Thermodynamic Study For Removing Of Crystal Violet Dye On Iraqi Porcelanite Rocks Powder

1Saad Imran .Al-Abadi *  , 1Muneer A .Al- Da’amy  and  2 Eman T. Kareem
1Department of Chemistry , College of Education for Pure Science, University of Kerbala, Iraq.
2Department of Public Health , College of Veterinary Medicine, University of Kerbala, Iraq.
saadomranalbade@gmail.com

Abstract

Natural Iraqi Porcelanite Rocks powder are better adsorbents due to better functionality , surface area , employed for the adsorption of crystal violet ( cv) dye from aqueous media. Crystal violet is used as dye in cotton ;silk and printing ink , crystal violet ( cv) dye is a water - soluble ,toxic , recalcitrant organic dye that cause several health problems and environment pollution. This study involves the adsorption of crystal violet ( cv) dye adsorbed from solution on the Iraqi Porcelanite Rocks powder surface was characterized by numerous techniques AFM. The Iraqi Porcelanite Rocks powder showed promising adsorption ability for Crystal violet dye. Batch experiments were designated to determine the effect of PH, dye concentration ,adsorbent dose ,temperature change and contact time in dye removal. Process variables were optimized and maximum dye adsorption of 31.38 mg /g was achieved at PH 8 , 0.02 g adsorbent dose, 20 min. contact time , 25°C for dye initial concentration of 30 mg/ L. The isothermal data obtained using batch adsorption technique were fitted using Langmuir ,Freundlich and Timken equation and it was found that the experimental data is well described by Freundlich isotherm model. Different thermodynamic parameters have shown natural Gibbs free energy ($\Delta G$) of the system showed increasing spontaneity with temperature while positive entropy value ($\Delta S$) implied random disorder of molecules featured at solution /solid interfase. Positive enthalpy value ($\Delta H$) confirmed endothermic nature of this adsorption process.

Keywords: Crystal violet dye Iraqi Porcelanite Rocks powder , Langmuir, Temkin and Freundlich isotherms

1. Introduction

Contamination with dyes during the manufacture of tissues is a major source of environmental pollution, and therefore the removal of dyes is an important consideration, not only because of the potential toxicity of the pigments, which pose environmental problems, but because of the effect of these dyes on the properties of natural water [1] and due to the ability of pigments to retain their dyes and structural formula when exposed to sunlight, as well as their high resistance to biodegradation, they have become a source of environmental pollution [2]. Industries produce a large amount of waste in the environment [3]. Most commercial dyes are chemically stable and difficult to remove from wastewater [4]. The industrial wastewater treatment carried out (applied) has been treated in various ways in order to remove dyes, heavy metals, and other biological organic pollutants[5]. In general, dyes were eliminated by several techniques, including (sedimentation, filtration, oxidation processes including free radicals, electrocoagulation, ion exchange and chemical oxidation [6,7]. Membrane filtration, electrochemical destruction, irradiation and ozone. Among these
methods are adsorption by far the most versatile and widely used method due to its low cost, ease of operation and easy nature. The Iraqi porcelain rocks represent one of the most adsorbents and the greatest because they contain high levels of silicon up to 50% [8]. In this research, locally low-cost rocks, which are Iraqi porcelains, as a dye absorbent surface Crystal violet.

2-EXPERIMENTS PROCEDURE:

2.1. Materials used:

- All chemicals were extremely pure and commercially available.
- We used Organic Crystal violet dye.
- NaOH, HCl, MgCl₂, NaCl, CaCl₂, KCl, Iraqi Porcelain Rocks,

2.2. Preparation the adsorbent

Porcelainite is a term used by Iraqi geologist to identify siliceous rock resemble to diatomite [9]. Porcelainite rocks in Iraq are from an Industrial bed of (0.5 to 1.5 m) thick layers associated with shale phosphorite and chert. These rocks are found in Iraq in different place. And are found in large areas within western Iraq in regions of Trebil and Akashat. Porcelainite rocks are largely composed of sponge spicules (pore). The adsorption capacity of Porcelainite is due to the large surface area within the composition of cristobalite and tridymite [11,10]. The Porcelainite samples were crushed and milled several time with deionized water and then dried through the drying oven to a consistent weight (110°C). Each sample was sieved for adsorption tests and the 75 μm and below fraction was collected.

