



Thermodynamic & Kinetic Study of the Adsorption of Glycolic acid using a Natural Adsorbent

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Abstract

Glycolic acid, is known as hydroxyl-acetate acid, is a vital chemical compound that have many applications, so, its recovery process of glycolic acid is mandatory and essential from its source of production, many processes are used to remove glycolic acid from its aqueous solution. In this article, adsorption process is applied via using grape leaf residues (GLR) as adsorbent. Thermodynamic and kinetic studies were applied to prove the optimal conditions of adsorption process.

Keywords: Glycolic acid, Grape leaf residues, Adsorption, Thermodynamic and kinetic studies.

1. Introduction

As a result of scientific and technological progress, one of the hazards that the global suffers from today is environmental pollution (water, soil, and air) [1-3]. Organic pollutants are widespread in the environment and directly led to adverse harmfulness effects, such as birth defects, dermatitis, emphysema, fertility problems, heart disease, kidney diseases, endocrine disruption, or even cancers [4]. Thus, many methods were used to remove these pollutants such as adsorption, oxidation, filtration, precipitation, electrochemical treatment, photochemical and irradiation methods. Each of these conventional techniques has some problems that delay its use, these obstacles may be represented by the need to provide high material and human capabilities [5, 6].

Recovery process of glycolic acid 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.[7-9] Among these technologies, there is adsorption technology that employed in waste water treatment for recovery certain vital products such as glycolic acid. [10] Also, adsorption of glycolic acid from aqueous solutions has been studied using many materials such as fly ash residues [11], adsorption resins (HPD 950, HPD 450 [12], and AB-8), and metallic surfaces [13].

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)

Besides, glycolic acid, is known as hydroxyl-acetate acid (GA, α -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.[14-16] It can be prepared, example by reaction of carbon monoxide with formaldehyde, preferably in the presence of water.[17, 18]

Also, glycolic acid 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 glycolic acid include sugar beets, sugar cane, cantaloupe, pine apple, and unripe grapes.[19]

In the same manner, adsorption was one of the chief common approaches used to remove pollutants, it is characterized by being an easy, safe, and economical method, and it does not require a high capital or the availability of complex equipment. [20, 21]

The aim of this article according to above survey is removal of glycolic acid from its aqueous solution by using grape leaf residues (GLR) as adsorbent. In order to attain the highest percentage of the adsorption, diverse conditions like the effect of concentration of the adsorbate material (glycolic acid), the effect of the weight of the adsorbent (GLR), shaking time, the acidity function of the reaction medium and, the effect of temperature were studied, a batch way was used in this study.

2. Experimental

2.1. Chemicals

The chemicals used in this study are of high purity, so no additional purification was performed on them, and these chemicals were as follows:-

- a. 0.1M glycolic acid was prepared.

- b. Sodium hydroxide solution (0.1, 0.01 and 0.001 M)

c. 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.

2.2. Instruments

- 1- Electric vibrator with water bath and thermometer (company Nüve).
- 2- Electrical conductivity meter type (company Hana).
- 3- pH-meter type (company Denver) .

2.3. Preparation of adsorbent

Grape leaves are characterized by their high moisture content, it is dried in an electric oven at a temperature of 313 K for 34 hours, then it was ground using an electric grinding machine, the layer comprising very small grains of grape leaves is separated from the other layers using very fine sieves designated for this purpose, and store in a place free of moisture (by using desiccants).

2.4. Preparation of Solutions:

- 1- Glycolic acid (0.1 M, 1lit.) was prepared by dissolving a certain weight of the acid in the distilled deionized water, to afford various concentrations.
- 2- To calculate the residual concentration from glycolic acid a standard solution of sodium hydroxide (0.1 M) was prepared, this secondary standard solution was calibrated with a primary standard potassium hydrogen phthalate (KHP) solution using phenolphthalein indicator.
- 3- The acidity of the solution was controlled by using hydrochloric acid and sodium hydroxide solutions.

3. Results and Discussion

3.1. Adsorption Optimal conditions

To have the net adsorption optimal conditions, concentration weight of the adsorbent were studied

together with acidity function of reaction medium and impact of temperature.

A. GA ideal concentration had been obtained with higher adsorption ratio via preparation of several concentrations of GA (0.001,0.003,0.005,0.007,0.009,0.015) M with **stabilization** of other practical conditions.

The highest percentage of adsorption process was at 0.009M of GA, from table 1, at 0.015M, that adsorption percentage begins to be stable (64 %) the reason for this is due to a decrease in the free adsorption sites located on the surface of GLR, as the glycolic acid molecules occupied all the adsorption sites on the surface [22, 23].

Figure 3B, higher the concentration of glycolic acid leads to adsorption capacity as increase in concentration which means an increase in GA ratio that will move towards the adsorbing surface [23].

Table 1: Changing the percentage of the adsorption glycolic acid, adsorption capacity, equilibrium constant, conductivity, and acidity function with changing the concentration of glycolic acid, other experiment conditions remained without any change.

Conc. (M)	Adsorp (%)	q_e (mg/g)	$k_{ads.}$	Cond. (μohm^{-1})		pH	
				Before adsorp.	After adsorp.	Before adsorp.	After adsorp.
0.001	20	0.0005	0.25	0.09	0.2	3.515	4.870
0.003	23	0.00017	0.30	0.16	0.2	3.322	4.296
0.005	28	0.00035	0.38	0.22	0.3	3.240	4.074
0.007	42	0.00075	0.75	0.26	0.3	3.173	3.896
0.009	64	0.0017	1.30	0.27	0.3	3.122	3.714
0.015	64	0.0028	3.00	0.30	0.4	2.996	3.491

q_e refers to the adsorption capacity (mg/g) which is calculated from the equation (1).

$$q_e = (C_i - C_e) * V / W \dots (1)$$

The symbol (C_i) represents the initial concentration of glycolic acid (mol/ L), and (C_e) indicates the concentration of the solution after a certain time has passed, (V) is the volume of the

