# Adsorption Isotherms of Lactoflavine on Mint Adsorbent in Water Samples

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## Abstract:

This study is concerned with the removal of *lactoflavin* pigment from water through its adsorption by Iraqi Mint that found in Iraqi soils. The optimum conditions like *PH*, temperature, doses of adsorb ate and adsorbent and contact time, were studied by following the change in concentration of *lactoflavin* in solution on the basis of UV-visible spectroscopy method. It is found that time t=60 min, temperature=60°C *P*H=9.0 and its initial concentration $C_o$=30 ppm are the best conditions to get high efficiency of removal percent of *lactoflavine* by the Mint surface.The adsorption process has been found as endothermic in nature depending on thermodynamic parameters of Gibbs's free energy, change in entropy and enthalpy. The Langmiur and Fruendlich isotherms of *lactoflavin* adsorption on Iraqi Mint have studied in the 30-60°C range, and it is found that the adsorption was endothermic heterogeneous processes.

**Keywords**: *Adsorption isotherms, lactoflavin, Mint as adsorbent.*

## 1-Introduction:

Pigments are organic pollutants introduced into water bodies from many industrial processes such as tanning, paint synthesis, fabrication and modification of polymers [1-3], and a result of side products formed from exerted materials to water, soils many subsequently generate colored wastewater[4].

Wastewater have been containing organic pollutants like dyes, and high concentrations of bimolecular derivatives such as vitamins soluble in water, is very difficult to treat, since the dyes are recalcitrant agamic molecules , resistant to aerobic digestion, that is stable to light [5]. The presence at bimolecular dyes derived from alkaloids, vitamins and Carotenes even in very low levels are highly visible and causes damage to the environment as they are toxic to aquatic life [6].

The abnormal levels of dyes such and methyl orange, methyl blue, *lanugo* and *lactoflav*in, could be considered as hazardous chemicals in waters, soils, for its highly toxicity[7].*Lactoflavin*, is the most commonly bioorganic molecule soluble in water and its significance in metabolism of human beings, other less, its levels after damages of biochemical reactions, needs to be removed from environment via green analytical methods involving various treatment techniques like precipitation, reduction, solvent extraction , ion exchange, and most of these techniques require high investment of capital and expensive apparatus. Previously some low cost plant waste had directly been used as adsorbent for dye adsorption from environment, and these need to modify procedure in order to increase its adsorption performance [7]. In the present study, we have focused, in using the Mint as natural adsorbent for removal of *lactoflavin* in aqueous solutions, as well as the isotherms of adsorption of *lactoflavin* on Mint adsorbent have studied on the basis of optimization the dose adsorbent, concentrations of adsorb ate, *PH* of the aqueous solution and temperature effects to deduce the thermodynamic parameters .

## 2-Experimental

### 2.1 Adsorbent:

The revised powder of Iraqi Mint was washed with distilled water, and boiled for 15 min. then, the suspended Mint were filtered out, before were dried in air for 48 hrs , in order to eliminate its moisture content. The dried Mint was grinded and sieved into (200-300) µm to reduce its size into fine power. The prepared adsorbent Mint was stored in air and referred as adsorbent Mint.

### 2.2 Adsorb ate:

Stock solutions were prepared by dissolving 0.2g in 20ml of de ionized water to prepare standard solutions of 10, 15, 20, 25 and 30 ppm of *lactoflavin*. The stocked solutions socked slowly to make sure that all powder of lactoflavin has been dissolved in de ionized water. These stock solutions were stored for further using. The maximum absorption for lactoflavin solution was in the visible region at 445nm.