2.3. Preparation of the dye:

For crystal violet, prepare a 100,000 μg.mL⁻¹ dye solution by dissolving 0.01g of dye in 100 mL of distilled water. the dye structures are shown in Fig. (1) and the properties of the dye selected are shown in Table (1)

![Fig.1:- Structural formula of crystal violet](image-url)
Table 1:- Characteristics of crystal violet

| Characteristics          | Value         |
|--------------------------|---------------|
| Empirical Formula        | C_{25}H_{30}N_{3}Cl |
| Class                    | Thiazine      |
| Source                   | Aldrich       |
| Water solubility         | Soluble       |
| Molecular Weight         | 407.979 g/mol |
| λ max                    | 590 nm        |
| C. I. No                 | 42555         |

2.4. Batch Adsorption

The adsorption experiments were performed in a shaker water bath at 105 rpm where the water bath contained 25mL of dye solutions at different concentrations ranging between (5.0000-30.0000 μg.mL⁻¹). The initial pH values of the solutions were previous adjusted with using hydrochloric acid at a concentration of 0.1M and 0.1M of Na OH. Iraqi Porcelain Rocks powder, weighing 0.0200g, was added to each beaker, and then the flasks were closed tightly to prevent any change in the volume of the solution inside these flasks during the experiments. After that, the flasks were placed in the shaker water bath for a predetermined time intervals (20 minutes), then the flasks were extracted from the shaker and the crystal violet dye solutions were separated from the absorbent material by filtration after centrifugation, then the absorbance were measured by a UV spectrophotometer, then the amount of adsorption of the crystal violet dye was calculated using the following equation:

$$Q_e = \frac{V(C_o - C_e)}{m} = \frac{x}{m}$$

Where: $Q_e$ (mg/g) is the amount of dye adsorbed at equilibrium (adsorbent capacity), $C_o$ and $C_e$ are (mg/L) the concentrations of dye at initial and equilibrium respectively, $V$ and $m$ is the volume of the solution (L) and m the adsorbent mass (g) respectively. Through the following relationship, the removal percentage was calculated [13]

Effects of each parameter (contact time, pH value, temperature and adsorbent dosage) were tested in a single parameter. Experiment by adjusting the parameter while keeping the other parameters constant.

3. RESULTS AND DISCUSSIONS:

Characterization Studies ATOMIC FORCE MICROSCOPE (AFM)

AFM is one of the important and popular techniques as a tool for enlarging, measuring and diagnosing, as it is used in the field of nanotechnology through which the topography of surfaces with nanoscale dimensions is defined and drawn, as it has an analysis capacity of up to nanoparticles that greatly exceeds optical microscopes by more than 1000 times. Fig.2
three-dimensional Photography of the surface of Iraqi porcelain, in which the distribution of layers and particles is shown to be irregular interspersed with gaps.\textsuperscript{[14]}

![AFM Photography of Iraqi Porcelanite Rocks](image)

**Fig. 2 AFM Photography of Iraqi Porcelanite Rocks**

### 3.1. Impact Contact Time

The relationship between contact time and adsorption capacity of Crystal Violet dye by Iraqi Porcelanite rocks was conducted through batch experiments to achieve the equilibrium as shown in Fig.3. The results showed that the equilibrium time was reached within 20 min.

![Influence of Dye Concentration on Percentage Removal of Crystal Violet by Iraqi Porcelanite Rocks](image)

**Fig.3**: Influence of Dye Concentration on Percentage Removal of Crystal Violet by Iraqi Porcelanite Rocks, temperature = 298 K, initial dye concentration = 100.0000 μg.mL\textsuperscript{-1}, pH = 8, and the adsorbent weight of 0.01 g.
3.2. Impact of Weight of Adsorbent

The change in surface weight of Iraqi Porcelanite rocks has an effect on the adsorption process of the Crystal Violet dye. The effect was studied using a constant concentration of 5.0000 μg.mL⁻¹ as the adsorbent and different weights ranged between (0.0050-0.0800 g) from the surface of the Iraqi Porcelanite Rocks at 298. Via the figure (4) We notice the increase in the removal rate with the increase in the amount of the adsorbent surface, and the reason is due to the provision of a larger area with the increase in the number of active sites prepared for adsorption of the dye on the surface, and then the amount of dye adsorbed from the solution increases and the percentage of removal increases. Weight (0.01g) gives the best percentage of removal of Crystal Violet on the surface of Porcelanite rocks therefore it was used in subsequent experiments.