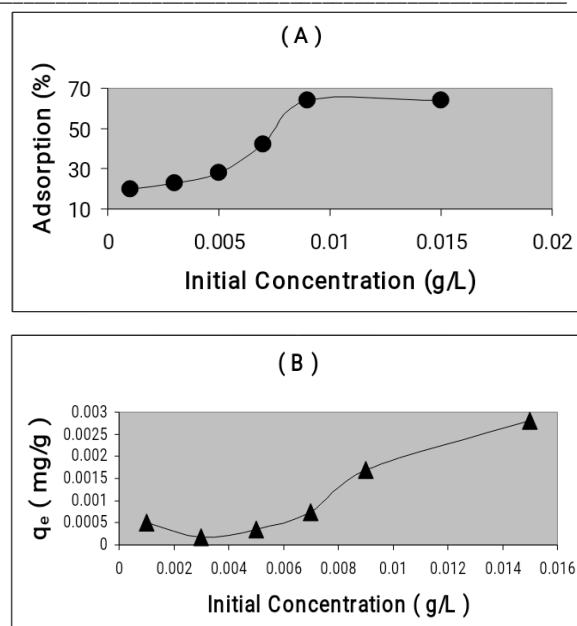


Fig.3. The relationship between the initial concentration of glycolic acid and (A) percentage of the adsorption process, (B) adsorption capacity, other experiment conditions remained without any change [weight of adsorbent (1.5) g GLR, the shaking time is equal to 75 minute, pH=2.5 (natural) and temperature 293K].

glycolic acid solution, (W) refers to the weight of the adsorbent material [25,26].

B. The electrical conductivity gradually increase with increasing concentration, due to increment of GA concentration and number of ionized molecules which cause occurrence of

electrical conduction due to their movement towards the adsorbing surface and their stability on it, which mean the electrostatic interferences decreases due to the increase in the distance between the ions in the solution (un adsorbed).

The results in table (1) show that the higher the concentration, due to dissociation of GA to minimize pH values for the solution, to be acidic medium. An increase in the pH values of the solution is observed after adsorption, due to the adsorption of some hydrogen ions on the surface of GLR [24].

Table 2: Changing the percentage of the adsorption glycolic acid with changing the weight of adsorbent, other experiment conditions remained without any change [0.009 M glycolic acid, shaking time is equal to 75 minute, pH= 2.5 (natural), and temperature 293K].

Weight of adsorbent substance (g)	Adsorption (%)
0.5 GLR	45
0.8 GLR	55
1.0 GLR	64
0.2 GLR + 0.8 charcoal	95
0.3 GLR + 0.7 charcoal	91
0.4 GLR + 0.6 charcoal	86
0.5 GLR + 0.5 charcoal	83
0.6 GLR + 0.4 charcoal	82
0.7 GLR + 0.3 charcoal	73
0.8 GLR + 0.2 charcoal	56

C. Impact of weight of the adsorbent material.

Increase of grape leaf residues (GLR) as an adsorbent material is accompanied by an increase of adsorption percentage. At 0.5g GLR, adsorption process is 46 %, at 0.8g GLR adsorption was 55 % and adsorption was at 64 % as equilibrium state, when 1g of adsorbent is used (Table 2).

In another way, a mixture of GLR and charcoal with different weight ratios was used to increase adsorption efficiency. At

0.2 g GLR with 0.8 g charcoal; adsorption percentage was 95 %. This is because of presence of charcoal. So, the optimal weight is at 1g (0.3 GLR + 0.7 charcoal) (Table 2).

D. Impact of shaking time.

The shaking time greatly affect the adsorption process so, at different times (2, 5, 10, 15, 30, 45, 60, 75 and 90 minute), the percentage of GA adsorption towards the surface of GLR is very high (26 % at a time of 2 minute), due to presence of free active sites on the surface of GLR until arriving at the equilibrium stage (the percentage of adsorption process equal 63 % and 64 % at time 75 and 90 minute) where the percentage of the adsorption process remains constant no matter how long the shaking time is because all the free sites located on the surface of GLR are associate with the glycolic acid molecules (Table 3).

Table 3: Changing the percentage of the adsorption glycolic acid, adsorption capacity with changing the shaking time, other experiment conditions remained without any change [0.009 M glycolic acid, weight of adsorbent (1)g GLR, pH =2.5 (natural) and temperature 293K].

shaking Time (minute)	Adsorption (%)	q _t (mg.g ⁻¹)
2	26	0.000120
5	34	0.000155
10	36	0.000165
15	42	0.000190
30	44	0.000200
45	51	0.000230
60	55	0.000250
75	63	0.000285
90	64	0.00030

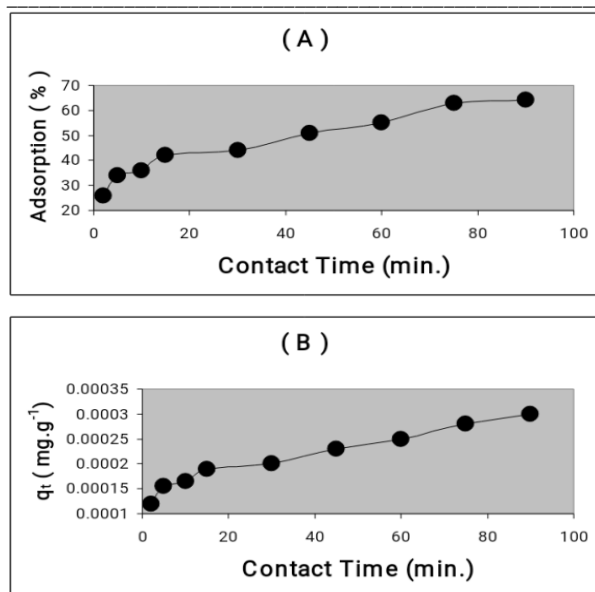


Fig.4. Changing the percentage of the adsorption glycolic acid (A), adsorption capacity (B) with changing the shaking time.