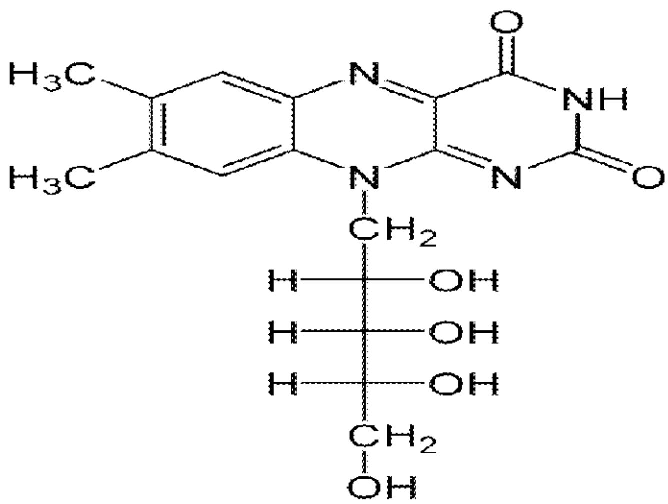



**Figure (1): structure of lactoflavin.**

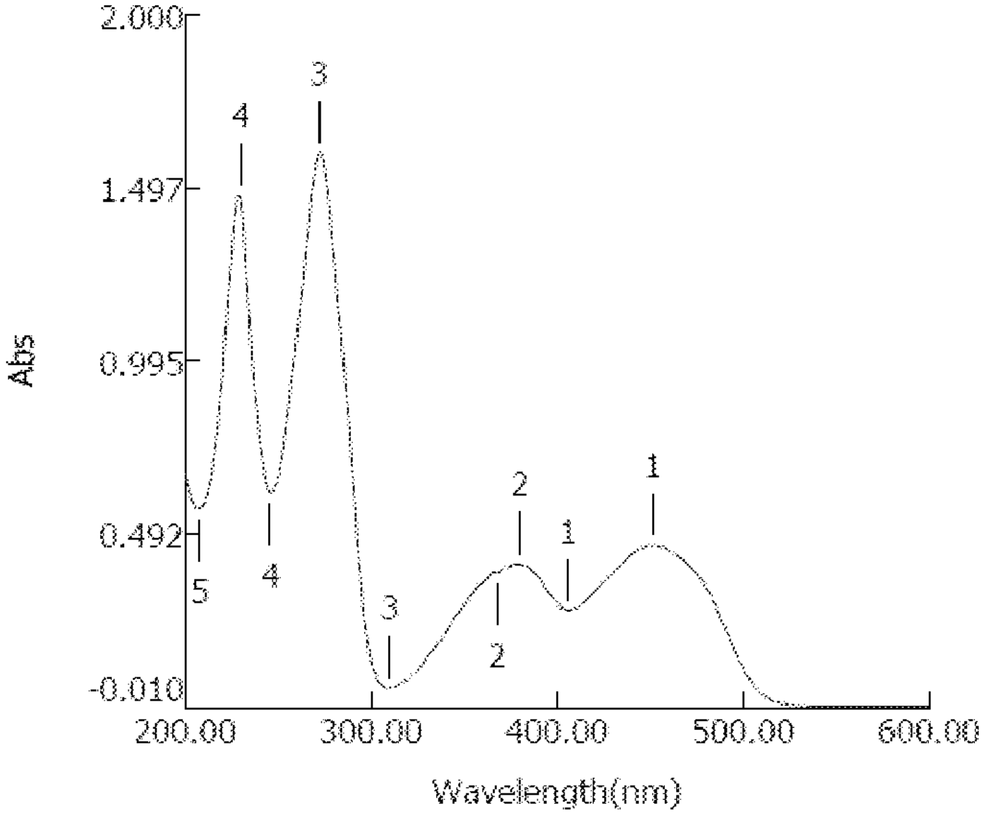



**Figure (2): Electronic spectrum scanning of aqueous lactoflavin solution (20ppm).**

## 2.3 Equilibrium Studies:

These experiments were carried out by adding 0.34gm,of Mint to a conical flask containing 20ml of *lactoflavin* (10,20,30, and 40 mg/L.) at constant *PH* and temperature. The flasks were placed in horizontal shaker and agitated at 150 rpm rate for internal periods of time 10 , 20 , 30 , 40 , 50 and 60 minutes to make sure that equilibrium has reached. Final concentration of dye solutions were analyzed using T80UV/vis spectrometer PG instruments model in the range 200-800nm, according to the following equation (1):

$$q_e = \frac{(C_o - C_e)v}{w} \times 100 \quad \text{-------------------- (1)}$$