![Fig.4:- influence of adsorbent dosage on the percentage removal of: Crystal Violet by Iraqi Porcelanite rocks. Temperature = 298 K, initial dye concentration 100.0000 μg.mL⁻¹, pH= 8, contact time (20 min) and agitation speed(105 rpm).](image.png)

3.3. Impact of pH

The pH is an important factor that affects the adsorption process, as the pH affects the effective adsorption sites on the adsorption surface, so if the surface contains sites that are partially charged with positive charge and others charged with negative charge, where in the acid medium the number of ions that will go to the negative charges[15] on the surface it increases so it has a bond with it. prevents adsorption and the same principle in the basic medium[16]. Figure (5) effect of the pH of the absorption of a Crystal Violet dye on the surface of Iraqi Porcelanite rocks in the pH range( 2-12). The removal of dyes was minimal at pH 2. The adsorbed dyes increased with increasing the pH from 2 to 8. Then, after pH 8, there was no notable change. For this reason, pH 8 was selected for further experiments.
3.4. Ionic strength impact

The results of the study of the effect of the ionic strength on the adsorption of the Crystal Violet dye on the Iraqi Porcelanite rocks indicate a decrease in the adsorption capacity with an increase in the ionic strength, which can be attributed to the solubility of the Crystal Violet dye, which is higher than the solubility of the salt used to increase the ionic strength. This factor in turn makes it a competition for ions salts. The results of the study indicated the difference in the effect of the different salts used in charge and volume on the Crystal Violet dye so note that the larger the charge and the larger the volume, the more it interferes with adsorption with the Crystal Violet dye in the following order:

\[
\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^{+} > \text{Na}^{+}
\]

Where the percentage of removing the dye from Crystal Violet with sodium chloride salt is higher than the percentage with calcium chloride salt. And the effect of the concentration of these salts used in concentrations ranging from \((0.0700-0.0200 \text{ M})\) of salts (NaCl, KCl, MgCl₂, CaCl₂). Concentration was used 0.01g from Crystal Violet dye, where the increase in the concentration is offset by a decrease in the percentage as shown in the study data in Figure (6) and Table(2).
| Adsorbate  | Salt Conc (M) | % Removal |
|------------|--------------|-----------|
| crystal violet |               | NaCl  | KCl  | MgCl<sub>2</sub> | CaCl<sub>2</sub> |
| 0.02       | 66.2%        | 65.4%  | 63.4% | 59.86% |
| 0.05       | 61.66%       | 61%    | 59.86% | 58.5% |
| 0.07       | 59.12%       | 58.6%  | 57.34% | 56.2% |

Table (2) Effect of ionic straight on the adsorption of Crystal Violet dye by Iraqi Porcelanite rocks. Equilibrium time =20 min, at 298 K

3.5. Effect of Temperature

The study of the effect of temperature on the adsorption process by which the values of the thermodynamic functions, Gibbs energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. The free energy of Gibbs ΔG may be calculated from the following equation:

\[ ΔG = -RT \ln K_{eq} \]  

Where:
- \( ΔG \): is a Gibbs energy change (kJ/mol),
- \( R \): is the ideal gas constant (8.314 J/mol K),
- \( T \): is the absolute temperature (K).
- \( K_{eq} \): is the equilibrium constant for the adsorption process at each temperature was calculated from the equation \[17\].

\[ K_{eq} = \frac{m \cdot Qe}{V \cdot C_e} \]  