E. Acidity of the reaction medium.

The type of medium is effective factor on adsorption process. So, at various acid concentrations [2.5, 4.5, 7, 10], by using 0.2 N HCl and 0.2 N NaOH.

Adsorption percentage is small at lower pH, and increase with increase of pH, this is because of acidic medium which leads to adding hydrogen ions to the reaction medium to bind to the active sites on the surface of GLR as competitor to glycolic acid molecule. The percentage of adsorption is high (80 % at pH=4.5) with lower of un-adsorbed GA residual (20 %), therefore it is not possible to apply the mathematical equations for

research because the application of these equations requires the presence of the value of the residual concentration, for this reason, this study has been completed at the natural acidity function since the percentage of the adsorption process is equals (65 %) and the percentage of the remaining glycolic acid in the solution is (35 %) thus it becomes possible to apply mathematical equations and complete the calculations for the research.

Table 4. Changing the percentage of the adsorption glycolic acid with changing the acidity function for the reaction medium, other experiment conditions remained without any change [0.009 M glycolic acid, weight of adsorbent (1) g GLR, shaking time is equal to 90 minute, and temperature 293K].

pH	Adsorption (%)
2.5 (natural)	65
4.5	80
7.0	89
10	96

F. Impact of temperature.

Optimum temperature is important factor in adsorption. So, thermodynamic functions ($\Delta H, \Delta S, \Delta G$) were measured with different temperature (288, 293, 303, 308, 313, 318, and 323K) with stabilization of other factors.

GA adsorption is 64% as increases as temperature at 288K then it gradually decreases with increasing temperature until arriving 23% at 323K, due to breakdown of bonds between GA and GLR as adsorbent (Table 5).[25]

Table 5. Changing the percentage of the adsorption glycolic acid, conductivity, and acidity function with changing the temperature for the reaction, other experiment conditions remained without any change [0.009 M glycolic acid, weight of adsorbent (1) g GLR, shaking time is equal to 90 minute ,and at a natural acidity function (pH=2.5)].

Temp. (K)	Adsorp. (%)	Cond. (μohm^{-1})		pH	
		Before adsorp.	After adsorp.	Before adsorp.	After adsorp.
288	64	0.1	0.7	3.330	4.962
293	63	0.2	0.7	3.320	4.866
298	51	0.2	0.8	3.203	4.819
303	44	0.2	0.8	3.186	4.800
308	38	0.2	0.8	3.180	4.797
313	35	0.2	0.9	3.172	4.673
318	27	0.3	0.9	3.132	4.639
323	23	0.3	0.9	3.096	4.581

Also, electrical conductivity gradually increase with raising the temperature, due to breaking of bonds that leads to free ions in the solution, which leads to an increase in the electrical conductivity values.

G. Acidity function of the solution supports electrical conductivity, at higher temperature with lower pH due to increase GA dissociation that causes increase of hydrogen ions and increase in pH is observed after occurrence of adsorption due to the adsorption of the free hydrogen ions present inside the solution on the surface of GLR [25]

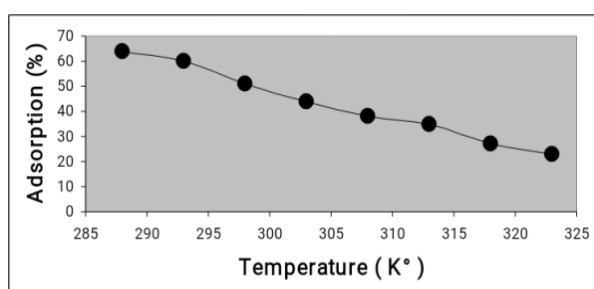


Fig.5. Effect of temperature on adsorption

3.2. Thermodynamic study

The thermodynamic study gives complete information about the nature of the reaction. Via the following equations

$\ln k_{eq} = -\Delta H / RT + \ln k \dots (2)$ (Vant't Hoff equation).

$$\Delta G = -RT \ln k_{eq} \dots (3)$$

$$\Delta G = \Delta H - T\Delta S \dots (4)$$

k_{eq} ($\text{mg} \cdot \text{gm}^{-1}$) represent the equilibrium constant which calculates from the equation (5).

$$k_{eq} = C_{ads} / C_e \dots (5)$$

C_{ads} , C_e (mg / L) are the concentrations at the equilibrium state for glycolic acid on the GLR and in the solution.

ΔH ($\text{kJ} \cdot \text{mol}^{-1}$) indicates the change in enthalpy value for the reaction, ΔS ($\text{kJ} \cdot \text{mol}^{-1}$) refers to the change in the value of enthalpy, ΔG ($\text{kJ} \cdot \text{mol}^{-1}$) represents the change in the value of Gibbs energy for the reaction, T (K) is the reaction temperature, R ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) expresses the gas constant, k refers to a constant value.

The value of ΔH is obtained by drawing a linear Van't Hoff equation since the slope of this relationship represents the value of ΔH , as shown in Fig. (6).

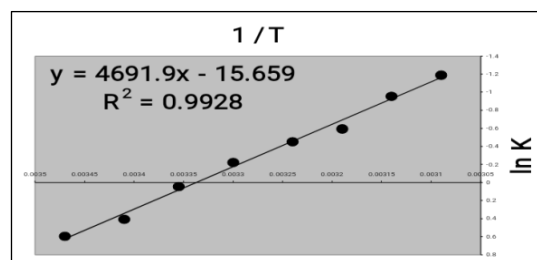


Fig.6. Application of the Van't Hoff equation to study the adsorption of glycolic acid by GLR.

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ΔH is negative that means GA adsorption is an exothermic process, due to formation of bonds between GLR and GA which leads increase of temperature (table 6).