Where $C_o$ and $C_e$ (mg.$L^{-1}$) are the liquid-phase concentrations of dye at initial and equilibrium, respectively, V (ml.) is the volume of the solution and w(g) is the mass of adsorbent Mint used. The percentage removal dye is defined as the ratio difference in dye concentration before and after adsorption,($C_o$ -$C_e$) to $C_o$ of dye in aqueous solutions and was calculated using the equation.

$$\%\ removal = \left[\frac{(C_o - C_e)}{w}\right] \times 100 \quad \text{--------------------- (2)}$$

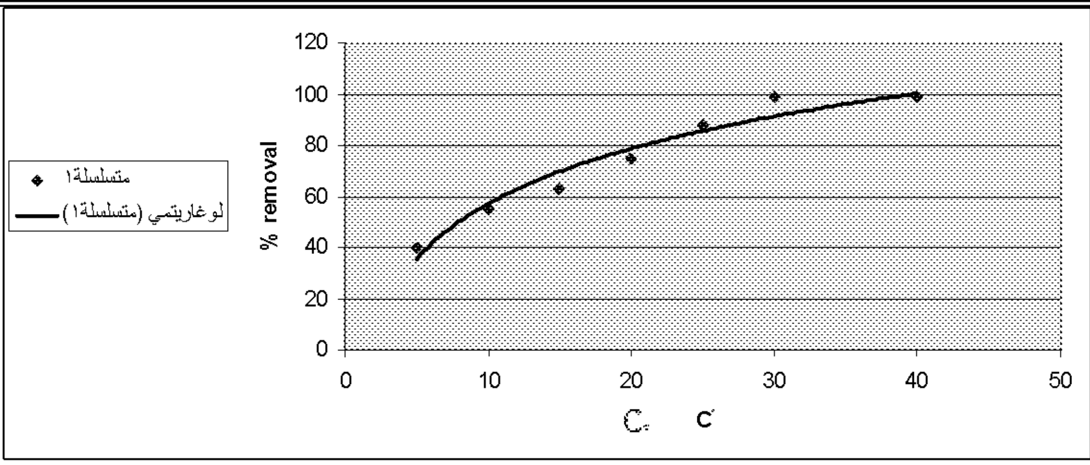



**Figure (3): Influence of initial concentration on % removal of adsorption.**

## 2.4 Adsorption isotherms:

The adsorption isotherm represents the relationship between the amount adsorbed by a unit weight of solid adsorbent and amount of lactoflavin remained in solution of equilibrium [8]. Langmuir and Freundlich isotherms are commonly used to describe the equilibrium characteristic of adsorption linear regressions were used to determine the best fit model and least squares has been widely used for obtaining isotherm constant.

Langmuir isotherm [9] refers to homogeneous adsorption ,in which the processes can only occur at a fixed number of definite localized sites,
with no transmigration of the adsorb ate in the plane of the surface. The Langmuir model can be given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}}C_e \text{ ---------------------- (3)}$$

Where $q_e$ is the amount of lactoflavin (mg/g) on surface of Mint $C_e$ is the equilibrium concentration (mg/L.), $q_{max}$(mg/g) and $K_L$ are the Langmuir isotherm constants related to free energy.

The linear form of Freundlich isotherm [10] model is derived from assuming heterogeneous surface of adsorption capacity, and adsorption intensity with an uniform distribution of heat of adsorption. The Freundlich model can be given as:

$$q_e = K_F . C_e^{\frac{1}{2}} \text{ ---------------------- (4)}$$

Rearranging equation 4,

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \text{ --------------------- (5)}$$

Where $K_F$ and $\frac{1}{n}$ are Freundlich isotherm constant (mg/g), $(dm^3/g)^n$ related to adsorption capacity. A plot of log $q_e$ vs. log $C_e$ yields a straight line, with a slope of $\frac{1}{n}$ and intercept of $\log K_F$.