Where: \( m \) is the weight of the adsorbent (0.02g of Iraqi Porcelanite rocks. Table (3) gives the values of LnK_{eq} at different temperatures. The heat of adsorption \( ΔH \) may be obtained from Vant Hoff’s equation \[18,17\] and determined from the slope and intercept of Van, t Hoff’s plot of Ln K versus 1/T Figure (12).

\[ \ln K_{eq} = \frac{-ΔH}{RT} + \text{con} \]  

The values of the change in entropy (ΔS) was calculated from Gibbs- Helmholtz equation

\[ ΔS = \frac{ΔH - ΔG}{T} \]
Table (4) shows the thermodynamic functions $G$, $H$ and $S$ for the removal of Crystal Violet dyes on Iraqi Porcelanite rocks at different temperatures.

| $\ln K_{eq}$ crystal violet | $T$ (K) | $1/T$ (K$^{-1}$) |
|-----------------------------|--------|-----------------|
| 1.288                       | 298    | 0.0033          |
| 1.5014                      | 308    | 0.0032          |
| 1.4054                      | 318    | 0.0031          |
| 1.67366                     | 328    | 0.0030          |
| 1.80647                     | 338    | 0.0029          |

Table (3) Values of equilibrium constant for removing crystal violet by using Iraqi Porcelanite rocks at different temperatures.

| $T$ (K) | $1/T$ (K$^{-1}$) | $\ln K_{eq}$ crystal violet |
|---------|-----------------|-----------------------------|
| 298     | 0.0033          | 1.288                       |
| 308     | 0.0032          | 1.5014                      |
| 318     | 0.0031          | 1.4054                      |
| 328     | 0.0030          | 1.67366                     |
| 338     | 0.0029          | 1.80647                     |

$y = -1.2092x + 5.2836$  
$R^2 = 0.8508$

Fig.7: Temperature Dependence of the Adsorption crystal violet on the Iraqi Porcelanite rocks. $(1/T \times 10^3)$

Table 4: Thermodynamic function $\Delta G$, $\Delta S$ and $\Delta H$ of crystal violet dye on the adsorbent surface Iraqi Porcelanite rocks at (298-328)K

| Adsorbate     | Temp. K | $-\Delta G$ (KJ/mol) | $\Delta H$ (KJ/mol) | $\Delta S$ (KJ/mol.K) |
|---------------|---------|----------------------|---------------------|----------------------|
| crystal violet| 298     | 3.1911               | 8.8211              | 0.00403              |
|               | 308     | 3.8446               |                     | 0.04112              |
|               | 318     | 3.7156               |                     | 0.03942              |
|               | 328     | 4.5641               |                     | 0.04491              |
|               | 338     | 5.0764               |                     | 0.04111              |
We note from Table 3 that the negative values of \( \Delta G \) over the temperature range(338 - 298) indicate that the adsorption of the crystal violet dye on the adsorption surface is spontaneous and the values of the adsorption inversion(\( \Delta H \)) are positive. When adsorption of crystal violet dye, which indicates the type of adsorption is endothermic, the apparent entropy change values are almost constant over the temperature range. The positive entropy characterized an increased random disorder of the system due to the loss of water which surrounding the dye molecules at the sorption on the Iraqi Porcelanite rocks \(^{19}\).

### Adsorption Isotherm

A crystal violet dye was studied on Iraqi Porcelanite rocks surface within the concentrations(5- 30 mg/L) of crystal violet dye and adsorption isotherms were obtained as shown in Table (5) at different temperatures within the range (298-328 K) and at the best conditions. The adsorption capacity \( (Q_e) \) was calculated from the following equation:

\[
Q_e = \frac{V(C_0 - C_e)}{m} = \frac{x}{m} \quad \text{.........}(7)
\]

The drawing of the relationship between the adsorption capacity \( (Q_e \text{ mg/g}) \) and the concentration at equilibrium \( (C_e \text{mg/L}) \) of the adsorbent gives the general forms of the adsorption isotherms of the adsorption at equilibrium as shown in the figure (8), which shows the adsorption isotherms of a crystal violet dye on surface Iraqi Porcelanite rocks.

