

Adsorption of Folic Acid on The Surface of Charcoal Extracted from Pomegranate Peels

Ayat Ahmed shukran^{1,*}, Lekaa Hussain Khadim²

¹M.Sc-Student, Part of Thesis., Department of Chemistry, College of Education for Girls, University of Kufa, Iraq

²Advisor, Department of Chemistry, College of Education for Girls, Kufa University, Iraq

*Corresponding author: dr.nagham_mj@yahoo.com

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Abstract Adsorption from aqueous solutions by employing Peel of pomegranates charcoal (PP) for folic acid as inexpensive and accessible adsorbent materials are explored in this research. The sorption behavior of (PP) toward folic acid was investigated using batch adsorption studies as a function of temperature, pH, reaction duration, dose of (PP) wastes, and beginning concentration. Time-dependent tests revealed that for (PP), adsorption achieved equilibrium after 90 minutes. Folic acid adsorption is reported to be more effective in acidic pH for (PP). Equilibrium isotherms were investigated by using Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) models and it was observed that the equilibrium data could be well explained by Temkin for the adsorption process on (PP) wastes. The experimental findings showed that the nine kinetics models, which included basic first-order, pseudo first-order, second-order, and pseudo second-order models, followed the Pseudo second-order equation for PP with strong correlation coefficients ($R^2 = 0.9997$). The determination of thermodynamic parameters, including ΔH° , ΔS° , and ΔG° , revealed a predominance of physisorption, according to the data. The adsorption's endothermic nature process is confirmed by the positive values of ΔH and ΔS , which also enhance the unpredictability of the system interface. The favorable and spontaneous adsorption process is shown by the negative value of ΔG . The results show that PP may be effectively employed as a pharmaceutical adsorbent to remove folic acid from liquid states.

Keywords: langmuir, temkin, dubinin, isotherm

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1. Introduction

Adsorption is the adhesion [1] of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. [2] This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the adsorbate) is dissolved by or permeates a liquid or solid (the adsorbent). [3,4] While adsorption does often precede absorption, which involves the transfer of the adsorbate into the volume of the adsorbent material, alternatively, adsorption is distinctly a surface phenomenon, wherein the adsorbate does not penetrate through the material surface and into the bulk of the adsorbent. [5,6,7,8] The term sorption encompasses both adsorption and absorption, and desorption is the reverse of sorption. The act of manufacturing itself causes pollution. Large amounts of waste, such as chemicals, solvents, and byproducts, can be produced throughout the pharmaceutical manufacturing process [9], which pollutes the air and water. Antibiotic resistance is further facilitated by the use of antibiotics in livestock production, which releases these compounds into the environment

through animal waste [11,12] and promotes growth and prevents sickness. [13] Illustration Folic acid is a water-soluble vitamin necessary for the development of cells and development. It is often referred to as vitamin B9 or folic acid. It plays a crucial role during times of rapid cell division and expansion [14,15,16], such as pregnancy or adolescence, in the synthesis of DNA and RNA, the building blocks of genetic material. The synthesis of new red blood cells and the avoidance of anemia depend on folic acid [17,19]. It is also necessary for the metabolism of homocysteine, an amino acid that can damage blood vessels in excess, and for the creation of some other amino acids. [20,21,22,23,24].

2. Materials and Methods

2.1. Preparation of Pomegranate Peel Charcoal Powder

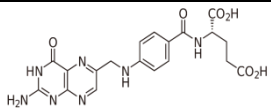
Pomegranate peel (pp) are collected from the Iraq city rinsed with water, and dried in the air for 48 h in an oven at a temperature of 80°C; the dried (pp) are placed in oven, also material crushed to produce a fine nutty powder. The

(IDC) powder is activated and carbonized in two phases (CA-P): chemical activation with phosphoric acid at a 5M concentration (1:1) for 24 h and physical activation with carbonization in an oven at 500 °C for two hours, washed with hot water and dried and Sifted to size by 600µm [5]

2.2. Preparation of Folic Acid Solution

This investigation was carried out in the Chemistry Department at the University of Kufa, Iraq's College of Education. The standard stock solution of folic acid was made by dissolved 0.5 g of weight in 500 ml of distilled water containing a measure of 1000 ppm. Next, various folic acid concentrations It was made between 50 and 500 parts per milliliter. The drug's spectrum was captured with an ultraviolet-visible spectrophotometer to determine its maximal adsorption, with pure water serving as the blank. Afterwards, a UV-visible spectrophotometer was used to test each of the ten samples in order to calculate the medicine's calibration curve. Folic acid.

Table 1. Properties of Folic acid

| Specification sheet | | Structure |
|------------------------------------------------------------------------------------|---------------------------------------------------------------|------------------------------------------------------------------------------------|
| Chemical formula | C ₁₉ H ₁₉ N ₇ O ₆ |  |
| Molecular Weight | 441.40 | |
| Appearance | Yellow | |
| Solubility | Water | |
| 2-[4-[(2-amino-4-hydroxypteridin-6-yl)methylamino]benzoyl]amino]pentanedioic acid. | | |

2.3. Effect of Contact Time

Using a Precision Scientific's shaker water bath (GCA) at a certain speed (150 rpm) and the necessary dosage of adsorbent (0.15 gm), 20 ml of solutions containing folic acid at a known concentration (500 mg/l) at pH =5 were shaken. The batch adsorption procedure was performed at 307 K. The solution was filtered using a Centrifuge (Magafuge 10, Herouse Sepatech) after every 30 minutes to estimate the time required to reach equilibrium. A spectrophotometer (Biochrom Ltd., United Kingdom) was then used to examine the solution. At λ_{max} = 279 nm. Based on the results, the time required to reach equilibrium was determined to be 90 minutes (Folic acid).

