = \frac{C_i}{C_o} * 100$$

C_i= is the concentration of adsorbate substance at equilibrium(mg.L^{-1}).

C_o = the initial concentration (mg. L^{-1}).

2-Effect of the Weight of Adsorbent Substance

At an optimal concentration for adsorbate substance, different weights of clay (0.02, 0.03, 0.05, 0.08, 0.1, 0.5) gm were used as adsorbent substance at 30C° and natural acidity function of ascorbic acid.

3-Effect of Contact Time

To study the effect of contact time on the adsorption process the same samples of ascorbic acid solutions with volume (50) ml were used and leave a limit time between them. The models studied at different times (2, 5, 8, 12, 15, 20, 25, 30, 45, 60, 75, 90) minute were filtrated. After that, the remain concentration of ascorbic acid was calculated for all samples by titrating with sodium hydroxide solution. This process produced at a favorite weight of an adsorbent substance and concentration for adsorbate substance at (30C°) using natural acidity function.

4- Effect of Acidity Function

The adsorption process was completed at different acidity functions (natural and pH = 4, 7, 11) to study the effect of (pH) on the efficiency of adsorption.

5- Effect of Temperature

The effect of temperature was studied at optimum condition for the adsorption process to obtain results which were employed to determine the thermodynamic parameters (ΔG, ΔH, ΔS) and range of temperatures between (15-40) C°.

Theoretical Study

The theoretical study of ascorbic acid was carried out using (DFT-B$_3$LYP/6.31G (d) using the (Chem. Office 2015 Gaussian program). Calculation of the Mulliken charge (which represent the difference between the negative electron density in orbits and the amount of positive protons in the nucleus) were calculated for ascorbic acid, the results are given in table (2) and the mechanical proposed by theoretical study.

It was found that ascorbic acid before dissociation has three states, the first before dissociation and the second intermediate in which the complex formed contains positive and negative charges. Whereas, if the intermediate state is left in place, it will lead to no adsorption and return to the first state and in the third case, ascorbic acid will lose ions and convert to the di-ketone product. But theoretical studies, which are in agreement with the practical results, have proven that ascorbic acid, after losing the negative charges and double bonds, turns into a more stable diketone compound, according to what was concluded from the theoretical study, as in the following table(2).

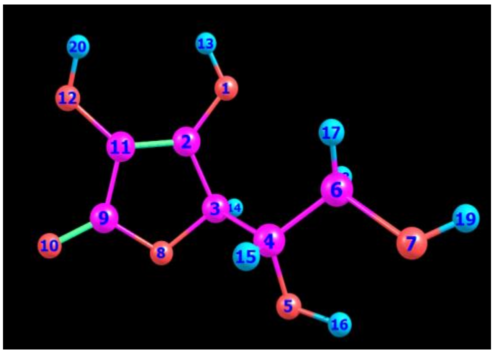


Table (2): The values of Mulliken charge of atoms of ascorbic acid calculated by DFT method

Numbers of atoms	Reactant	Activated Complex	Product
1	O -0.582192	O -0.774619	O -0.32489
2	C 0.275068	C 0.169716	C 0.290908
3	C 0.040843	C 0.010963	C 0.012928
4	C 0.140161	C 0.147265	C 0.177230
5	O -0.646827	O -0.667227	O -0.639616
6	C -0.036905	C -0.024595	C -0.035774
7	O -0.656049	O -0.670383	O -0.662234
8	O -0.483688	O -0.532179	O -0.483525
9	C 0.459373	C 0.309666	C 0.490902
10	O -0.458539	O -0.564006	O -0.335373
11	C 0.253488	C 0.164718	C 0.286453
12	O -0.584171	O -0.836925	O -0.265363
13	H 0.400340	H 0.115545	H 0.229651
14	H 0.217115	H 0.110448	H 0.157388
15	H 0.155979	H 0.380912	H 0.397996
16	H 0.396172	H 0.142464	H 0.143281
17	H 0.162461	H 0.123236	H 0.165196
18	H 0.153485	H 0.395001	H 0.394851
19	H 0.403419		
20	H 0.390469		

3. Results and Discussion

A good adsorption rate was obtained through practical study, and this percentage increased in the basic medium or by increasing the pH value in the medium. Basic as increasing the OH value in solution increases the dissociation of ascorbic acid according to the Le-Chatelier's base.

As a result of the importance of ascorbic acid in our life and its wide uses in drugs such as vitamins to resist infections [1], simple methods in laboratories were utilized to study the removal of this vitamin from solution by adsorption on the surface of the clay. The titration method with sodium hydroxide solution was considered as a simple one to determine the concentration of ascorbic acid which gives good results in a short time.

To study the removal of ascorbic acid from their solutions with a selection of the better conditions of removal it. Some factors were studied that affected on adsorption process as following:-

3.1. Effect of Initial Concentration.

One of the important factors affecting the adsorption process is the initial concentration of ascorbic acid, as the increasing concentration impacts the movement of ions in solution and prevents the transition of these ions toward the adsorbent material (clay surface). The increasing concentration leads to an increase in the interferences between ions by physical forces which causes a decrease in the percentage of adsorption. The initial concentration also affects the value of the equilibrium constant. Furthermore, the increase of concentration causes decreasing in the number of ions transition to the surface of clay leading to a decrease in adsorption percentage. Hence, the competition between ions starts to adsorb on the active sites on the surface of the clay, which leads to the coming back of some ions from the surface to the solution, the results were listed in the table (3).

TABLE 3. Effect of the initial concentration on percentage adsorption of ascorbic acid, use 0.1 gm clay, contact time is 30 min. , at a natural acidity function and 30 C$^{\circ}$.