Table 6. The values of thermodynamic parameters ΔG , ΔH , and ΔS for the adsorption of glycolic acid on the surface of GLR.

Temp. (K)	ΔG (kJ/mole)	ΔH (kJ/mole)	ΔS (kJ/mole)
288	-1.4239	-39.2	-0.130
293	-0.9877		-0.130
298	-0.1100		-0.131
303	+0.5621		-0.131
308	+1.1576		-0.131
313	+1.5477		-0.131
318	+2.5263		-0.131
323	+3.1949		-0.133

ΔG in the range (288-298)K are negative values, which indicates that the process of adsorption of glycolic acid on GLR is spontaneity process, these values change to positive in the range (303-323)K which refers to that the adsorption process is not spontaneity at this range of temperatures. This is attributed to the difference in the type of the bonds formed between the GA material and the adsorbent surface, the formed bonds in the range (288-298) K are physical, and since the physical bonds do not require high energy, so these bonds can form automatically, the adsorption, in this case, is called physical adsorption. After that and as a result of the high temperature for the reaction medium (303-323) K some of the physical bonds will be changed to the chemical bonds, as the process of forming chemical bonds is an endothermic process, meaning that the reaction medium must be provided with additional energy in order to form these bonds. For this reason, ΔG will be changed to positive, and the adsorption is known in this case as chemical adsorption [24].

The movement of glycolic acid from the solution and its attachment to the surface of GLR led to a decrease in the randomness of the system, therefore ΔS has a negative sign [26].

3.3. kinetic study

This study was conducted by using first-order pseudo and second-order pseudo sample which can be represented by the equations (6) and (7) [27].

$\text{Log}(q_e - q_t) = \text{Log } q_e - (k_1/2.303) t \dots (6)$ (pseudo-first-order equation)

q_e and q_t (mg/g) represent the adsorption capacity of glycolic acid on the GLR at equilibrium state and at a certain time(min), k_1 is the rate constant(min^{-1}). The value of the theoretical adsorption capacity was calculated for the adsorption process, as it is equal to (0.000183) mg.g^{-1} and the experimental value is (0.00029) mg.g^{-1} as the difference between them is about (0.000107) units, the value of the rate constant was also calculated ($k = 0.0297087$) min^{-1} . when notice Fig. (7,A) it appears that it has a high correlation coefficient value ($R^2 = 0.9077$) (Figure 7).

Another model was used in conducting this study is the pseudo-second-order model which can be represented by the equation (7) [27].

$$t / q_t = 1/k_2 q_e^2 + (1/q_e) * t \dots (7)$$

The adsorption capacity at the equilibrium state can be represented by the symbol (q_e) (mg/g), while it can represent the adsorption capacity at a certain time by using the symbol (q_t), the symbol (k_2) (g/mg.min) indicates the value of the rate constant for the reaction from pseudo-second-order.

The above equation was used in calculating the values of (q_e) and (k_2), drawing (t/q_t) versus (t) will give a linear relationship, the value of (q_e) is calculating from the slope while the intercept for this relationship is equal to the value of the rate constant (k_2), note Fig. (7, B).

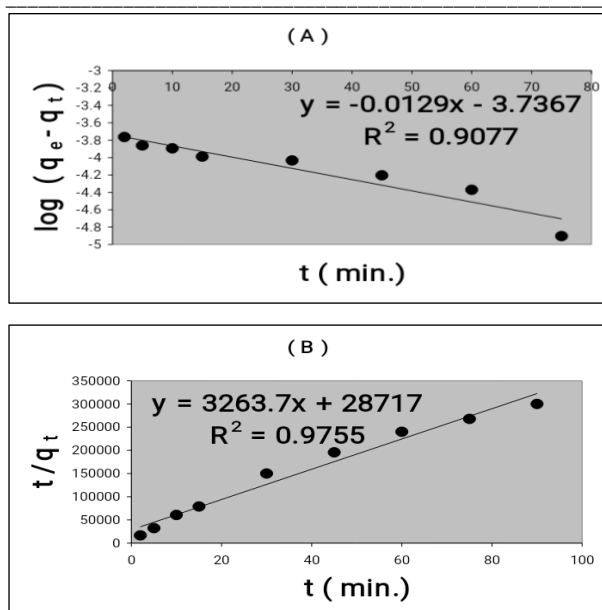


Fig.7. The kinetic model from pseudo-first-order (A) and pseudo-second-order (B) for the adsorption of glycolic acid on the GLR, the experimental conditions are (0.009)M glycolic acid, weight of adsorbent (1) g GLR, shaking time is equal to 90 min., pH = 2.5 (natural acidity function), and temperature 288K.

The theoretical adsorption capacity according to this model is (0.00030) mg.g⁻¹, while the experimental adsorption capacity value is (0.00029) mg.g⁻¹, the difference between them is very small (0.00001). The rate constant for the adsorption process is also calculated ($k = 370 \text{ min}^{-1}$), it is clear from Fig.(7,B) that it has a high correlation coefficient ($R^2 = 0.9755$).

From all these results, it can be arrive at an important fact, which is that the pseudo-second-

Table 7. Change the values of the Langmuir constants with temperature, the experimental conditions is (0.009 M) glycolic acid, weight of adsorbent (1) g GLR, shaking time is equal to 90 minute, and pH = 2.5 (natural acidity function).

Temp. (K)	q_{\max} (mg.g ⁻¹)	b (L/mg)	k_L (L/mg)	R^2
288	0.000814	42	0.0341	0.9622
293	0.000364	55	0.0200	0.9407
298	0.000352	57	0.0200	0.9191
303	0.000279	63	0.0175	0.9773
308	0.000277	112	0.0310	0.9725

order model is the most compatible model with this study, and there are many scientific studies that agree with these results [28, 29].