2.4. Effect of Activated Charcoal Weight

In order to determine the ideal weight of the active surface on which folic acid medicine can be adsorbed at a temperature of 307 K, the impact of the weight of the activated charcoal on its adsorption capabilities was investigated. Following 130 minutes in a shaking water bath with varying weights of activated charcoal (0.05, 0.1, 0.15, 0.2, 0.3, 0.4, and 0.5 gm), fixed volume (20 ml), and concentration (500 ppm for folic acid), the mixture was filtered through filter paper (110 mm), and the absorbance of the filtrate was measured using a spectrophotometer at predetermined λ_{max}. [6]

2.5. Effect of Zero Charge Point

In order to determine the optimal surface charge of the adsorbent, ten medicine samples were prepared in a volume of twenty milliliters at a concentration of five hundred part per million. Following this, forty milliliters of NaNO₃ salt solution were supplemented with a concentration of one micromole (0.1 M). The PH of the ten samples was then adjusted to (2,3,4,5,6,7,8,9,10,11) utilizing a basic NaOH solution at a concentration of (0.1M) and an acidic (HNO₃)-solution, respectively. Prior to mixing. The adsorption was determined. Recent research works reported activated carbon as an effective agent to adsorb cationic species of toxic materials from multi-pollutant systems and also proposed possible adsorption mechanisms with supporting evidences ., The adsorption surface was then put at room temperature with a set weight of 0.2 grams and left for 24 hours. Following filtering, the filtrate's absorbance was determined, and the acidity function was then adjusted [7].

$$\Delta Ph = pH_f - pH_i \quad (1)$$

2.6. Adsorption Isotherms

The findings of the isothermal adsorption model can be expressed using a variety of isotherm models. In the current work Langmuir, Freundlich, Elovich, Harkin-Jura, Temkin, and Dubinin isotherms are employed to examine the practical data [8]. A fixed 0.1 grams of activated charcoal in weight was added to ten prepared medication samples. The medication samples are placed in a water bath shaker for the predetermined amount of time. Each sample is then filtered through filter paper, and a spectrophotometer measures the absorbance of the filtrate at the relevant λ_{max}. The concentration of the adsorbent for each was determined (at equilibrium) using the following quantitative formula [9].

$$(C_0 - C_e) * V \text{ sol} / M = Q_e \quad (2)$$

In this case, Q_e stands for the quantity of adsorbate (mg/g).

C₀: Indicate the amount of primary material adsorbent in milligrams per liter.

C_e: It displays the concentration under ideal circumstances (mg/L),

V sol: the adsorbent solution's volume (L), and

M: Adsorbent weight (g).

3. Results and Discussion

3.1. Calibration Curve for Folic Acid

The UV spectrum for Folic acid medication were displayed in figure (1) Reordering the maximum wavelengths using a two-beam visible ultraviolet spectrometer, the results were (279 nm) for Folic acid and these results are similar to the previous references [10,22]. The folic acid calibration curve produced was displayed in figure (2) with an R² of 0.9505, indicating the linearity of the curves that follow the Beer-Lambert Law at the specified concentration.

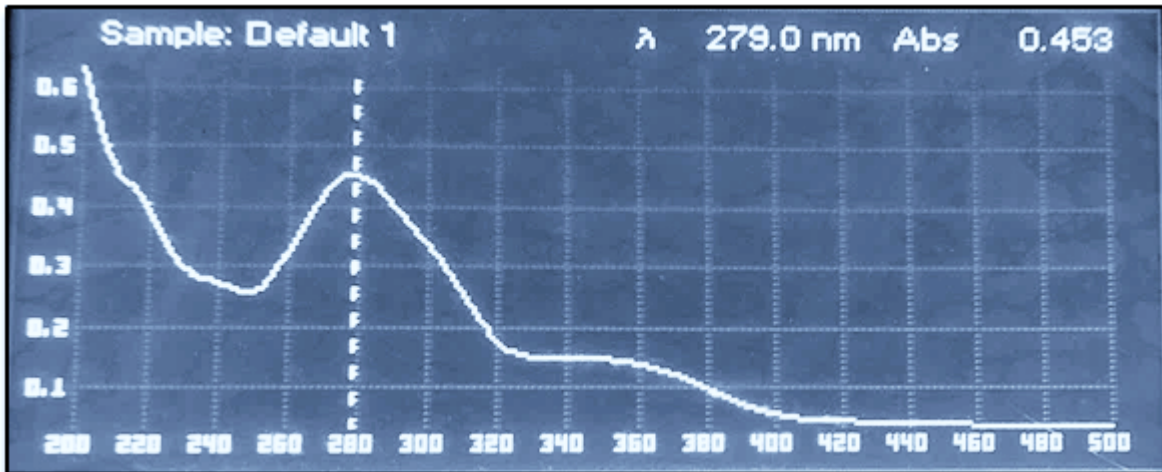


Figure 1. UV-visible spectra of Folic acid in distilled water pH (7)

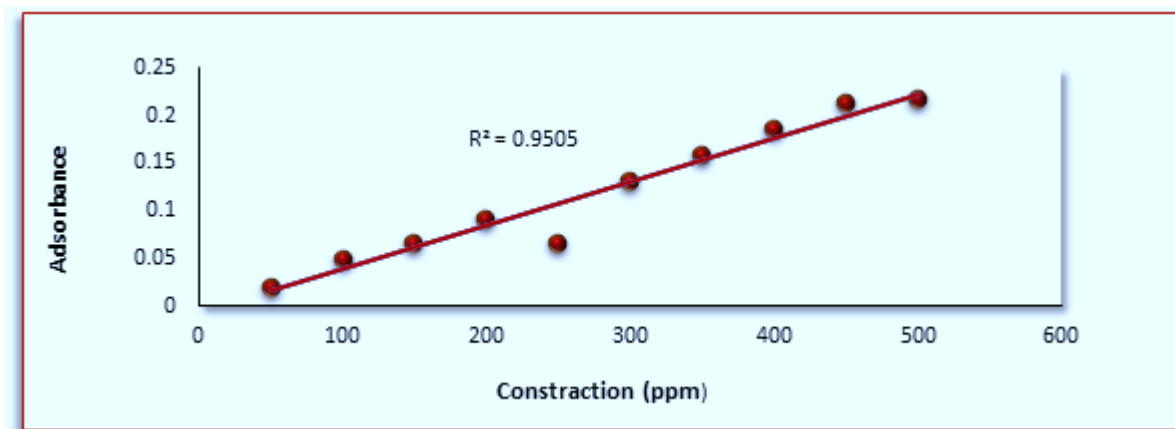


Figure 2. Calibration curve of Folic acid in distilled water at pH = 5



Figure 3. Impact of contact duration on the process of adsorption of 500mg/L of treatment at 307K and pH = 5