Conc. (M)	$K_{ads.}$	Adsorp.%
0.005	24	96
0.009	21.5	95
0.010	15.6	94
0.013	7.1	87
0.015	3.1	76
0.02	2.1	68
0.04	0.9	49
0.05	0.6	38.4
0.09	0.6	38.2

3.2. Effect of Adsorbent Substance.

Using different weights of clay in the adsorption process was employed to obtain an ideal weight of clay which gives a high percentage of adsorption at optimum conditions.

The efficiency of adsorption in ascorbic acid increases with the increase of the amount of adsorbent substance, due to the presence of more active sites on clay which give a high percentage of adsorption.

TABLE 4. The relation between the weight of clay and percentage of adsorption, use (0.005) M ascorbic acid, contact time is 30 min. , at a natural acidity function and 30 C$^{\circ}$.

Weight of Clay (gm)	Adsorp.%
0.02	28
0.03	56
0.05	76
0.06	80
0.08	84
0.10	96
0.50	98

3.3. Effect of Contact Time.

The contact time means the time of contact between the adsorbate and adsorbent substance. It is important to study the nature of the adsorption system such as the ability of adsorbate substance to be adsorbed on adsorbent substance until reaching the equilibrium. The contact time for ascorbic acid with clay at a natural acidity function listed in table (5) described the concentration of ascorbic acid adsorbed on clay. Ascorbic acid concentration increases with increasing contact time, and the adsorption capacity leads to an increase in the efficiency of adsorption. At initial minutes of adsorption, the efficiency of adsorption was very high because a large number of ascorbic acid ions transferred from solution to the surface of clay until reach equilibrium, instead of stay of the ascorbic acid with clay for a long time. The reason for obtaining a high percentage of adsorption at an initial time because of the availability of active sites on the surface of the clay, and with increasing the contact time between ascorbic acid solution and clay the competition between ions increases to adsorb on the surface until arriving at equilibrium. Fig.(1) Shows the relation between the capacity of adsorption (q_e) and time. The (q_e) increased with time until reach a constant value between (60-75) min.

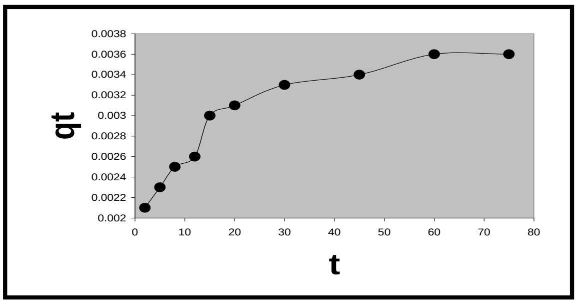


Fig. 1. Effect of contact time on the capacity of adsorption for ascorbic acid on clay, use (0.005) M ascorbic acid, 0.06 gm clay, at a natural acidity function and 30 C°.

TABLE 5. The effect of contact time on the efficiency of the adsorption process, use (0.005) M ascorbic acid, 0.06 gm clay, at a natural acidity function and 30 C°.

Time (min)	C_{ads} (mg/L)	q_t mg. g^{-1}	Adsorp.%
2	0.0025	0.0021	52
5	0.0027	0.0023	56
8	0.0030	0.0025	60
12	0.0031	0.0026	64
15	0.0037	0.0030	74
20	0.0037	0.0031	76
30	0.0040	0.0033	81
45	0.0041	0.0034	83
60	0.0043	0.0036	86
75	0.0043	0.0036	86

3.4. Effect of Acidity Function.

The acidity affects the nature of the charges that present in the solution and on the clay surface for this it will affect the efficiency of the adsorption process. Changing the value of acidity (from 2.5 to 4) will increase the efficiency of the adsorption process (from 68 % to 76 %) due to the addition of (positive or negative) ions.

Hydrogen ions and water molecules (resulting from the use of water as a solvent) impact the nature of the charges on the clay surface from the negative (due to the presence of metal oxides) to the positive ones. The dissociation of ascorbic acid will be resulting in the negative ions that can be easily transferred from the solution to the clay surface. The addition of (OH^-) to the acidic solution of ascorbic acid shifts the value of pH to be more alkaline. Consequently, the positive ions will decrease in the solution (H^+) leading to the dissociation of ascorbic acid. This dissociation will increase the positive charges. Thus, moving these charges to the clay surface leads to an increase in the efficiency of the adsorption process, this is what has been proven at (pH (7) and pH (11), as shown in table (6).

Where pH (7) gives freedom of movement for ascorbic acid to decompose in the largest possible amount and reach the level of equilibrium, while the highest percentage of adsorption obtained is at pH(11), so increasing the hydroxide ion concentration increases the amount of adsorption, since pH_{11} will dissociate the largest amount of ascorbic acid by withdrawing the positive hydrogen ion.

TABLE 6. Values of adsorption percentage at different acidity functions use (0.005) M ascorbic acid, 0.06 gm clay, contact time equal 90 min. , and at 30 C°.

pH	Adsorp.%
Natural (2.5)	68
4.0	76
7.0	82
11.0	96

3.5. Effect of Temperature.

The effect of temperature was studied at optimum conditions of adsorption. The increasing of temperature leads to remove the physical interactions and associations between ions and water molecules. It is supposed to increase the ionization of ascorbic acid also give more freedom for ions to transfer from solution to the clay surface. Table (7) illustrates the percentage of adsorption that decreased with increasing temperature. This means the further energy to the adsorption system leads to the desorption process by means the adsorbate ions leave the surface to inside in solution by breaking of the physical bonds between ions and surface. This conclusion gives that the adsorption of ions on the surface has physical.

TABLE 7. Effect of temperature on adsorption percentage, use (0.005) M ascorbic acid, 0.06 gm clay, contact time equal 90 min. and at pH = 4 .