**Figure (8)** adsorption isotherms of crystal violet at PH = 8 using 0.02 g from the surface of Iraqi Porcelanite rocks and equilibrium time = 20 min and at different temperatures.
The general shape of the crystal violet dye isotherm on the surface of Iraqi in the figure (8). The shape of dye adsorption isotherms were found to coincide with the S-type isotherm reported by Giles, which indicates that the orientation of the active sites on the surface is tilted or perpendicular to the high affinity of the dye on the surface.

**Isotherm Langmuir**

The adsorption of crystal violet equilibrium with increase in initial dye concentration at (298-328 K) has been fitted in Langmuir model, Freundlich and Temkin isotherms. The Langmuir isotherm is represented by the following equation: [20]

$$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{C_e}{a} \quad \ldots \ldots \ldots (8)$$

Where: (b) is the sorbent binding capacity, that is the maximum sorption upon complete saturation of adsorbent surface, and (a) is binding constant, i.e., related to the adsorption/desorption energy. a and b are Langmuir constants related to the adsorption capacity and energy of adsorption respectively [21]. The (a) and (b) values are calculated from the slopes (1/a) and intercepts (1/ab) of linear plots of $Ce/Qe$ [22] versus $Ce$ are shown in Figure 9.

**Table (5) the values of adsorption amplitudes of crystal violet on the surface of Iraqi at different temperatures**

| Temp. (K) | Adsorbate | \(C_o\) (mg/L) | \(C_e\) (mg/L) | \(Q_e\) (mg/g) | \(C_o\) (mg/L) | \(C_e\) (mg/L) | \(Q_e\) (mg/g) | \(C_o\) (mg/L) | \(C_e\) (mg/L) | \(Q_e\) (mg/g) | \(C_o\) (mg/L) | \(C_e\) (mg/L) | \(Q_e\) (mg/g) |
|-----------|-----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 298       | crystal violet | 5 | 0.4522 | 5.6800 | 0.3730 | 5.7800 | 0.3090 | 5.6600 | 0.4680 | 5.6600 |
|           |            | 7 | 0.7100 | 7.8620 | 1.0700 | 7.4100 | 0.9950 | 7.5000 | 1.3580 | 7.0500 |
|           |            | 10 | 0.9109 | 11.3600 | 1.9100 | 10.1100 | 1.8380 | 10.2000 | 1.5013 | 10.6200 |
|           |            | 15 | 2.5500 | 15.5600 | 2.3970 | 15.7500 | 2.0960 | 16.1300 | 1.6960 | 16.6300 |
|           |            | 18 | 2.9500 | 18.8000 | 2.7920 | 19.0100 | 2.2900 | 19.3600 | 2.6900 | 19.1370 |
| 308       | crystal violet | 20 | 3.5090 | 20.6130 | 3.2930 | 20.8800 | 2.5560 | 21.8050 | 3.1000 | 21.1250 |
|           |            | 23 | 3.8900 | 23.8800 | 3.6360 | 24.2050 | 2.6900 | 25.3800 | 4.0000 | 23.7500 |
|           |            | 25 | 4.1100 | 26.1100 | 3.7600 | 26.5500 | 3.1300 | 27.3300 | 4.8200 | 25.2250 |
| 318       | crystal violet | 28 | 4.3100 | 121.08 | 3.6151 | 121.92 | 3.3885 | 123.05 | 4.7488 | 116.25 |
|           |            | 30 | 4.8900 | 128.3 | 4.1897 | 129.09 | 4.5851 | 127.07 | 5.0542 | 124.72 |

\[R_L = \frac{1}{(1 + b C_o)} \quad \ldots \ldots \ldots (9)\]
Where: RL is the separation component. Where: RL values represent the type of adsorption to be permanent (RL = 0), favorable (0 < RL < 1), linear (RL = 1) or unfavorable (RL > 1), RL [23].

### Freundlich Isotherm

Freundlich adsorption isotherm model used to describe the adsorption process is represented by the following equation:

\[
\log Qe = \log Kf + \frac{1}{n} \log Ce 
\]

………………(10)

Where: \( Kf \) and \( 1/n \) are empirical constants and indicate adsorption capacity and intensity, respectively. The values of \( Kf \) and \( n \) determine the steepness and curvature of the isotherm [24].