Activated carbon is usually derived from waste products such as coconut husks; waste from paper mills has been studied as a source. [22,23] These bulk sources are converted into charcoal before being 'activated'. When derived from coal, it is referred to as activated coal. Activated carbon is used in methane and hydrogen storage, air purification, [24,25,26] capacitive deionization, supercapacitive swing adsorption, solvent recovery, decaffeination, gold purification, metal extraction, water purification, sewage treatment [27,28,29,30].

3.2. Effect of Contact Time

The optimal duration of contact between the medication and the activated charcoal surface was determined in this study, and the findings indicated that ninety minutes was the ideal duration for folic acid medication. As shown in figure (3), the amount being adsorbed was high at first and then started to decrease. This could be because the medicine molecules were able to adhere to the unsaturated

active sites on the surface, increasing the amount of adsorption; however, when the activated surface's these locations became saturated, the amount of material to be adsorbed started to decrease. [31,32,33,34], Activated carbon treatment removes such impurities and restores plating performance to the desired level., The customization of adsorbents makes them a potentially attractive alternative to absorption. Because adsorbents can be regenerated by temperature or pressure swing, this step can be less energy intensive than absorption regeneration methods.

3.3. Effect of Activated Charcoal Surface Weight

Figure (4) illustrates the positive association that was found when the activated charcoal weight was examined. Additionally, the results demonstrated that the proportion of folic acid medication eliminated from the solution rose from 48% to 80% as the adsorbent dose increased. This

might be the result of a rise in the quantity of adsorption sites and surface area. [24]

3.4. Adsorption Isotherm Model Study

The adsorption isotherm, which represents the connection between a substance's concentration in the equilibrium solution and the quantity adsorbed at constant temperature, is significant from both a theoretical and practical standpoint [25]. Finding the right model to utilize for design reasons requires analyzing the isotherm data and fitting it to several models. The coefficients of correlation, or R^2 values, were used to analyze how well the isotherm models applied to the completed adsorption research [26]. A collection of isotherm models have been evaluated; Freundlich, Langmuir, Tempkin and Dubinin-Radushkevich (D-R). The process of adsorption isotherm is depicted in Figure (5).

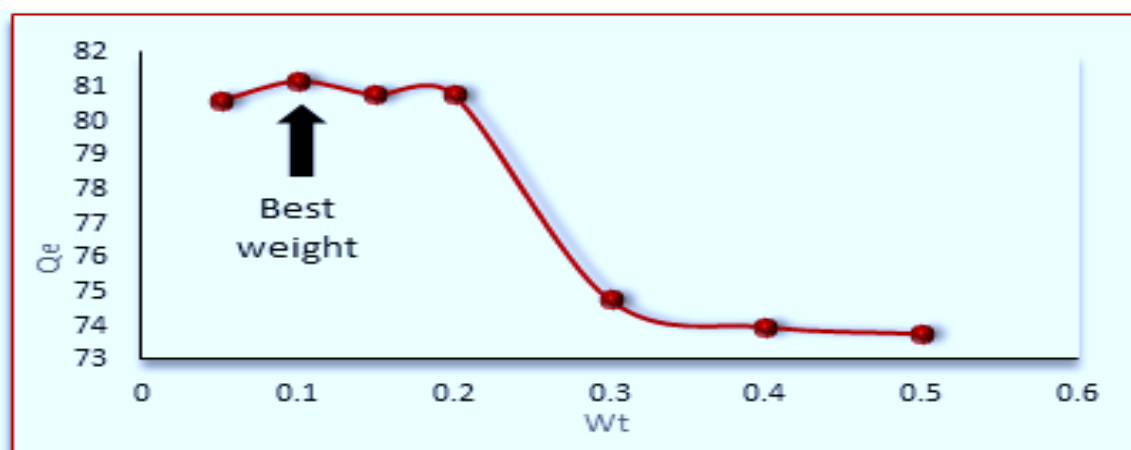


Figure 4. Impact of the weight of activated charcoal on the process of adsorption of 500mg/L of medicine at 307 K and pH =5

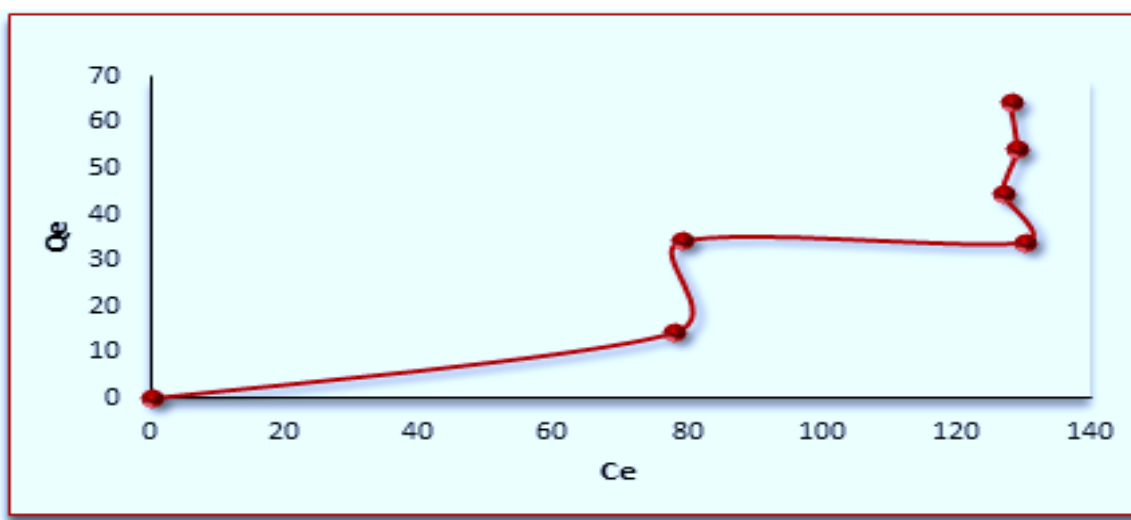


Figure 5. Adsorption isotherms of folic acid drug on the surface of pomegranate peel charcoal at a temperature of 307 K and an acidic pH = 5