Temp. (C°)	Adsorp.%
15	80
20	72
25	68
30	56
35	40
40	20

Studying the adsorption process at different temperatures is useful to calculate the thermodynamic parameters which describe the state of the adsorption system thermodynamically, the results were tabulated in table (8).

TABLE 8. Thermodynamic parameters for adsorption process.

Temp. (K°)	ΔG (KJ/mole)	ΔH (KJ/mole)	ΔS (KJ/mole)
288	-3.318		-0.2783
293	-2.231		-0.2772
298	-1.835		-0.2739
303	-0.458	-83.472	-0.2769
308	+1.305		-0.2759
313	+4.187		-0.2800

From the results in a table (8), the ΔG values were converted from negative to positive values. This means the adsorption process is converted from a spontaneous process to a non-spontaneous one. Studying the effect of temperature on the efficiency of adsorption was shown in the inverse of adsorption percentage with the temperature reaching up to (20%). The easily breaking of weak bonds will lead to an increase in the temperature consequently, ascorbic acid (anions) will be adsorbed on the surface of the clay. This is called (physical adsorption). The positive values of ΔG at (308, 313) K° refer to the further energy to adsorption system can convert the physical adsorption for some ions to chemical adsorption but generally, most of the ions leave the surface of the clay and come back to the solution. These conclusions will confirm the future study in this paper.

It is clear that the enthalpy of the adsorption process has a high negative value; this refers to that the adsorption process is exothermic naturally. This leads to a decrease (ads. %) with increasing temperature.

All the ΔS values have the same negative values at all temperatures, this means that the adsorbate ions on the surface were systematic more than the ions in the solution.

4. Kinetic Study

4.1.Pseudo First Order Model: -

This model of kinetic which known Lagergren equation use to describe the average adsorption process [18]. It is a complex process that has done through more than one step and depends on the adsorption capacity as shown in the equation below.

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

q_e = capacity of adsorption at equilibrium ($mg.g^{-1}$) .

q_t = capacity of adsorption at time (t) ($mg.g^{-1}$).

K_1= rate constant (min^{-1})

The value of experimental capacity of adsorption is (0.0161) mg.g-1, this value does not equal the theoretical value (0.0027) $mg.g^{-1}$, the rate constant is (K = 0.0112) min^{-1}. This result represents one step of the adsorption process but it does not represent all the steps of adsorption kinetic.

4.2.Psedue Second-Order Model:-

This model of kinetic depends on the capacity of the adsorbent substance and the behavior of the adsorbate substance along the time of the adsorption process as shown in the equation below:-

$t / q_t = 1 / K_2 q_e^{2} + (1 / q_e) * t$

K_2 = rate is constant of adsorption ($L. mol^{-1}. min^{-1}$).

q_e = capacity of adsorption at equilibrium ($mg. g^{-1}$).

t = time (min.).
q_t = capacity of adsorption at time (t) (mg. g^{-1}).
From the above equation, it can be obtained the initial rate constant of the adsorption process through the relation:-
$h = K (q_e)^2$

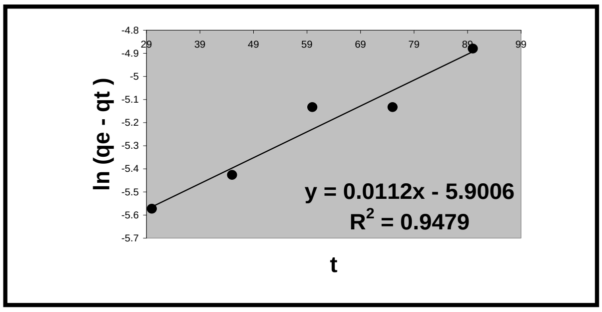


Fig. 2. The Lagergren first-order kinetic model for the adsorption of ascorbic acid on clay, use (0.005) M ascorbic acid, 0.06 gm clay, at a natural acidity function and 30 C°.

The results were obtained from this relation in Fig.(3) which gave a good relationship with the correlation coefficient ($R^2 = 0.9992$). It was found that the theoretical capacity is the same as the experimental capacity up to (0.0160 mg. g^{-1}). These results were confirmed that the adsorption process of ascorbic acid is consent with this model. As can be seen that the adsorption process varies in the ordinary kinetics of chemical reactions due to the complexity of the process. The process passes through more than one step with several activation energies. Because of these reasons, the results of adsorption agree to the pseudo-first and second-order model which is similar to other studies [19,20].

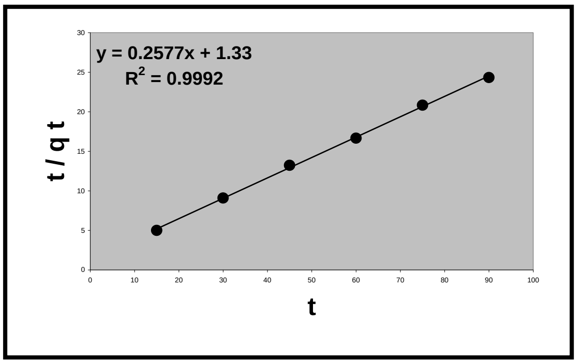


Fig. 3. The pseudo-second-order kinetic model for the adsorption of ascorbic acid ions on the surface of the clay uses (0.005) M ascorbic acid, 0.06 gm clay, at a natural acidity function and 30 C°.

5. Application of Isotherms Models

5.1. Langmuir Isotherm Model.

In this isotherm the adsorption of molecules or ions occur on a certain number on active sites of the surface that possess certain energy, these molecules or ions lead to form one layer on the surface and there is no interaction between these molecules or ions, the Langmuir equation was written as follows.