### Temkin Isotherm

The Temkin isotherm is regularly determined by Eq. 11.

\[
q_e = \ln (\frac{KT}{Ce}) \quad \text{……….. (11)}
\]

The Temkin isotherm (Eq. 11) can be simplified to the following Eq. 12 [25].

\[
q_e = \beta \ln KT + \beta \ln Ce \quad \text{……….. (12)}
\]

where \( \beta = \frac{RT}{b} \)

(T) is the thermodynamic temperature in Kelvin degrees and (R) was the universal gas constant, 8.314 J mol\(^{-1}\) K\(^{-1}\). The consistent (b) is identified with the adsorption heat.

The experimental data for removing a crystal dye was applied to the Langmuir equation, Freundlich and the Temkin equation to see how applicable it was to the assumptions of the equations. Table (6) and Figures (9) show the exclusion of the Langmuir equation in the adsorption mechanism because there is no linear relationship (\( Ce / Qe \)) and the (Ce) values, while the equilibrium data showed the applicability of the Freundlich equation clearly when drawing log \( Qe \) versus log Ce as in Table (7), Fig. (10) Comparison with the Langmuir equation. Figures (11, and Table (8) also show the applicability of Temkin equation well when plotting \( Qe \) against the values of \( \ln Ce \).
Table (6) Data for adsorption of crystal violet on the surface of Iraqi Porcelainite rocks at different temperatures according to the application of Langmuir equation.

| Temp. | 298 K | 308 K | 318 K | 328 K |
|-------|-------|-------|-------|-------|
| Adsorbate | LogCe | LogQe | LogCe | LogQe | LogCe | LogQe | LogCe | LogQe |
| crystal violet | -0.3446 | 0.7543 | -0.4282 | 0.7619 | -0.5100 | 0.7678 | -0.3297 | 0.7528 |
| | -0.4052 | 1.0553 | 0.28103 | 1.004 | 0.26434 | 1.0086 | 0.17646 | 1.02612 |
| | 0.4065 | 1.1920 | 0.37966 | 1.197 | 0.32139 | 1.2076 | 0.2294 | 1.2208 |
| | 0.4698 | 1.2741 | 0.4459 | 1.2789 | 0.3598 | 1.29292 | 0.42975 | 1.28187 |
| | 0.54518 | 1.31414 | 0.51759 | 1.3197 | 0.40756 | 1.33855 | 0.49136 | 1.32479 |
| | 0.58994 | 1.3780 | 0.56062 | 1.38390 | 0.42975 | 1.40449 | 0.60205 | 1.37529 |
| | 0.61384 | 1.41680 | 0.57518 | 1.42406 | 0.49554 | 1.43663 | 0.68304 | 1.40183 |
| | 0.63447 | 1.47319 | 0.63042 | 1.47217 | 0.59217 | 1.5787 | 0.7226 | 1.4533 |
| | 0.68930 | 1.4966 | 0.6901 | 1.4903 | 0.70842 | 1.49276 | 0.78804 | 1.47508 |
| | -0.3446 | 0.7543 | -0.4282 | 0.7619 | -0.5100 | 0.7678 | -0.3297 | 0.7528 |
Table (7) data for adsorption of crystal violet on the surface of the Iraqi Porcelanite rocks at different temperatures according to the application of the Freundlich equation.

![Figure (10) isotherm Freundlich for adsorption of crystal violet on the surface of Iraqi Porcelanite rocks.](image)