## 2.5 Kinetic Studies:

Batch kinetic experiments were carried out by mixing 0.3gm of Mint to each conical flask containing 20ml. of (10-40 mg/L.) ppm. Of *lactoflavin* pigment at 30°C . A series of such conical flasks were then, shaken at a constant speed of 80rpm in a water bath shaker and samples were collected at different time intervals.

The concentration of pigment in the super ant solution was analyzed by UV-visible spectroscopy at $\lambda_{max}$ =445nm and the capacity of adsorption of equilibrium were calculated from the following relationship:

$$q_e = \frac{(C_o - C_e)V}{W} \quad \text{------------------- (6)}$$

Where $q_e$ is the equilibrium adsorption capacity (mg.$g^{-1}$) ,$C_e$ is the pigment concentration (mg.$L^{-1}$) at equilibrium, V is the volume (mL.) of solution and w is the weight (g) of adsorbent.

## 2.6 Effect of *PH* on Flavin adsorption:

The influence of *PH* on pigment adsorption was studied in range 2.5 to 10.5. which was adjusted up on addition of 0.1 M HCl and NaOH solutions to mixture of pigment and Mint. In this study, 25 mL.of pigment (30 ppm) was agitated with (0.30 gm) of Mint for 120 min at 30°C .In the subsequent investigations, experiments were performed at solution *PH* value up to 9.0, to avoid any possible transformations of pigment to anionic or salt form.

## Result and Discussion:

## A- Calibration Curve of Latoflavin:

Solutions of different concentrations were prepared by serial dilutions of *lactoflavin* in deionizer water of range 5, 10, 15,20,25,35 and 40 mg/lit.

Absorbance values of these solutions were measured at specific wave length of $\lambda_{max}$ =445nm, and plotted the initial concentrations ($C_o$) vs. absorbance that fall in the region applicability of Lambert Beers law, which were then used in subsequent quantitative estimation [11], figure (4).

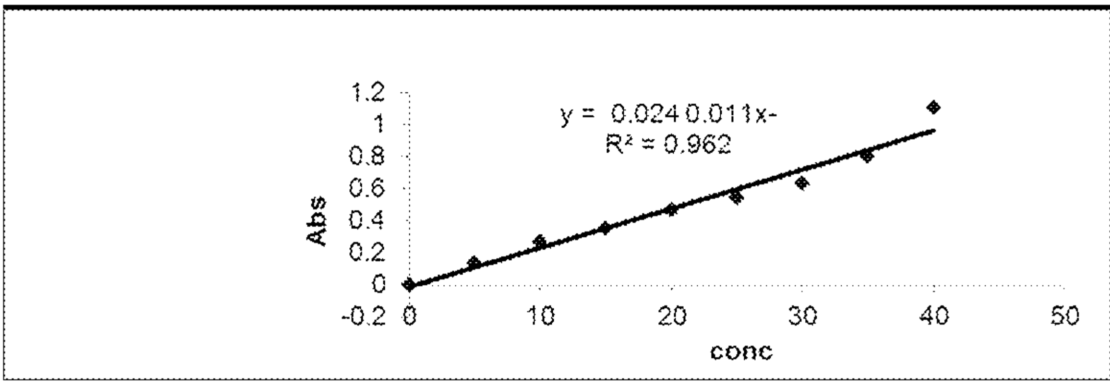



**Figure (4): Calibration Curve** of *lactoflavine* at 445nm in distilled water.

## B- Equilibrium contact time:

Figure (5), showed the amount of *lactoflavin* adsorbed by Mint as a function of time. The saturation curve rises sharply in the initial stages (10-20) minutes, confirming that there are plenty of functional accessible sites that binds strongly by electrostatic forces between hydroxyls groups and nitrogen atoms, of lactoflavin to negative charger on adsorbent Mint,until reaches plateau value at infinite time in 60 min.[12].