$C_e / q_e = 1 / b\, q_{max} + C_e / q_{max}$

b = Langmuir constant (L/mg) and have a relation with adsorption energy.

q_{max} represents a maximum capacity of adsorption (mg. g^{-1}).

The results of the application Langmuir isotherm equation listed in the table (9).

TABLE 9. Values of Langmuir isotherm at different temperatures, use (0.005) M ascorbic acid, 0.06 gm clay, and contact time equal 90 min.

Temp. K°	q_{max} (mg. g^{-1})	b (L/mg)	K_L (L. mg^{-1})	R_2
293	0.0187	60.6	1.133	0.9206
298	0.0169	746.2	12.610	0.9909
303	0.0114	136.9	1.560	0.9869
308	0.0088	531	4.672	0.9987
313	0.0066	228	1.504	0.8688

$K_L = q_{max} * b$

Langmuir constant (b) can be used to obtain some parameters which give information about the shape of the isotherm and the success of this isotherm on experimental results of adsorption through the separation factor (R_L).

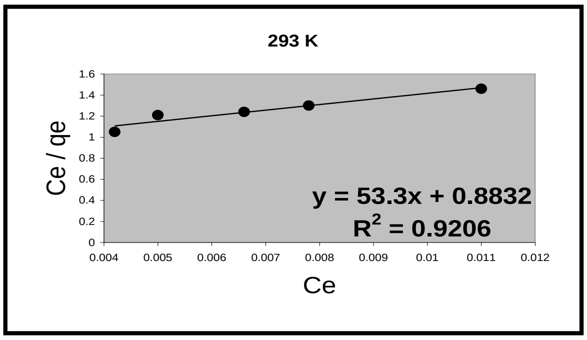
$R_L = 1 / (1 + b * C_i)$

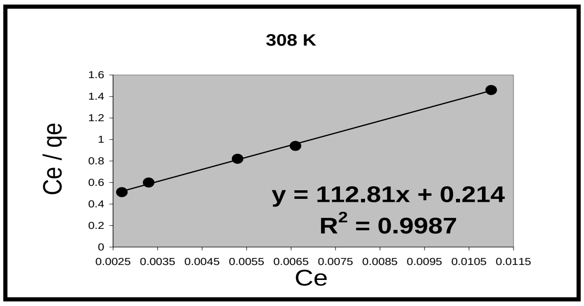
The (R_L) value refers to the range of the acceptable model and this value is preferred at range ($1 > R_L > 0$) since the adsorption process is linearity at value (1). This value refers to the range of acceptance isotherm. It is ideal at a value less than one and non-preferable at a value of more than one, therefore the zero value indicates a non-reversible equilibrium. When the RL value is equal to one and this refers to a linear relationship of the adsorption process, the results were listed in table (10).

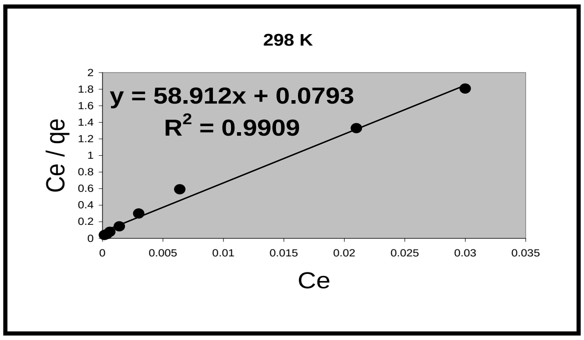
The results in a table (9) show that the increased temperature leads to a decrease in the maximum capacity of adsorption to form one layer of ions on the surface. Langmuir value constant has a relation with adsorption energy, which decreases with increasing temperature because of broken physical bonds between ions and the surface of the clay. This is in agreement with the experimental results which have related to the effect of temperature on the adsorption process.

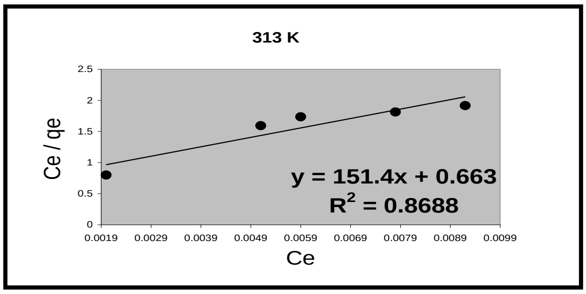
TABLE 10. Values of (R_L) at different concentrations and temperatures, use 0.06 gm clay, and at contact time equal 90 min.

Conc.	R_L				
	Temp. (K°)				
	293	298	303	308	313
0.009	0.647	0.129	0.448	0.173	0.327
0.010	0.622	0.118	0.422	0.158	0.304
0.013	0.559	0.093	0.359	0.126	0.252
0.015	0.523	0.082	0.327	0.111	0.226
0.020	0.452	0.062	0.267	0.086	0.179









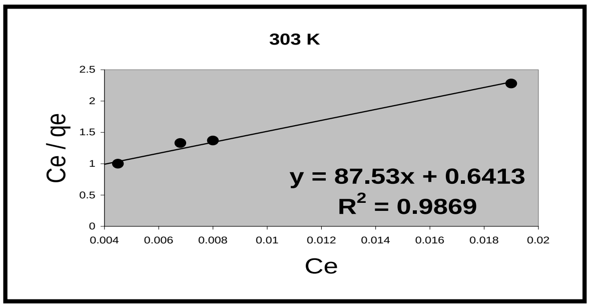


Fig. 4. Langmuir isotherms linear adsorption for ascorbic acid at different temperatures, use (0.005) M ascorbic acid, 0.06 gm clay, and contact time equal 90 min.