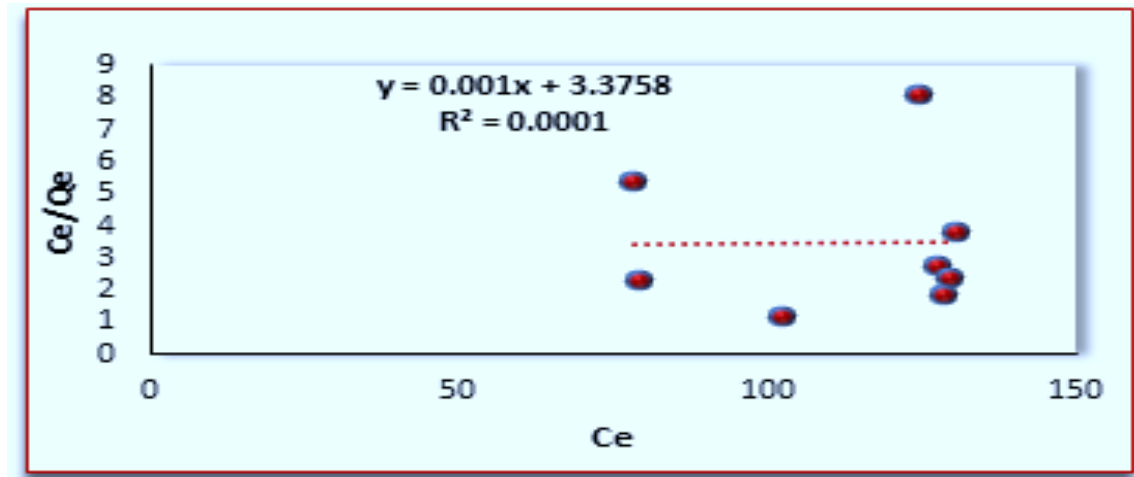


Figure 6. Langmuir isotherms at 307 K for adsorption of 500 mg / L of medicine on Activated Carbon from Pomegranate peel at pH=5

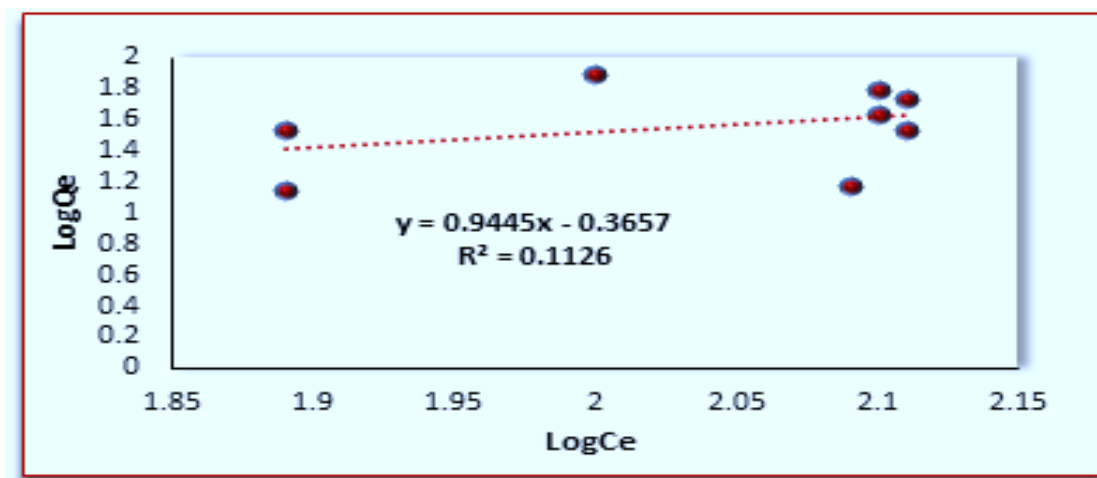


Figure 7. Freundlich isotherms at 307 K for adsorption of 500mg / L of medicine on Activated Carbon from Pomegranate peel at pH=5

3.4.1. Langmuir Isotherm Model

The Langmuir equation, with its strong theoretical foundation and ease of application, is arguably the most extensively used model for understanding the adsorption isotherm [16]. According to this hypothesis, sorbet molecules do not interact with one another during monolayer sorption on a homogenous surface. In addition the model assumes homogeneous energies of sorption on to the surface and no transmigration of the adsorbate. The Langmuir isotherm equation is expressed as follows in its linearized version [17]:

$$Ce / qe = 1 / K_L \cdot q_m + Ce / q_m \quad (3)$$

The formula is as follows: Ce (mg l^{-1}) is the equilibrium concentration of folic acid in solution; q_m (mg g^{-1}) is the adsorbent's monolayer adsorption capacity; K_L (L mg^{-1}) is the adsorption energy; and q_e (mg g^{-1}) is the quantity adsorbed per unit mass of adsorbent corresponding to full covering of sites. A summary of the relevant parameters may be found in Table 2, and Figure 6 displays the linearized Langmuir equation. The findings show that, with inadequate fitting on both wastes, the Langmuir model is unable to adequately characterize the experimental data.