| Adsorbate | Temp. | 298 K | 308 K | 318 K | 328K |
|-----------|-------|-------|-------|-------|------|
| crystal violet | -0.7936 | 5.6800 | -0.9861 | 5.7800 | -1.1744 | 5.8600 | -0.7592 | 5.6600 |
| | -0.3424 | 7.8620 | 0.0676 | 7.4100 | -0.0050 | 7.7000 | 0.30601 | 7.0500 |
| | -0.0933 | 11.3600 | 0.6471 | 10.1100 | 0.60867 | 10.2000 | 0.40633 | 10.6200 |
| | 0.93609 | 15.5600 | 0.8742 | 15.7500 | 0.74003 | 16.1300 | 0.52827 | 16.6300 |
| | 1.08180 | 18.800 | 1.0267 | 19.0100 | 0.82855 | 19.6300 | 0.98954 | 19.1370 |
| | 1.25533 | 20.6130 | 1.1917 | 20.8800 | 0.93844 | 21.8050 | 1.13140 | 21.1250 |
| | 1.3564 | 23.8800 | 1.2908 | 24.205 | 0.98954 | 25.3800 | 1.38629 | 23.7500 |
| | 1.41342 | 26.1100 | 1.3244 | 26.5500 | 1.14103 | 27.3300 | 1.57277 | 25.2250 |
| | 1.46093 | 29.7300 | 1.4516 | 29.6600 | 1.36533 | 30.1100 | 1.66392 | 28.4000 |
| | 1.58719 | 31.3800 | 1.5904 | 31.3600 | 1.63119 | 31.100 | 1.80992 | 29.8600 |

Table (8) isotherm Temkin for adsorption of crystal violet on the surface of Iraqi Porcelanite rocks at different temperatures.
Figure (11) isotherm Temkin for adsorption of crystal violet on the surface of Iraqi Porcelanite rocks at different temperatures.

Then the isotherm constants (a, b, RL) for Langmuir and (n, Kf) were calculated for the Freundlich model, as well as the Temkin model (B, AT) with linear correlation coefficients as shown in Table (9).

| Temp.K | Langmuir isotherm | Freundlich isotherm | Temkine isotherm |
|--------|-------------------|---------------------|------------------|
|        | a (mg/g) | b (mg/L) | r² | RL | Kf | n | r² | B | A_T | r² |
| 298    | 50.5000  | 0.2469   | 0.5614 | 0.4475 | 10.0138 | 1.522 | 0.9624 | 9.7035 | 3.2600 | 0.8786 |
| 308    | 99.0000  | 0.0870   | 0.2115 | 0.6960 | 9.00322 | 0.746 | 0.9924 | 10.386 | 2.6860 | 0.7887 |
| 318    | 81.3000  | 0.01314  | 0.24500 | 0.9384 | 6.32969 | 1.382 | 0.9023 | 10.242 | 3.3260 | 0.7721 |
| 328    | 62.1100  | 0.1523   | 0.5614 | 0.5676 | 10.3800 | 1.432 | 0.8568 | 10.323 | 2.4902 | 0.9012 |

Table.9:- Parameters of Isotherms of Adsorption of crystal violet at( 298-328) KLangmuir, Freundlich and Temkin .

Conclusion:-
- Existing research has shown that Iraqi Porcelanite rocks can be used as an optimal adsorbent for aqueous solution elimination, from a crystal violet dye.
- The outcomes also include additional advantages, in addition to reducing waste.
- The equilibrium data was found to be very consistent with Freundlich isothermal data Model, suggesting a homogeneous surface adsorption of a monolayer wastewater treatment for agricultural waste.
- Thermodynamic experiments indicated that the adsorption process was endothermic and that at solid-liquid values, the degrees of freedom in naturally decreased.
References

1. K.S. Al-Bassam, A.A. Saleh, N.A. Rashid, M.M. Shaker, and S.Korkess. (The Use of Iraqi rocks as filter aids for sulfur refining and food products as substitute for celite). Internal report, Som. (1993).

2. Patterson, A. L. "The Scherrer formula for X-ray particle size determination." Physical review 56.10 (1939): 978.

3. J.R.Baeri, P.N.Palanisamy and P.S.Kumar, (Adsorption of Basic Dye from Synthetic Textile Effluent Activated Carbon Prepared from Thevetia Peruviana), Indian J. Chemical Technology, Vol.19, pp.311-21, 2012.

4. Santhi, Thirumalaisami, and Subbayan Manonman. "Adsorption of methylene blue from aqueous solution onto a waste aquacultural shell powders (Prawn Waste)." Sustain Environ Res 22 (2012): 45.