5.2. Freundlich Isotherm Model .

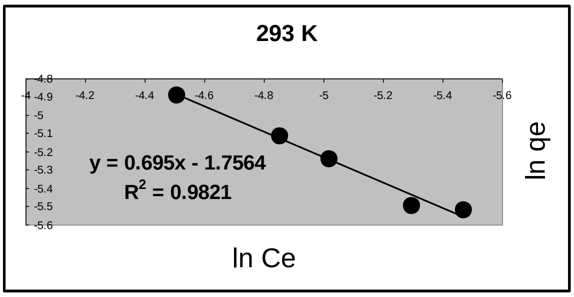
This model of isotherm is different from those have related to Langmuir isotherm by the formation of several layers of adsorbate ions on the surface of the clay. The Freundlich isotherm has two constants , (K_f) which has a relation with adsorption capacity and the (n) constant which has a relation with the intensity of adsorption, these values prefer a range between (1-10). The results were listed in table (11). the Langmuir equation was written as follows.

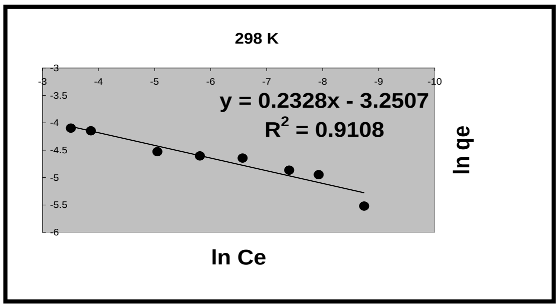
$$\log q_e = \log K_F + 1/n \log C$$

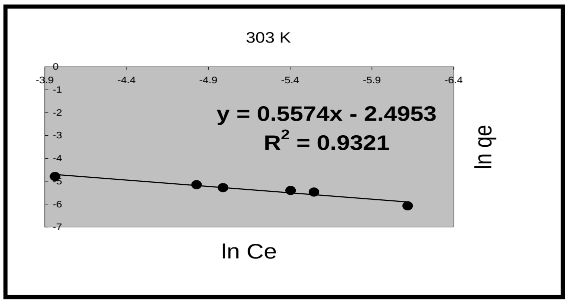
where K_F = adsorption capacity (L/mg) and (1/n) is adsorption intensity.

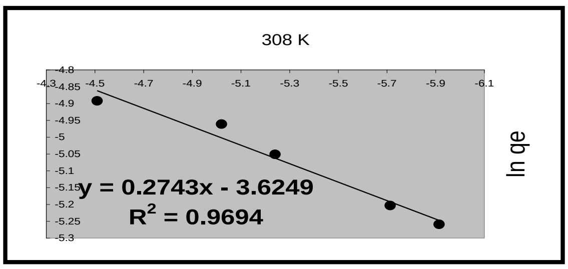
TABLE 11. Values of Freundlich constant for ascorbic acid on the surface of clay at different temperatures, use (0.005) M ascorbic acid, 0.06 gm clay and at contact time equal 90 min.

Freundlich Isotherm Constant			
Temp. (K°)	K_F	n	R^2
293	5.7	1.438	0.9821
298	25.8	4.290	0.9108
303	12.1	1.790	0.9321
308	37.5	3.640	0.9694
313	32.8	2.430	0.9075









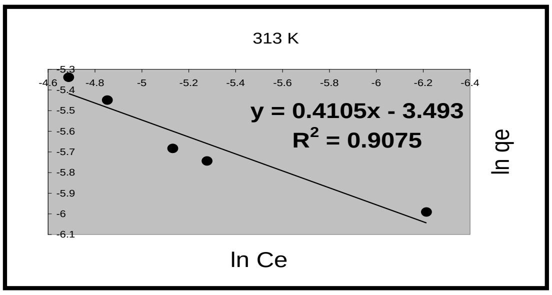


Fig.5. Freundlich isotherms linear adsorption for ascorbic acid at different temperatures, use (0.005) M ascorbic acid, 0.06 gm clay, and contact time equal 90 min.

Study the Probability of Sticking on the Surface of Clay [21-22]. This study depends on the coverage of ions or molecules on the surface of clay at different temperatures, the development Arrhenius equation was written as follows.

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

This relation gives a linear relationship with intercept (ln S*) and slope (-Ea/R) from Fig.(6). The (S^*) value is (0.29287) that refers to the presence of a mixture of physical and chemical adsorptions. This system is close to chemical adsorption more than physical adsorption. This point confirms the results of thermodynamic parameters (ΔG, ΔH). The (Ea) value represents the apparent activation energy (AAE) which is equal (+28.5051) K.J that confirms the conversion of adsorption system from spontaneous adsorption and exothermic to non-spontaneous and endothermic by converting the natural of bonded for some ions on the surface from the physical bond of adsorption to the chemical bonded of adsorption. Because of the presence of metal oxide on the surface of the clay, that will facilitate the occurrence of physical adsorption such as the adsorbed ions that are attracted to the oxygen atom. The obtaining metal oxide leads to occur physical adsorption which later turns to chemical adsorption.

TABLE 12. The values of Ln (1-Ɵ) and 1/T at different temperatures.

T	1 / T	Ln (1-Ɵ)
288	0.00347	-0.2231
293	0.00341	-0.3285
298	0.00335	-0.5798
303	0.0033	-0.7339
308	0.00324	-0.9162

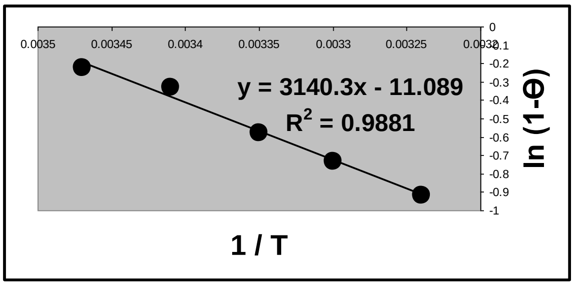


Fig.6. The relation between Ln (1-Θ) and 1/T at different temperatures from a development Arrhenius equation.