3.4.2. Isotherm Freundlich

Figure (7) illustrates how the adsorption takes place on multi-layered, heterogeneous surfaces. The Freundlich adsorption equation was utilized to apply folic acid medication to the Pomegranate Peel Coal surface at a temperature of 307 K. The adsorption intensity was expressed by the Freundlich constants, denoted by (n), which were calculated. the degree to which the surface is saturated with the curve's curvature. and (Kf), which derives from the slope and intercept and reflects the surface's adsorption capability. According to the following equation [18], the constants are displayed in Table (2) when plotting $\ln Q_e$ versus $\ln C_e$.

$$\text{Log } Q_e = \text{Log } K_f + 1/n \text{ Log } C_e \quad (4)$$

where K_f and n are the system's Freundlich Constants, which correspond to the adsorption intensity and capacity, respectively.

3.4.3. Elovich Isotherm

The equation that describes Elovich's The model is based on kinetic data and explains the relationship in the following equation under the supposition that the number

of adsorption sites increases exponentially with adsorption, indicating that adsorption is multilayered. [19,27], the result are revealed in Figure (8).

$$\ln q_e / C_e = \ln K \cdot q_m - 1 / (q_m \cdot Q_e) \quad (5)$$

3.4.4. Harkin-Jura Adsorption Isotherm

The basis of the Harkin-Jura isotherm model, which is suitable for systems using solid fuels (Iyer and Kunju, 1992), is the notion that multilayer adsorption may take place on the adsorbents' surface where the distribution of pores is not uniform. Here is how this Harkin-Jura isotherm model is expressed.

$$1 / Q_e^2 = B / A - 1 / A \cdot \log C_e \quad (6)$$

where the Harkin-Jura constants A and B are used. The Harkin-Jura isotherm model has been utilized in the research of kinetics, adsorption isotherms, and the

elimination of Folic acid from aqueous solution using activated charcoal [20,28], figure (9) displays the isotherm of Harkin-Jura isothermal model for Folic acid .

3.4.5. Temkin Isotherm

Additionally, by using the following equation , Temkin parameter also describes the isothermal work of the adsorption process [21]:

$$Q_e = B \ln A + B \ln C_e \quad (7)$$

Plotting Q_e vs. $\ln C_e$ can be used to compute A and B, which are the Temkin constants. The correlation coefficient in conjunction with the parameters A and B. Figure (10), which displays the investigation's findings, shows that the adsorption process primarily follows the physical type [22,29].

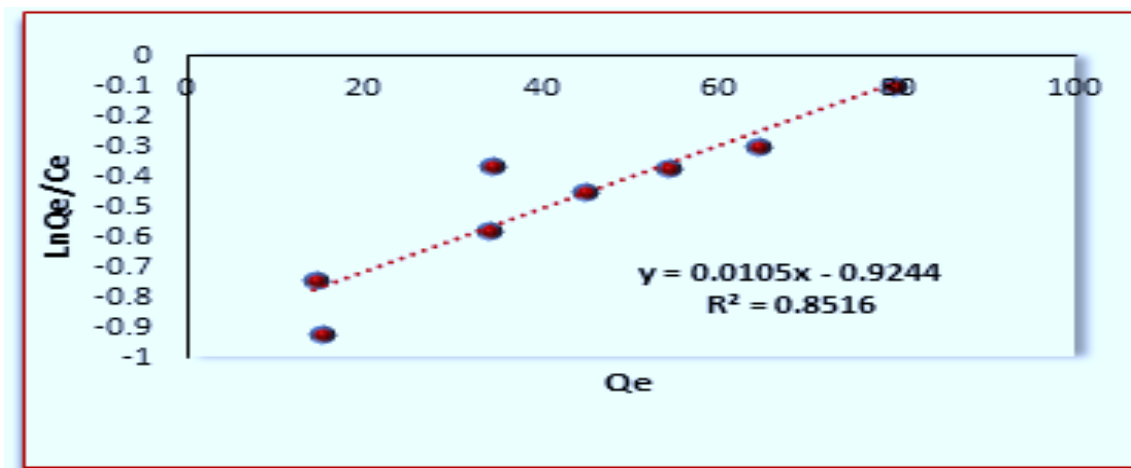


Figure 8. Elovch isotherms at 307 K adsorption of 500 mg / L of medicine on Activated Carbon from Carbon from Pomegranate peel at pH =7

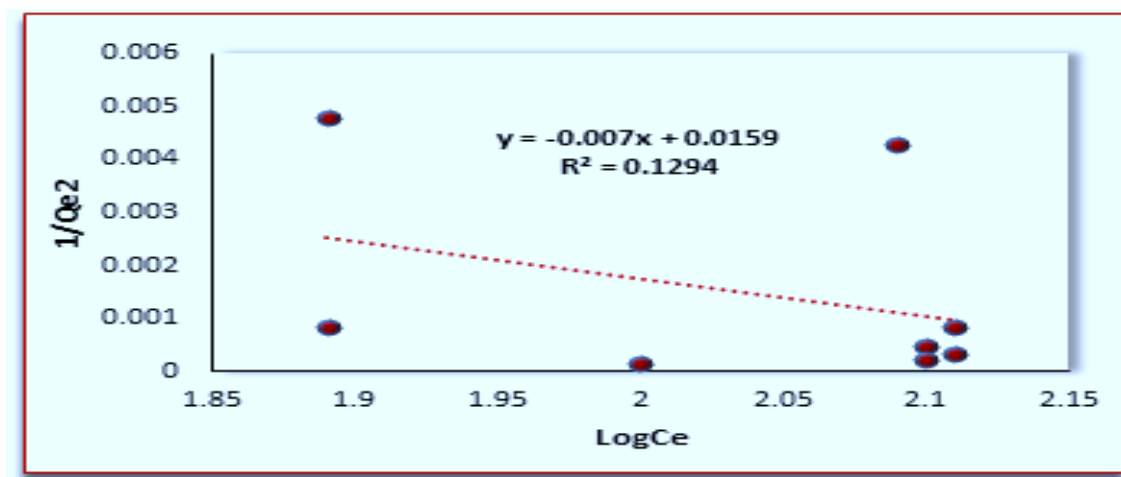


Figure 9. Harkin-Jura isotherm at 307 K for adsorption of 500 mg/L of medicine at pH =5