3.4. Adsorption Isotherms

Two isotherm models, Langmuir and Freundlich were fitted to the experimental data of adsorption. The thermodynamic Function (ΔH , ΔG , ΔS) are estimated. The results of the thermodynamic study showed that the forces controlling the adsorption process of the systems under considerate are physical in nature. The adsorption process are exothermic, occur spontaneously in the direction of connecting the dye to the clay surface, and forming less random system.[30, 31]

$$C_e / q_e = 1 / b \cdot q_{\max} + C_e / q_{\max} \dots (8)$$

(q_{\max}) represents the highest value of adsorption capacity (mg/g), the amount of material adsorbed on the adsorbent surface can be expressed using the symbol (q_e) (mg/g), (C_e) is the concentration at the equilibrium state (mg/L), (b) = Langmuir constant (L/mg) [34].

The Freundlich equation can be expressed as follows[33,41,42].

$$\text{Log } q_e = \text{log } k_F + 1/n \text{ log } C_e \dots (9)$$

(k_F) represent a constant value (mg/g)(adsorption capacity), the surface which containing active sites unequal in the energy is represented by the symbol (1/n), and (n) is a constant value (adsorption intensity) represents the number of adsorbed layers on the surface [33,41,42].

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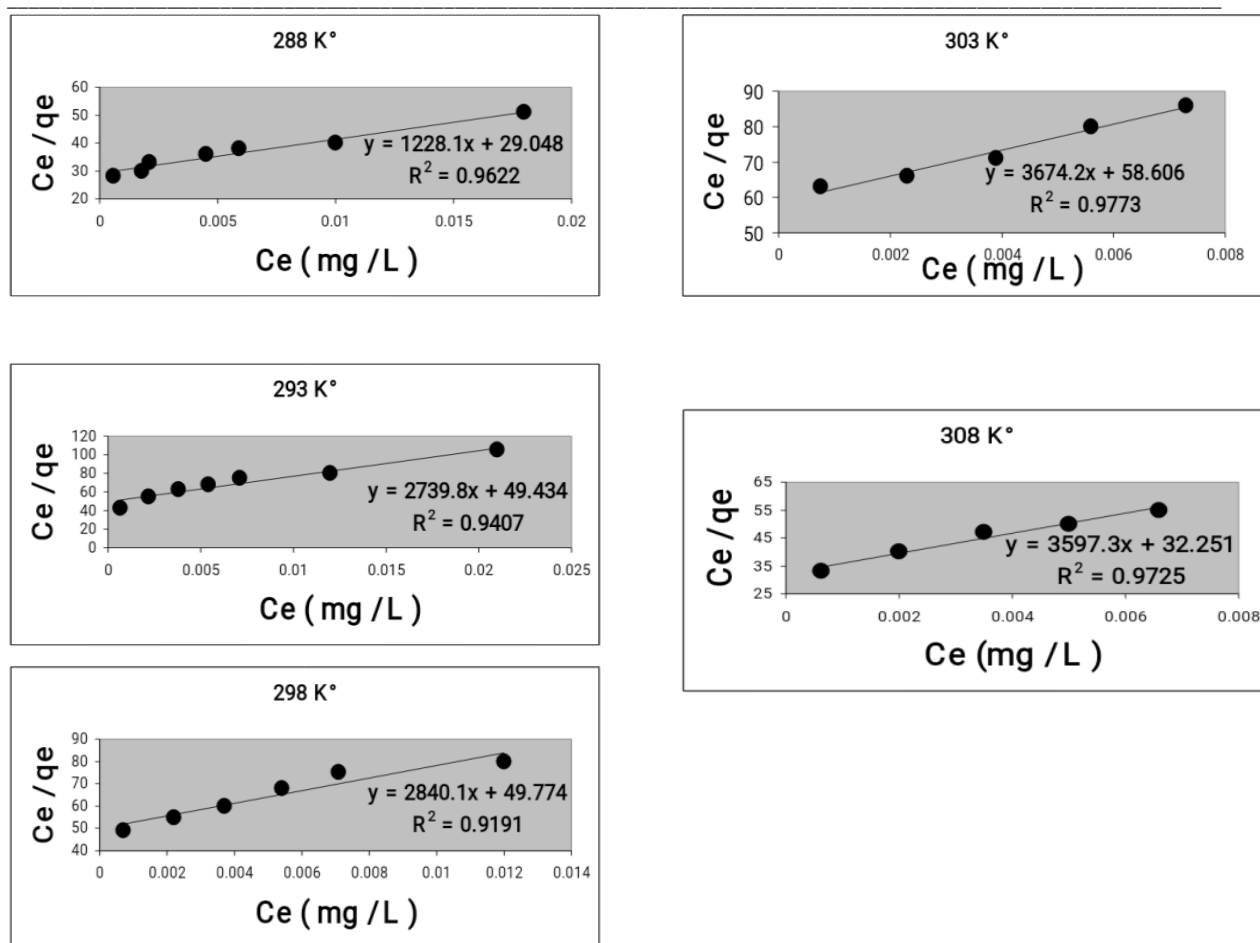


Fig.8. Drawing the Langmuir equation for the adsorption of glycolic acid by GLR.

Table 8. Separation factor (R_L) with temperatures and concentrations, weight of adsorbent (1) g GLR, shaking time is equal to 90 minute , and pH = 2.5 (natural acidity function).

R_L					
Conc.	Temp.(K)				
	288	293	298	303	308
0.001	0.959	0.947	0.946	0.940	0.899
0.003	0.888	0.858	0.853	0.841	0.748
0.005	0.826	0.784	0.778	0.760	0.641
0.007	0.772	0.722	0.714	0.693	0.560
0.009	0.725	0.668	0.660	0.638	0.498
0.015	0.613	0.547	0.539	0.514	0.373
0.025	0.487	0.421	0.412	0.388	0.263

(k_L) represent a constant value called the Langmuir constant (L/mg), which can be calculated from the equation (10) [27].

$$k_L = q_{\max} * b \dots (10)$$

It is clear from table (7) that the values of (q_{\max}) gradually decrease with the increase in temperature and that this is a natural result agree with the fact that the reaction is exothermic ($\Delta H = -$ value) as increasing the temperature means an increase in the kinetic energy present in the adsorbed material, which leads to the breaking of the bond that binds the glycolic acid with GLR [31].