Using the Changing of Electrical Properties to Describe the Mechanism of Adsorption.

As can be seen, the increase of the concentration of acidic solution causes increasing in electrical conductivity because of present free ions such as (H^+) ions and anions. The increasing of ascorbic acid concentration leads to increasing the dissociation of acid which decrease the acidity function for this solution leads to an increase in electrical conductivity of an acidic solution, all the physical properties of the solution will changes after the adsorption process, because the transition of (H^+) ions from solution to surface by adsorption cause increasing of acidity function (pH) of the solution, this represents the first step of adsorption [8-10]. The water molecules adsorbed on the surface of clay in this step of adsorption, because the surface of clay carries negative charges on oxygen atoms which belonged to the presence of metal oxide in it, this step is useful to activation the metal oxides surface to help the acidic anions which carry negative charge to be adsorbed on the surface of clay after that this step represents the second step of adsorption. The transition of anions and numbers of (H^+) ions leads to an increase in dissociation of ascorbic acid molecules and that will cause increasing of free ions because the interaction and interference between ions and water molecules decrease by adsorption of (H^+) ions and anions on the surface of clay for these reasons the conductivity increases after adsorption by free adsorbate ions which stay in solution, see table (13) which are showing the changing of (pH) and electrical conductivity after adsorption at different concentrations [23-24].

The increasing temperature will ease the dissociation of ascorbic acid by increasing of (H^+) ions in the solution. This leads to a decrease in acidity function and an increase in the electrical conductivity of the acidic solution. The increased temperature will cause a weakness in the physical bonds between adsorbed ions and the surface. This weakness leads to the breakdown of those bonds and the possibility to return these ions from the surface to the solution again. Also, the interference and interactions in the solution will decrease. In this case, the mechanism of adsorption will be changed because the conversion of the adsorption process to desorption process continuously with increasing of the temperature.

The results reveal that the effect of temperature is evident on values of (pH), conductivity, and the percentage of adsorption which decreases by increasing temperature, as shown in table (14) [25-27].

TABLE 13. Values of (pH) and electrical conductivity for an ascorbic acid solution before and after adsorption using different concentrations, use 0.06 gm clay, contact time equal 90 min. and at 30 C°.

Conc.	pH*	pH**	Cond.* (μohm^{-1})	Cond.** (μohm^{-1})	Adsorp.%
0.005	3.24	5.95	0.14	0.2	96
0.009	3.12	5.68	0.16	0.3	95
0.010	3.10	5.48	0.17	0.3	94
0.013	3.08	5.06	0.23	0.5	87
0.015	3.05	4.54	0.23	0.5	76
0.02	2.98	4.43	0.25	0.5	68

* before adsorption.

** after adsorption.

TABLE 14. The effect of temperature on changing of physical properties, use (0.005) M ascorbic acid, 0.06 gm clay, and contact time equal 90 min.

Temp.	pH*	pH**	Cond.*	Cond.**	Adsorp.%
15	3.83	7.57	0.16	0.8	80
20	3.70	7.62	0.34	0.9	72
25	3.64	7.64	0.38	1.0	68
30	3.54	7.73	0.44	1.0	56
35	3.44	7.90	0.49	1.3	40
40	3.33	7.92	0.57	1.4	20

* before adsorption.

** after adsorption.

6. Infrared spectrum

The IR spectrum of the ascorbic acid compound was measured before and after adsorption, relative to measuring the compound before adsorption, it was noted that ascorbic acid gives a band at 3336 re-stretching of an alcoholic OH group and a band at 2985 CH alph. Stretchable returns and a wide band 2564-2644 cm^{-1} of the two OH groups on the double bond (in keto-enol form), The double bond appears at 1670cm-1 and finally the frequencies of C-O ester at

1735cm^{-1} and C-O-C at 1156,1216 cm^{-1} as in Figure(7).

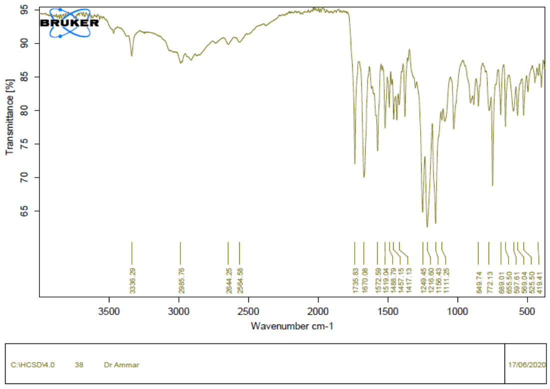


Fig (I): IR spectra for ascorbic acid

As for the compound produced after adsorption, it gave a band of 3235 back to the alcohol stretch OH and a band at 2977, 2932 of CH alph. stretchable returns, The C=O ester band appear in 1741, and C-O-C give band at 1150, 1249 and two similar bund at 1667 and 1718 refer to the C=O formed at the alpha beta sites as in Figure(8), Note the disappearance of the c = c stretch, This prove the mechanism which has been proposed as a product of the adsorption process.