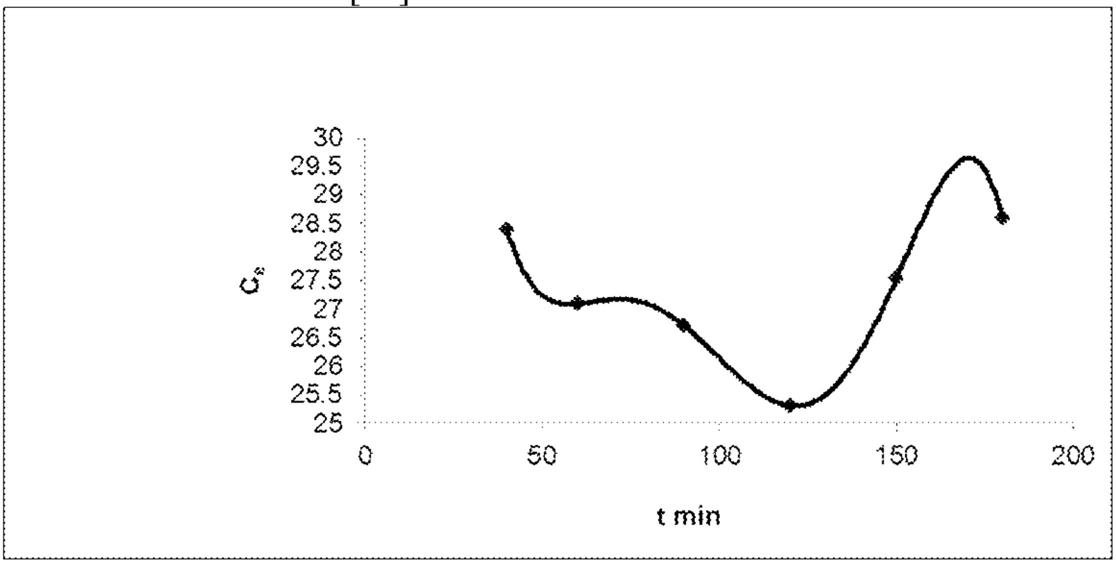



**Figure (5): Effect of time on adsorption of lactoflavine on Mint.**

## C-Effect *of PH* on adsorption:

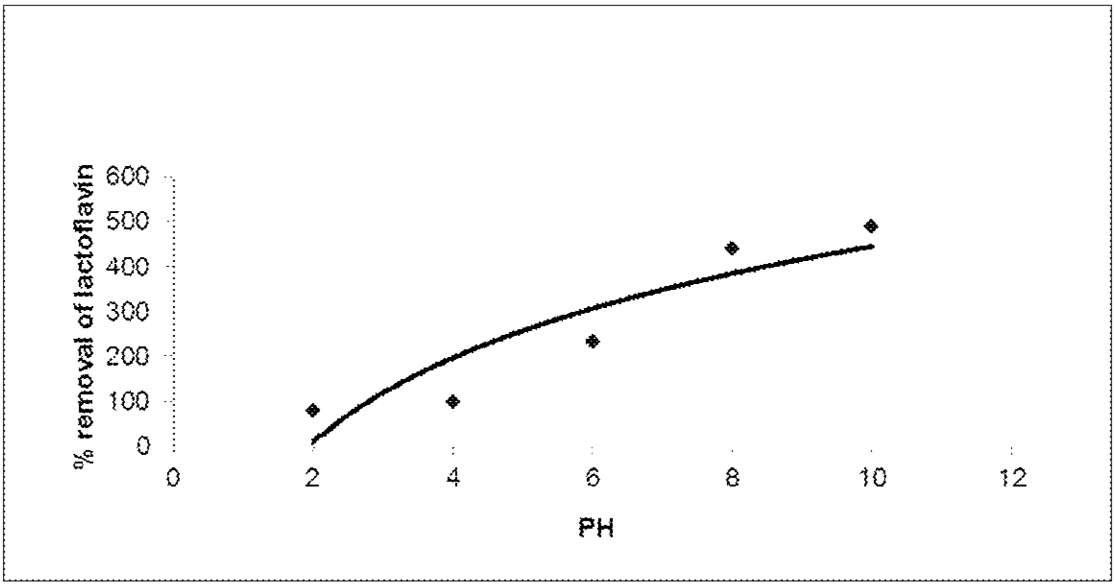
The adsorption characteristics of lactoflavin by spearmint adsorbent were studies at variable *PH* range from 2 to 10.0 by using standard solutions of HCl or NaOH. The profile, (Fig.6) concerning PH, showed that in the observed PH range, the adsorption capacity was much protonated at lower PH=2, while as the PH increases, adsorption enhances, due to performance of negatively charged sites on Mint adsorbent. [13].