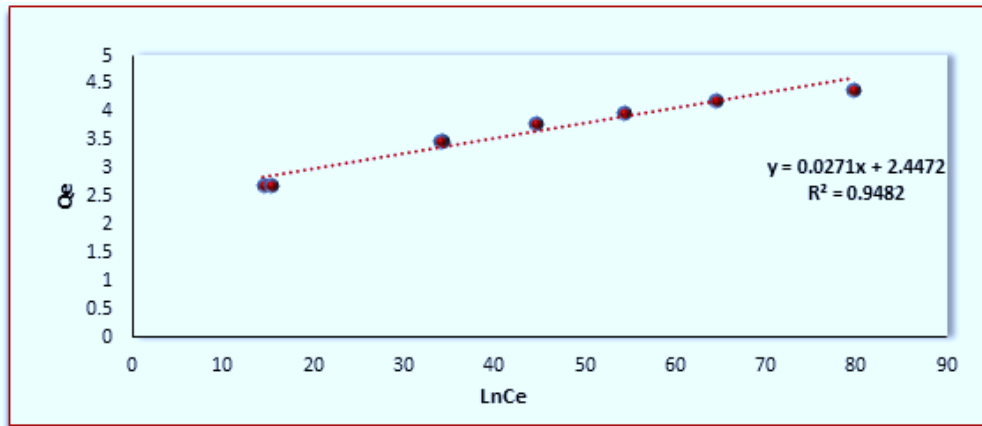


Figure 10. Temkin isotherm at 307 K for adsorption of 500 mg/L of medicine at pH =5

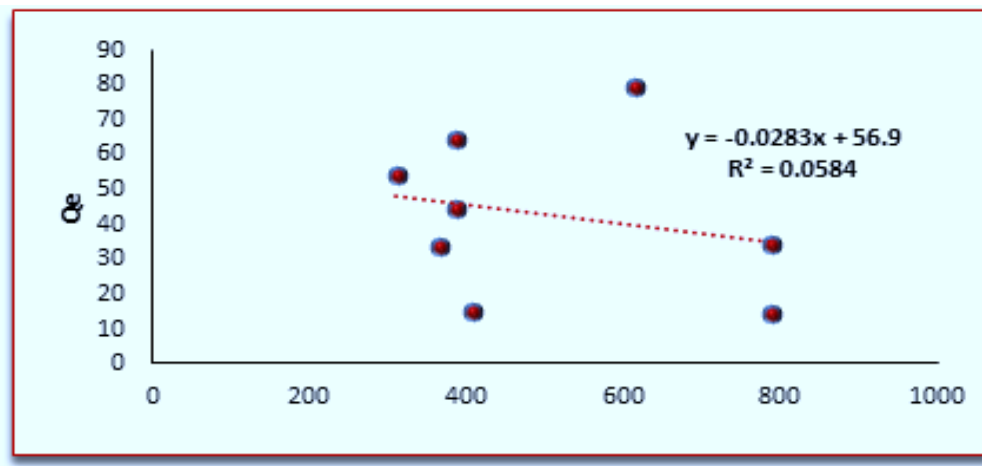


Figure 11. Dubinin isotherm at 307 K of 500 mg/L of folic acid at pH =5

3.4.6. Dubinin Isotherm

This model is only suited for intermediate-range of adsorbate concentrations as it demonstrates unrealistic asymptotic performance and at low pressure does not anticipate Henry's laws. may also be used to compute the sorption energy, which is the average free energy of adsorption for each adsorbate molecule. All pertinent data can be acquired by graphing the adsorption data as a function of the logarithm of the amount of adsorbate adsorbed vs the square of potential energy, as the Dubinin model is temperature-dependent. Figure 11 illustrates Dubinin's [23,35] findings.

$$\ln Q_e = \ln Q_m - B \epsilon^2 \quad (8)$$

$$\epsilon = R T \ln(1 + 1/C_e) \quad (9)$$

All related data in table (2) can be acquired by graphing the adsorption data as a function of the logarithm of the amount of adsorbate adsorbed vs. the square of potential energy, as the Dubinin model is temperature-dependent.

3.5. Effect of pH

At different pH values between 2 and 12 at 307K, the effect of pH on the adsorption of folic acid on pomegranate peel charcoal was examined. The percentage of folic acid removed in relation to pH variation is displayed in Figure 12. As can be seen in Figure 5, the

amount of adsorption rose as the pH of the folic acid solution increased up to pH. 6, after which it declined as the pH value climbed., Activated carbon is used for adsorption of organic substances[28] and non-polar adsorbents and it is also usually used for waste gas (and waste water) treatment. It is the most widely used adsorbent since most of its chemical, it depends on pH.

Table 2. Isotherms parameters of folic acid sorption on to Pomegranate Peel charcoal at 307 K and pH =5

| Folic acid | Linear equation isotherm model | parameters | Temperature 307 K |
|------------|------------------------------------------------------------------------|----------------------------------------------------------------------------------|-----------------------------|
| Folic acid | Langmuir $\frac{ce}{qe} = \frac{1}{KL \cdot q_m} + \frac{ce}{q_m}$ | KL(L/mg) q _m (mg/g) R ² | 0.000296 1000 0.0001 |
| | Freundlich $\ln q_e = \ln k_f + \frac{1}{n} \ln c_e$ | n K _f (l/mg) R ² | 1.0593 0.4308 0.1126 |
| | Tempkin $Q_e = B \ln \tau + B \ln c_e$ | KT(L/mg) B(J/mol) R ² | 4.503 0.0271 0.9482 |
| | Elovich $\ln \frac{q_e}{c_e} = \ln k \cdot q_m - \frac{1}{q_m} q_e$ | q _m (mg/g) K R ² | -95.238 4.635 0.8516 |
| | Harkins-Jura $\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A} \log C_e$ | A B R ² | 142.857 2.2714 0.1294 |
| | Dubin $\ln q_e = \ln q_m - \beta \epsilon^2$ | Q _m (mg/g) β(mol ² /KJ ²) R ² | 4.0412 -0.0283 0.0584 |