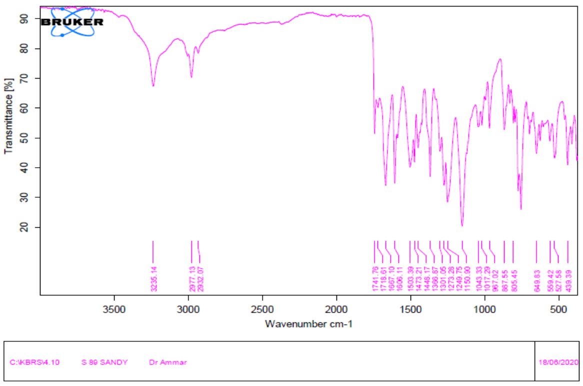
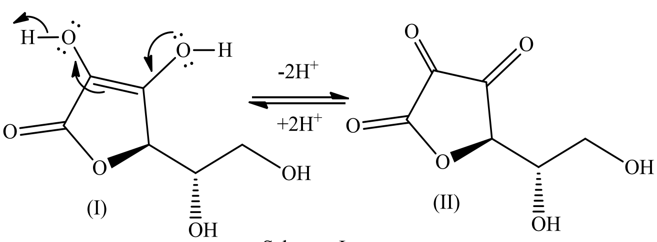


Fig (II): IR spectra for product Adsorption diketone

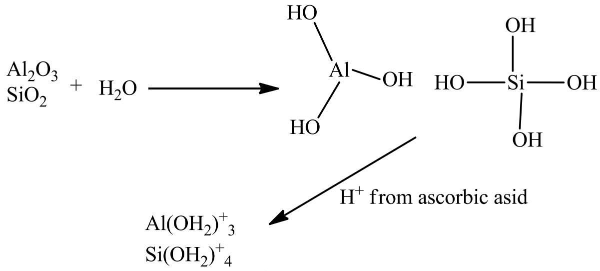
7. Conclusion

Through the theoretical study of ascorbic acid, we noticed that its loss of the positive hydrogen ion gives it a form of 1,2 diketone, which is more stable: scheme (1)



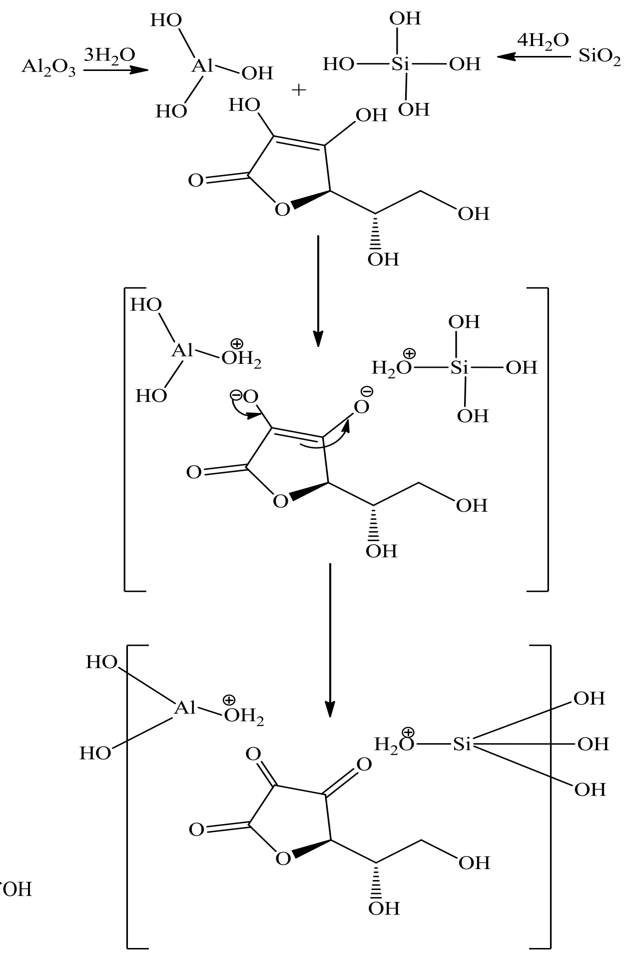
Scheme -I-

Since the clays or adsorbent matter are composed of metallic semi-oxides with high electrical negativity, they work on attracting the positive hydrogen ion from the acid, where the oxides are transformed into basic compounds in the presence of water as an adsorption medium. Thus, the surface has a high electron density and is the reason for the adsorption of positive ion scheme 2



scheme -II-

Through practical and theoretical results, what happens on the surface of the adsorbent material can follow the following suggested mechanism scheme 3



Scheme -III-

In the third case, ascorbic acid will lose ions and convert to di-ketone product. Dissolving clays containing semi-metallic oxides in water gives a surface rich in high electron density hydroxyl groups, and since ascorbic acid contains hydrogen ions, the surface of the clay serves to attract and adsorb these ions.

Adding the base increases the dissociation of ascorbic acid and thus increases the adsorption process. We also conclude that the positive hydrogen ions returning to the ascorbic acid are the ones that stimulate the clay and increase its adsorption capacity.

8. References

1- Farag, A. M., Rizk, M. S., El-Bassel, H. A., & Youssif, M. H. (2019). Fast and Efficient RP-HPLC Method for Simultaneous Determination of Water-soluble Vitamins in Some Nutraceutical Supplements. *Egyptian Journal of Chemistry*, *62*(12), 2195-2211.

2- Sudha, J. D., & Raveendran, R. L. (2017). Vitamin C: Sources, functions, sensing and analysis.

3- Duru, C., Nnabuchi, M., & Duru, I. (2019). Adsorption of Cu onto Maize Husk Lignocellulose in Single and Binary Cu-Zn Solution Systems: Equilibrium, Isotherm, Kinetic, Thermodynamic and Mechanistic Studies. *Egyptian Journal of Chemistry*, *62*(7), 1295-1305.