As much as, all subsequent studies, were performed at approximately PH=9.0, which is the optimum value for adsorption.

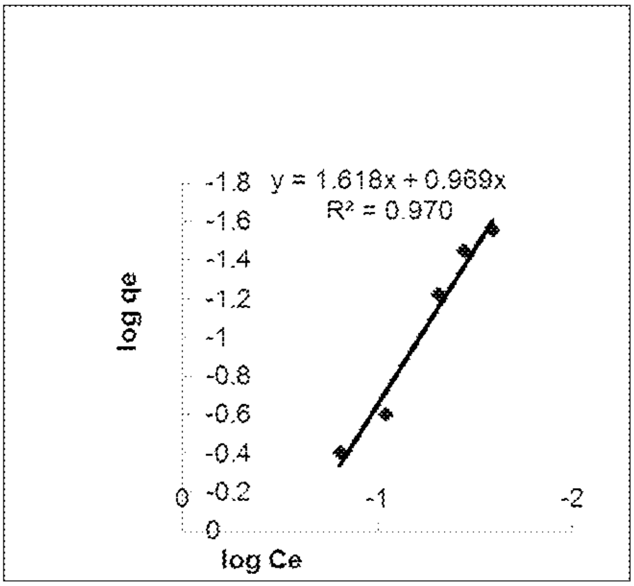
The adsorption of *lactoflavin* dye was also recorded in the concentrations range from (5-40) ppm, at a fixed *PH* of 9.0 and temperature 30, 40, 50 and 60C.

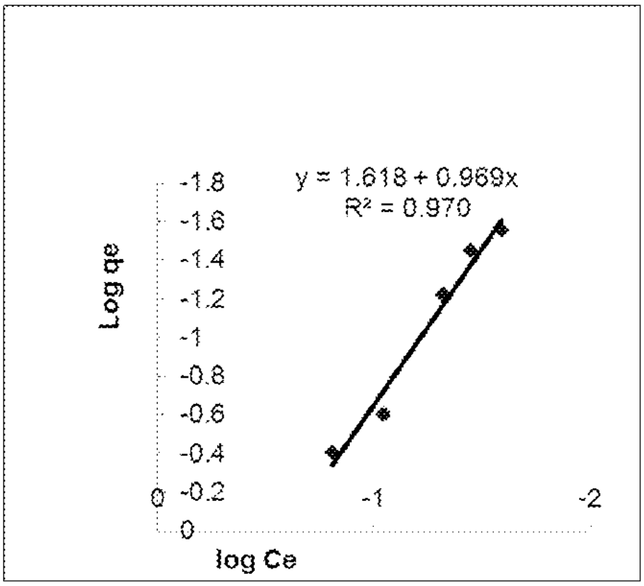
**Figure (6): Effect of *PH* on %adsprption of lactoflavine on Mint surface.**

Figure (6), also indicates that the adsorption of *lactoflavin* pigment in aqueous




solution by Mint adsorbent enhance with the increasing of temperature, indicating that the process was to be endothermic in nature [14].




A: Freundlich isotherm of *lactoflavin* on Mint at 30 **°C** **B**: Freundlich isotherm of *lactoflavin* on Mint at 40 **°C**

C: Freundlich isotherm of *lactoflavin* on Mint at 50 °C D: Freundlich isotherm of *lactoflavin* on Mint at 60 °C