The Langmuir model may be suitable for application in certain cases, and in other cases, it may not be suitable for the application. The thing which determines this is the separation factor (R_L), which can be calculated from the equation (11).

$$R_L = 1 / (1 + bC_i) \dots (11)$$

The symbol (C_i) represents the concentration of the adsorbate material at the beginning of the reaction, (b) represent Langmuir constant [32].

There are several ranges for the value of the separation factor (R_L) each one from these ranges has a specific interpretation, it can be said that the Langmuir models fit the current study when the value of the separation factor is equal (1), and in the case that the value of the separation factor is very large ($R_L \gg 1$) which indicates that it is not possible to apply the Langmuir model to this study, and there are some cases in which the value of the separation factor may be low ($R_L < 1$), in this case, the Langmuir model can be used to apply to this study [32].

It is clear from the values of the separation factor in table (8) that despite the different temperatures and the difference in concentrations, all the values of (R_L)

are characterized by being less than (1), this indicates that there is a fit between the Langmuir model and the practical results in this study [33].

Table 9: Freundlich constants with temperature, the experimental conditions is (0.009) M glycolic acid, weight of adsorbent (1) g GLR, shaking time is equal to 90 minute, and pH = 2.5 (natural acidity function).

Freundlich isotherm constants				
Temp. (K)	K_F	$1/n$	n	R^2
288	0.0022	0.7053	1.417	0.9987
293	0.0038	0.7483	1.336	0.0075
298	0.0040	0.7562	1.322	0.9971
303	0.0078	0.8960	1.116	0.9655
308	0.0093	0.9144	1.093	0.9300

When notice the values of (n) in the above table, it turns out that they are greater than (1) indicating that the bonds formed between the glycolic acid and GLR are bonds of a physical nature [32]. The values of ($1/n$) are higher than (0.1) and less than (1), which indicates the adsorption of glycolic acid on the surface of GLR is preferred [33-35].

One of the most important conclusions which reached from the above information is the possibility of using both the Langmuir and Freundlich isotherms in studying the adsorption of glycolic acid on the surface of GLR. This is in agreement with previous studies [36,37].

3.5. Nature of the adsorption by calculating the propability of sticking and apparent activation energy.

The sticking probability refers to the extent to which the adsorbate is bound to the adsorbent surface so that a layer of adsorbate material is formed that

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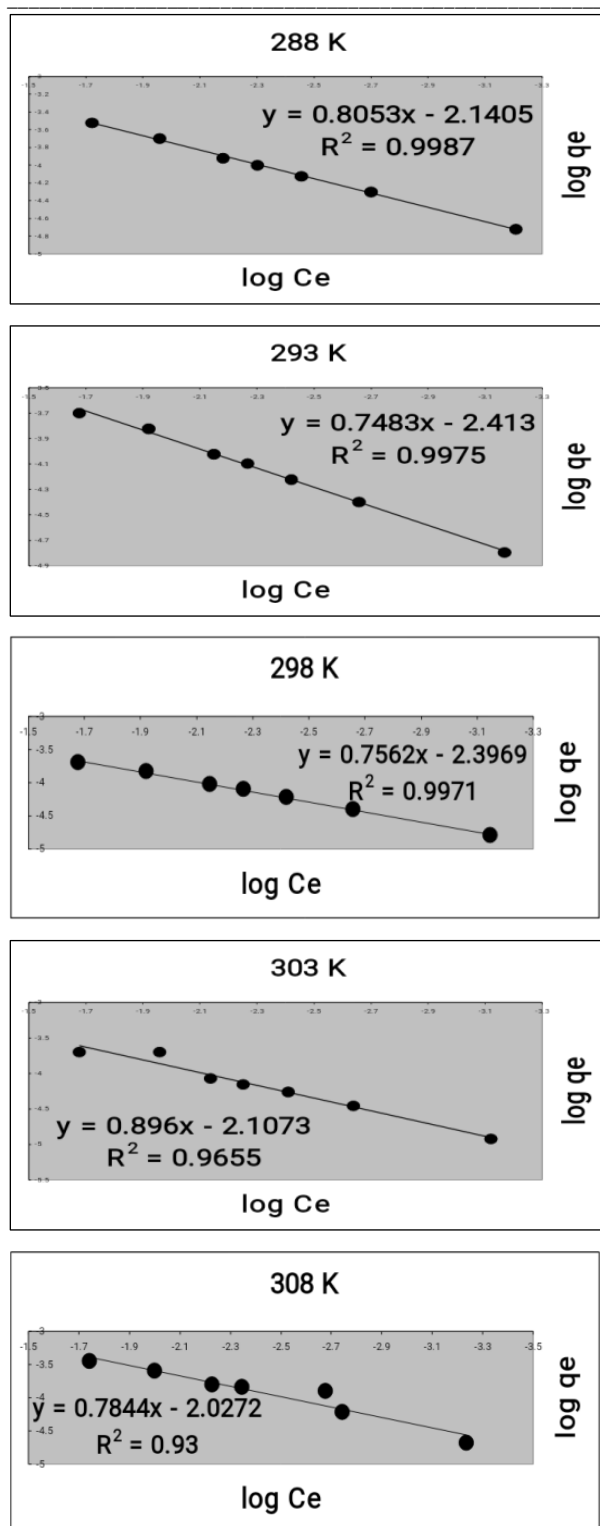


Fig.9. Drawing the Freundlich equation for the adsorption of glycolic acid by GLR.

surrounds the surface of the adsorbent material [32]. This study is one of the important studies in adsorption because it provides important information about the nature of the adsorption process, such as identifying the thermodynamic behavior of adsorption, whether it is an endothermic or an exothermic, and knowing the type of bond which formed between the adsorbate and the adsorbent [26]. There is a special equation for this study known as the developed Arrhenius equation which is written as shown below.[38]

$$\ln(1-\Theta) = \ln S^* - E_a / RT \dots (12)$$

The symbol (Θ) expresses the amount of the adsorbate that will cover a percentage of the surface for the adsorbent material (GLR), the sticking probability can be indicated by using the symbol (S^*), while (E_a) represents the apparent activation energy ($\text{kJ}\cdot\text{mol}^{-1}$), (R) is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$), and (T) is the absolute temperature for the adsorption (K).

plotting the x-axis ($1/T$) versus y-axis [$\ln(1-\Theta)$] for the above equation will give a linear relationship, the intercept for this relationship can be used to calculate the value of sticking probability (S^*), while the value of the (E_a) is calculated from the slope [38].