4- Al-Allaq, E., Al-Lami, H., & Al-Mowali, A. (2020). Synthesis and Adsorption Study of some Chitosan Acid Derivatives as Dispersants for Ceramic Alumina Powders. *Egyptian Journal of Chemistry*, *63*(7), 14-15.

5- Mahmoud, G., Abdel Khalek, M., Shoukry, E., Amin, M., & Abdulghany, A. (2019). Removal of Phosphate Ions from Wastewater by Treated Hydrogel Based on Chitosan. *Egyptian Journal of Chemistry*, *62*(8), 1537-1549.

6- - Mizhir, A., Abdulwahid, A., & Al-Lami, H. (2020). Chemical Functionalization Graphene Oxide for The Adsorption Behavior of Bismarck Brown Dye from Aqueous Solutions. *Egyptian Journal of Chemistry*, *63*(5), 1679-1696.

7- Keshawy, M. E., Fathy, M., Gaffer, A., Hosny, R., & Abdel Moghny, T. (2019). Low-cost Bio-Adsorbent Based on Amorphous Carbon Thin Film/Chitosan Composite for Removal of Methylene Blue Dye from Aqueous Solutions: Kinetic and Isotherm. *Egyptian Journal of Chemistry*, *62*(12), 2313-2329.

8- Gawande, S. M., Belwalkar, N. S., & Mane, A. A. (2017). Adsorption and its isotherm–theory. *International Journal of Engineering Research*, *6*(6) ,312-316

9- Anah, L., & Astrini, N. (2018, June). Isotherm adsorption studies of Ni (II) ion removal from aqueous solutions by modified carboxymethyl cellulose hydrogel. In *IOP Conference Series: Earth and Environmental Science* (Vol. 160, No. 1, p. 012017). IOP Publishing.

10- Abd El Salam, H., & Sharara, T. (2019). A novel microwave synthesis of manganese based MOF for adsorptive of Cd (II), Pb (II) and Hg (II) ions from aqua medium. *Egyptian Journal of Chemistry*, *62*(5), 837-851.

11- - Tanzifi, M., Kolbadi Nezhad, M., & Karimipour, K. (2017). Kinetic and isotherm studies of cadmium adsorption on polypyrrole/titanium dioxide nanocomposite. *Journal of Water and Environmental Nanotechnology*, *2*(4), 265-277.

12- Al-Abady, F. M., & Saeed, N. H. (2017). Quantum-chemical calculation methods to determine the ionization constants of N-substituted amine acid derivatives . *European Chemical Bulletin*, *6*(8), 343-349.

13- Abbas, A. M., Mohammed Taib, A. S., & Saeed, N. H. (2020). Synthesis and Characterization of Linear Thermally Stable polyester contain Schiff Bases. *Egyptian Journal of Chemistry*, *63*(8), 45-52.

14- Hassan, Y. I., & Saeed, N. H. M. (2012). Kinetics and Mechanism of Oxidation of Diethyl Ether by Chloramine-T in Acidic Medium. *E-Journal of Chemistry*, *9*(2), 642-649.

15- Karam, F. F., Saeed, N. H., Al Yasasri, A. H., Ahmed, L. M., & 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), 5-8.

16- Saeed, N. H. (1999). Kinetics and Mechanism of Chlorination of N-Acetylglycin by Chloramine-T In Acidic Medium. *Journal of education and science*, *24*(3), 41-50.

17- Hassan, Y. I., & Saeed, N. H. (2010). Kinetic study of chlorination of p-methoxyacetanilide by chloramine-T in hydrochloric acid medium. *Oriental Journal of Chemistry*, *26*(2), 415.

18- Ho, Y. S., & McKay, G. (2002). Application of kinetic models to the sorption of copper (II) on to peat. *Adsorption Science & Technology*, *20*(8), 797-815.

19- Al-Neimi, K. I., & Ahmed, A. G. (2019). 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), 23-39.

20- AL-Niemi, K. I. (2019). Mechanism, Kinetic And Thermodynamic For Transport Of Citric Acid Ions To Removal By Adsorption Using Electrical Conductivity, Potential Difference And Acidity Function. *Journal of education and science*, *28*(2), 85-102.

21- Swelam, A. A. (2019). Removal comparative study for Cd (II) ions from polluted solutions by adsorption and coagulation techniques using Moringa oleifera seeds. *Egyptian Journal of Chemistry*, *62*(8), 1499-1517.

22- Al-Niemi, K. I. (2019). 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), 246-272.

23- Ridha, N. A. S., Kamal, N. M., & Ridha, M. A. S. (2020, November). Effect of Adsorption on Electrical Conductivity Values, Ionization Constant and Degree to Di Hydroxy Benzoic acid By Using Natural Surfaces. In *Journal of Physics: Conference Series* (Vol. 1660, No. 1, p. 012021). IOP Publishing.

24- Musso, T. B., Parolo, M. E., & Pettinari, G. (2019). pH, Ionic Strength, and Ion Competition Effect on Cu (II) and Ni (II) Sorption by a Na-bentonite Used as Liner Material. *Polish Journal of Environmental Studies*, *28*(4).

25- Saleh, M., Ayoub, A. I., & Hammady, A. O. (2020). Synthesis biological studies of some new heterocyclic compound derived from 2-chloro-3-formyl quinoline and 4-(benzyl sulfonyl) acetophenone. *Egyptian Journal of Chemistry*, *63*(12), 4-6.

26- Al-Niemi, K. I. A. (2020). Changing of Electrical Conductivity, Acidity Function Voltage of Potential Difference for Salicylic Acid and Substituted to Study Adsorption Mechanism on Alumina Surface and the Factors Affecting it. *interaction*, *14*(1), 6-12.

27- Alniemi, K. I. (2020). 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), 76-89.