5. Nirmala, D. V., P. Saraswathi, and M. Makeswari. "Removal of dyes and heavy metals from aqueous solution using ricinus communis as an adsorbent—a review." European Journal of Pharmaceutical and Medical Research (EJPMR) 3 (2016): 395-398.

6. Gupta, V. K. "Application of low-cost adsorbents for dye removal—a review." Journal of environmental management 90.8 (2009): 2313-2342.

7. Benadjemia, Millière, et al. "Preparation, characterization and Methylene Blue adsorption of phosphoric acid activated carbons from globe artichoke leaves." Fuel Processing Technology 92.6 (2011): 1203-1212.

8. Afaj, Adnan H. "Study of Removal of Pb, Zn, Cu and Ni Ions from Iraqi factories wastewater using local porcelanite rocks." Iraqi National Journal Of Chemistry 39 (2010).

9. S.Z. Jassim and J.C. Goff, (Geology of Iraq), Published by Dolin, Prague and Moravian Museum, Brno 1st ed., 299, 2006.

10- F. A.Uday, (Scavenging of Organic and Inorganic Water Pollutants by Iraqi Clay Minerals) Ph.D. Thesis, University of Baghdad, (2009).

11- A.S.Al-Saqqar and B.M.Al-Bayaty,(Porcelanite Rocks as a Dual Filter Media in Water Treatment Plants),J.of Engineering,4(3)(2008),2643-2653.

12. Color Index 3rd Edition Volume 4 (PDF), Bradford: Society of Dyers and Colors, 1971, page 4391, archived from the original (PDF) on June 18, 2019

13. Atkins, Peter William, and Julio De Paula. Fisicoquímica. No. 541 A85Y 1981. Fondo Educativo Interamericano, 1986.

14. S.P. Raghuvanshi, A.K. Raghav, R.Singh and A. Chandra, (Investigation of Sawdust as Adsorbent for the Removal of Methylene Blue Dye in Aqueous Solution. Proceedings of international Conference for Water and Wastewater Perspectivesin Developing Countries (NAPDEC) International Water Association, U.K.;99, 1053-1062, 2002.

15. Ramakrishna, Konduru R., and T. Viraraghavan. "Use of slag for dye removal." Waste Management 17.8 (1998): 483-488.

16. B. H.Hamed, M. I.El-Khaiary,( Kinetics and Equilibrium Studies of Malachite Green Adsorption on Rice straw-derived char), J.Hazard. Mater.,153, 701-708, (2008 )

17. Bratianu, Constantin, and Ivona Orzea. "The entropic intellectual capital model." Knowledge Management Research & Practice 11.2 (2013): 133-141.

18. AL-Rubaey, Eman TK, and Rusul AJ AL-Myali. "Removal of Azure Dyes with Novel PMF Polymer from Aqueous Solution."

19- AL-Rubaey, Eman TK, and Rusul AJ AL-Myali. "Removal of Azure Dyes with Novel PMF Polymer from Aqueous Solution."

20. I. Langmuir, (The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum), J. Am.Chem.Soc., Vol.40, No.3, pp.1361-1403, 1916.

21. N. Muhammad, J. Farr, M.D. Smith and A.D. Wheatly, (Adsorption of Heavy Metals in Slow Sand Filters), 24th ed., WEDC Conference, T water treatment, Islamabad, Pakistan, pp.346-349, 1998.

22. Gregg, Sidney John, Kenneth Stafford William Sing, and H. W. Salzberg. "Adsorption surface area and porosity." Journal of The electrochemical society 114.11 (1967): 279C.

23. AL-Da’amy, Muneer A., Noor A. AL-Khazali, and Eman TK AL-Rubaey. "Removal of Malachite Green from Aqueous Solution by Iraqi Porcelanite Rocks." Journal of Global Pharma Technology 10 (2017): 150-156.
24. Gaikwad, R. W. "Removal of Cd (II) from aqueous solution by activated charcoal derived from coconut shell." Electron J Environ Agric Food Chem 3.4 (2004): 702-709.
25. Yang, Xiaoyan, and Bushra Al-Duri. "Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon." Journal of Colloid and Interface Science 287.1 (2005): 25-34.