There are several probabilities for the value of (S^*). The first is when ($S^* > 1$) that is mean the adsorbate does not stick to the adsorbent surface. The second probability is ($S^* = 1$) which refers to that the adsorption process takes place and depending on the presence of chemical and physical bonds. While the

third probability is ($S=0$) which is a sign of the presence of the chemical bonds linking the adsorbate material with the adsorbent surface, and the chemical bonds are strong comparing with the physical, and that makes the adsorption process continues for a long period of time. The last possibility is ($0 < S^* < 1$) indicates that the probability of sticking the adsorbate material to the adsorbent surface is high and that the bonds connecting them are of a physical nature [39-40].

The temperature greatly affects the value of (S^*) [40-41], and in order to know how temperature affects the sticking probability of glycolic acid to the surface of GLR, the sticking probability has been studied at a range of temperature (288-323 K), the obtained results showed that the sticking probability value is ($S^* = 0.0562$) which indicates that the sticking probability of glycolic acid to the surface of GLR is big [42]. The apparent activation energy was calculated for this study ($E_a = -6.409 \text{ kJ.mol}^{-1}$), this value will lead to arrive at two conclusions, the first is that the sign of the apparent activation energy is negative which means that the adsorption of glycolic acid on the surface of GLR is an exothermic process, the proof for the correctness of this value is that it matches with the negative enthalpy change sign ($\Delta H = -$ value) which was calculated from the thermodynamic study.

The second conclusion is that although the process of adsorption of glycolic acid on the surface of GLR is done through the formation of physical and chemical bonds (the chemical bonds form in some cases and at high temperatures), the percentage of the physical bonds is higher than the chemical bonds, and evidence of this is the value of apparent activation energy is ($E_a < 40 \text{ kJ.mol}^{-1}$) [41,43].

TABLE 10. The values of the x-axis ($1/T$) and y-axis [$\ln(1-\Theta)$] of the developed Arrhenius equation which was calculated at various temperatures.

Temp.(K)	1 / T	Ln (1- Θ)
288	0.00347	-0.209
293	0.00341	-0.244
298	0.00335	-0.303
303	0.00330	-0.327
308	0.00324	-0.367
313	0.00319	-0.412
318	0.00314	-0.470
323	0.00309	-0.497

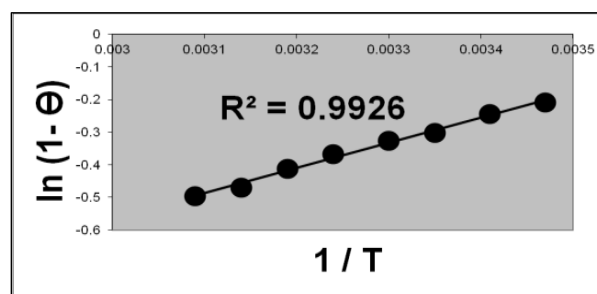


Fig.10. Drawing the x-axis ($1/T$) versus y-axis [$\ln(1-\Theta)$] for the developed Arrhenius equation.

Conclusion

From pervious results in this article, it can be concluded that grape leaf residues can be used in removing glycolic acid from aqueous solutions. Optimum conditions are use of (0.009M) glycolic acid, weight of the adsorbent material is (0.2 g GLR + 0.8 g charcoal), and shaking time is 90 minute, the percentage of the adsorption process increases at a high acidity function and using 288 K. Also, The thermodynamic study showed that the adsorption

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process is exothermic ($\Delta H = -39.2 \text{ kJ.mol}^{-1}$), spontaneous at the range of temperature (288-298 K) and the adsorption of glycolic acid causes a decrease in the randomness of the adsorption system.

Also, kinetic study of pseudo-second-order model is more in agreement with the experimental results and isotherms indicates the possibility of using both Langmuir and Freundlich models to express the adsorption system.

Sticking probability of glycolic acid to the surface of GLR is big (0.0562) and the general character of the bonds formed in the adsorption process is that they are physical.