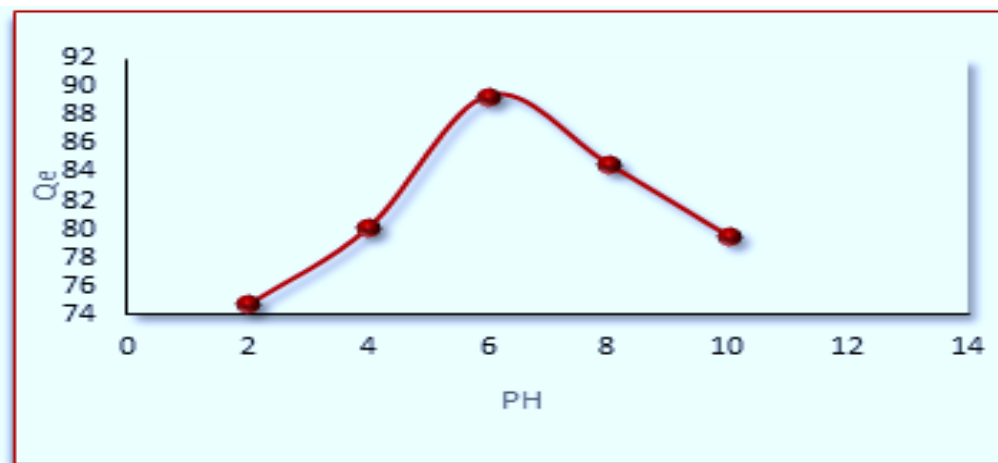


Figure 12. Effect of pH on percentage removal of Folic acid on to pomegranate peel charcoal at 307K and conc. 500mg/L

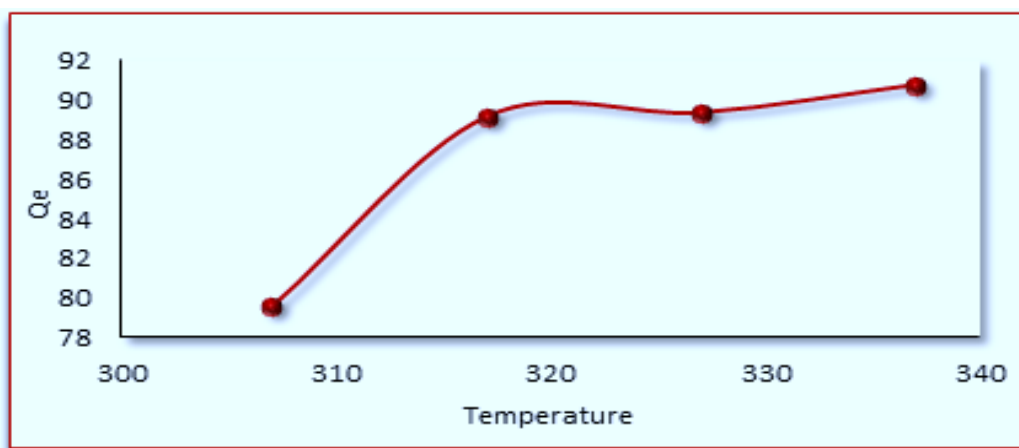


Figure 13. Effect of temperature on adsorption of Folic acid of 500mg/L at pH =5

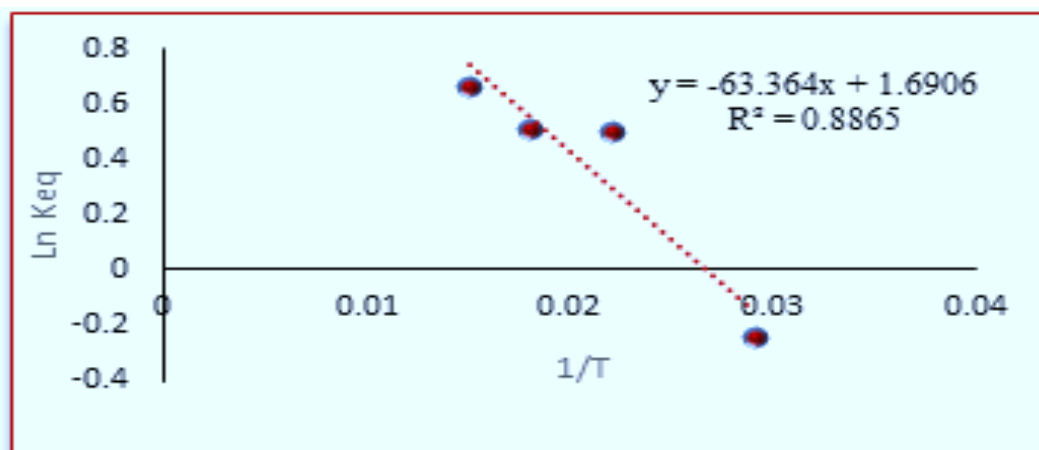


Figure 14. Relationship between the reciprocal of temperature and the equilibrium constant for the adsorption of (20ml) at a concentration of (500mg/L) of the pomegranate peel charcoal

3.6. Effect of Temperature

The efficacy of the adsorption process on the activated charcoal surface is largely dependent on temperature. Figure 13 shows the effect of temperature on the adsorption of folic acid. The obtained results showed that the adsorption of folic acid increased with temperature increment, especially at (327, 337 K). This could be

connected to the surface's activation at high temperatures or the enlarged pore size. These studies were carried out at various temperatures (307, 317, 327, and 337 K) to observe how this variable affected the ability of the adsorption process for medication on the surface. [24,36].