Refereneces

1. E.R. Rene, E. Sahinkaya, A. Lewis, P.N. Lens, Sustainable heavy metal remediation, Principles and Processes 1 (2017) 1-283.
2. A.M. Abdel-Satar, M.H. Ali, M.E. Goher, Indices of water quality and metal pollution of Nile River, Egypt, The Egyptian Journal of Aquatic Research 43(1) (2017) 21-29.
3. J. Karpińska, U. Kotowska, Removal of organic pollution in the water environment, Multidisciplinary Digital Publishing Institute, 2019, p. 2017.
4. P.N. Omo-Okoro, A.P. Daso, J.O. Okonkwo, A review of the application of agricultural wastes as precursor materials for the adsorption of per-and polyfluoroalkyl substances: a focus on current approaches and methodologies, Environmental Technology & Innovation 9 (2018) 100-114.
5. M. Patel, R. Kumar, K. Kishor, T. Mlsna, C.U. Pittman Jr, D. Mohan, Pharmaceuticals of emerging concern in aquatic systems: chemistry, occurrence, effects, and removal methods, Chemical reviews 119(6) (2019) 3510-3673.
6. W.N.W. Ismail, S.U. Mokhtar, Various Methods for Removal, Treatment, and Detection of Emerging Water Contaminants, Emerging Contaminants (2020).
7. 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.
8. 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.
9. L. Reyes, C. Nikitine, L. Vilcocq, P. Fongarland, Green is the new Black—A review of technologies for carboxylic acids recovery from black liquor, Green Chemistry (2020).
10. 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.
11. A. Soni, A. Keshav, V. Verma, S. Suresh, Removal of glycolic acid from aqueous solution using bagasse flyash, (2012).
12. 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.
13. 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.
 14. R.C. Tung, W.F. Bergfeld, A.T. Vidimos, B.K. Remzi, α -Hydroxy acid-based cosmetic procedures, American journal of clinical dermatology 1(2) (2000) 81-88.
 15. I. Eroglu, These are The Worst Skincare Ingredients For People with Rosacea.
 16. J. Sharad, Glycolic acid peel therapy—a current review, Clinical, cosmetic and investigational dermatology 6 (2013) 281.
 17. 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.
 18. 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.
 19. C.R. Noll Jr, R. Burris, Nature and Distribution of Glycolic Acid Oxidase in Plants, Plant physiology 29(3) (1954) 261.
 20. D. Lakherwal, Adsorption of heavy metals: a review, International journal of environmental research and development 4(1) (2014) 41-48.
 21. R.V. Kandisa, K.N. Saibaba, K.B. Shaik, R. Gopinath, Dye removal by adsorption: a review, Journal of Bioremediation and Biodegradation 7(6) (2016).
 22. N.K. Mondal, S. Chakraborty, Adsorption of Cr (VI) from aqueous solution on graphene oxide (GO) prepared from graphite: equilibrium, kinetic and thermodynamic studies, Applied Water Science 10(2) (2020) 1-10.
 23. V.T. Trinh, T.M.P. Nguyen, H.T. Van, L.P. Hoang, T.V. Nguyen, L. Ha, X.H. Vu, T. Pham, T.N. Nguyen, N. Quang, Phosphate adsorption by silver nanoparticles-loaded activated carbon derived from tea residue, Scientific reports 10(1) (2020) 1-13.
 24. R.T. Ali, K.I. Al-Niemi, N.H. Mohammedthajji, A practical and theoretical study of the mechanical kinetics of ascorbic acid adsorption on a new clay surface, Egyptian Journal of Chemistry 64(8) (2021) 4569-4581.
 25. 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.
 26. K.I. AL-Niemi, 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) (2019) 85-102.
27. J.-P. Simonin, On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics, *Chemical Engineering Journal* 300 (2016) 254-263.
 28. S. Iftexhar, D.L. Ramasamy, V. Srivastava, M.B. Asif, M. Sillanpää, Understanding the factors affecting the adsorption of Lanthanum using different adsorbents: a critical review, *Chemosphere* 204 (2018) 413-430.
 29. N.S. Al-Kadhi, The kinetic and thermodynamic study of the adsorption Lissamine Green B dye by micro-particle of wild plants from aqueous solutions, *The Egyptian Journal of Aquatic Research* 45(3) (2019) 231-238.
 30. H.-K. Chung, W.-H. Kim, J. Park, J. Cho, T.-Y. Jeong, P.-K. Park, Application of Langmuir and Freundlich isotherms to predict adsorbate removal efficiency or required amount of adsorbent, *Journal of Industrial and Engineering Chemistry* 28 (2015) 241-246.
 31. T.S. Khayyun, A.H. Mseer, Comparison of the experimental results with the Langmuir and Freundlich models for copper removal on limestone adsorbent, *Applied Water Science* 9(8) (2019) 1-8.
 32. E. Ajenifuja, J. Ajao, E. Ajayi, Adsorption isotherm studies of Cu (II) and Co (II) in high concentration aqueous solutions on photocatalytically modified diatomaceous ceramic adsorbents, *Applied Water Science* 7(7) (2017) 3793-3801.
 33. G.M. Al-Senani, F.F. Al-Fawzan, Adsorption study of heavy metal ions from aqueous solution by nanoparticle of wild herbs, *The Egyptian Journal of Aquatic Research* 44(3) (2018) 187-194.
 34. 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.
 35. Abdullah, L. W., Saied, S. M., & Saleh, M. Y. (2021). Deep eutectic solvents (Reline) and Gold Nanoparticles Supported on Titanium Oxide (Au-TiO₂) as New Catalysts for synthesis some substituted phenyl (substituted-3-phenyloxiran) methanone Enantioselective Peroxidation. *Egyptian Journal of Chemistry*, 64(8), 4381-4389.
 36. 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.
 37. G. Ciobanu, S. Barna, M. Harja, Kinetic and equilibrium studies on adsorption of Reactive Blue 19 dye from aqueous solutions by nanohydroxyapatite adsorbent, *Archives of Environmental Protection* 42(2) (2016) 3--11.
 38. S.E. Abechi, Studies on the mechanism of adsorption of methylene blue onto activated

-
- carbon using thermodynamic tools, *Science World Journal* 13(2) (2018) 17-19.
39. Karam, F. F., Saeed, N. H., Al Yasarri, 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.
40. T.S. Najim, S.A. Yassin, Removal of chromium from aqueous solution using modified pomegranate peel: mechanistic and thermodynamic studies, *E-journal of Chemistry* 6(S1) (2009) S153-S158.
41. A. Swelam, 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) (2019) 1499-1517.
42. 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.
43. Saied, S., Mohammed, S., Khaleel, B., Saleh, M. (2021). Comparative Studies between Conventional Techniques and Green Chemistry to Synthesis of Novel Piperidinium Salts Ionic Liquids (PBSILs). *Journal of Chemical Health Risks*, 11(4), 451-456. doi: 10.22034/jchr.2021.686640