Probability is $S \ll 1$, indicating physisorption as the mode of adsorption. To assess the thermodynamic viability of folic acid adsorption, thermodynamic parameters were

computed. Thermodynamic considerations are required to determine whether the process is spontaneous or not, and one crucial criteria for non-spontaneity is the Gibbs free energy change [35], ΔG° . The following equation was used to derive the entropy ΔS and enthalpy ΔH° parameters, which are necessary to estimate the process's Gibbs free energy:

$$\ln k_{eq} = \Delta S/R - \Delta H/RT$$

$$\Delta G = \Delta H^\circ - T\Delta S^\circ$$

Table 3. Thermodynamic Parameters and sticking probability for Folic acid sorption on to (Pomegranate peel charcoal)

| T(K) | 1/T(K ⁻¹) | ΔG KJmol ⁻¹ | ΔH KJmol ⁻¹ | ΔS JmolK ⁻¹ |
|------|-----------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 307 | 0.029 | -3788.115 | 526.77 | 14.055 |
| 317 | 0.022 | -3928.665 | - | - |
| 327 | 0.018 | -4069.215 | - | - |
| 337 | 0.015 | -4209.765 | - | - |

Where T is the temperature (K), R is the ideal gas constant (8.314 J mol⁻¹), and Keq is the linear sorption distribution coefficient. The link between temperature and K is depicted in Figure 14. The adverse values of ΔG demonstrate that The process of adsorption is spontaneous., and the positive value of ΔS° indicates that there is an increase in randomness at the solid-solution interface during the adsorption of folic acid. Table 3

displays the surface coverage, and thermodynamic characteristics of folic acid adsorption on pomegranate peel [36] in a temperature range of (307, 317, 327, and 337 K) and pH=5.

3.7. Adsorption Kinetics

To evaluate the adsorption kinetics of folic acid onto Pomegranate Peel charcoal wastes, various kinetic models are used to suit the experimental data, which were analyzed using fundamental first-order, pseudo-first-order, second-order, and pseudo-second-order equations as provided [25,26,27].

$\ln q_t = K_1 t + \ln q_0$ First-order simplicity

$\ln (q_e - q_t) = \ln q_e - K_1 t$ Pseudo first-order

$1/q_t = K_2 t + 1/q_0$ Second-order

$t/q_t = 1/K_2' q_e + 1/q_e t$ Second-order pseudo

Where k_1 , k_1' , (min⁻¹) and K_2 , K_2' (g mg⁻¹ min⁻¹) are the simple first-order, pseudo first-order, second-order, and pseudo second-order adsorption rate constants, in that order; q_0 is the initial amount of folic acid sorbed (mgg⁻¹). In Figure 15 Figure 16, the models plots are displayed. The findings show that the major folic acid adsorption process on pomegranate peel charcoal is pseudo-second-order adsorption.

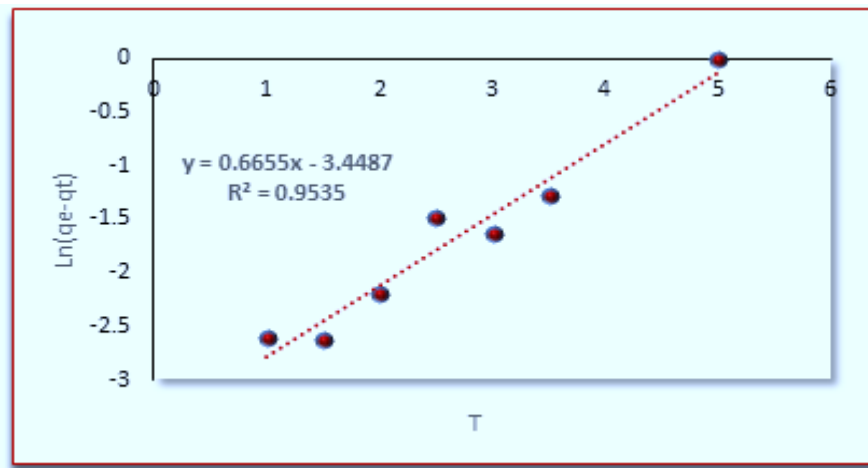


Figure 15. Simple first order adsorption of folic acid on Pomegranate Peel charcoal in 307 K , pH= 5

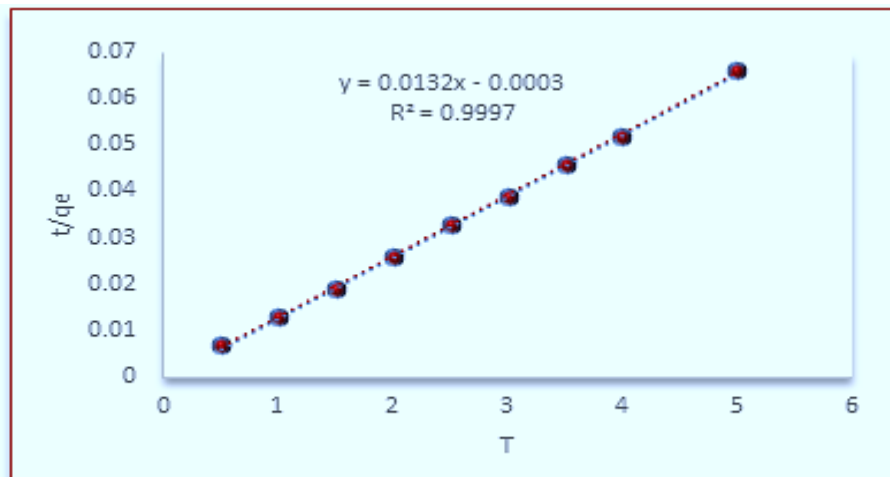


Figure 16. Second-order adsorption of folic acid on Pomegranate Peel charcoal in 307 K ,PH=5

4. Conclusion

Studies have been conducted on the adsorption of folic acid onto (PP) wastes. Adsorption tests were conducted at different temperatures, sorbent dosages, contact times, pH values, and concentrations of folic acid. The findings of the analysis of the equilibrium data using the Freundlich, Langmuir, Temkin, and D-R isotherm models suit the Temkin equations rather well. It was discovered that the equilibrium for (PP) was reached in 90 minutes, and that 5 was the ideal pH for folic acid adsorption. The pseudo-second-order adsorption process, which is the result of kinetic studies that adhere to a temperature model, demonstrates that adsorption is endothermic, spontaneous. This investigation concludes showed agricultural wastes (PP) are superior adsorbents for removing folic acid from water-based solutions.

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