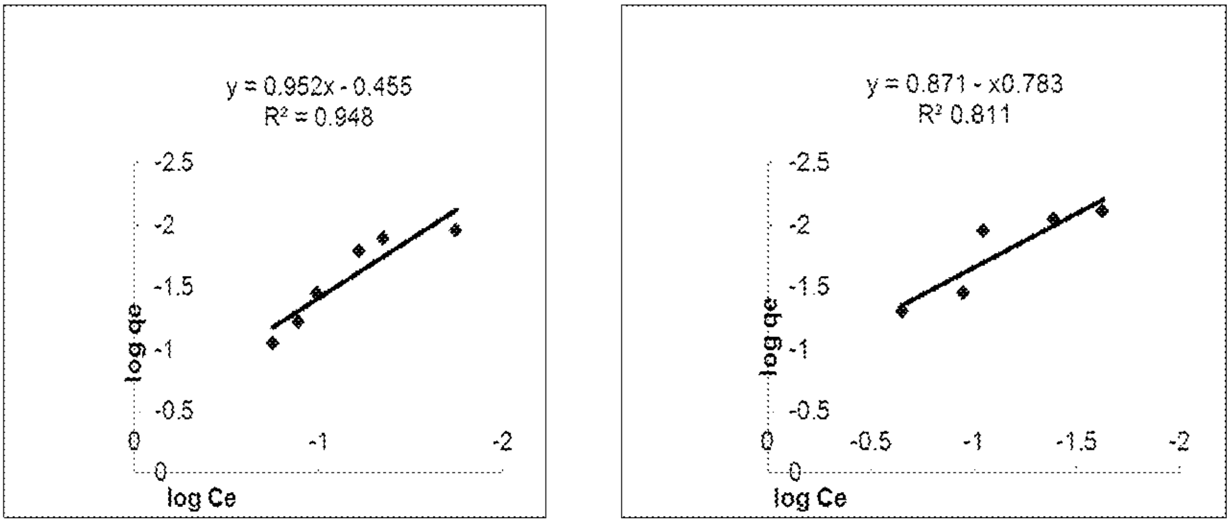
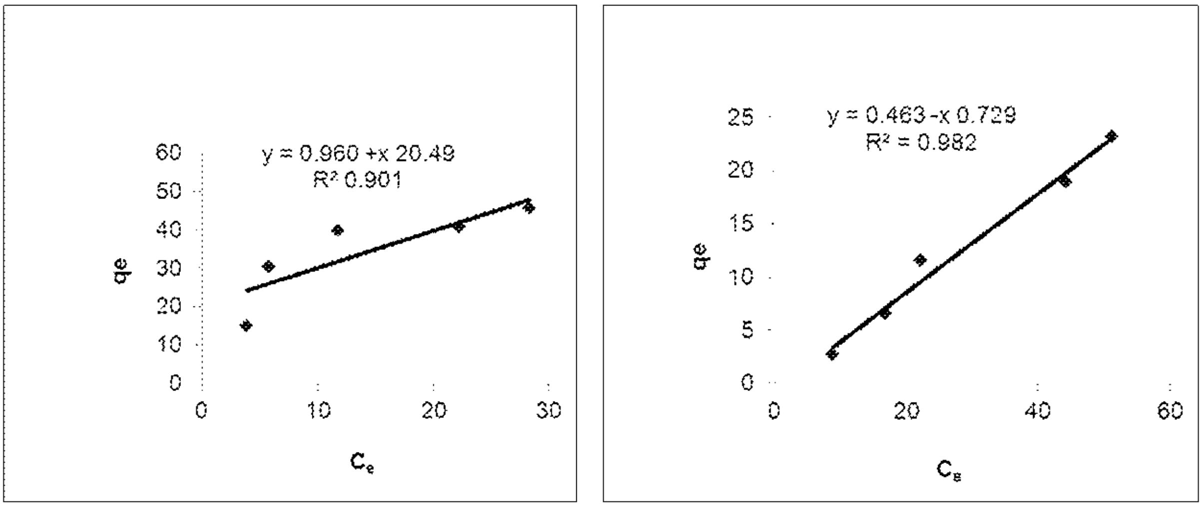



**Figure (7): Freundlich isotherm of l*actoflavin* on Mint at different Temperatures.**




C: Langmuir isotherm of *lactoflavin* on at Mint at 50 °C D: Langmuir isotherm of *lactoflavin* on at Mint at 60 °C

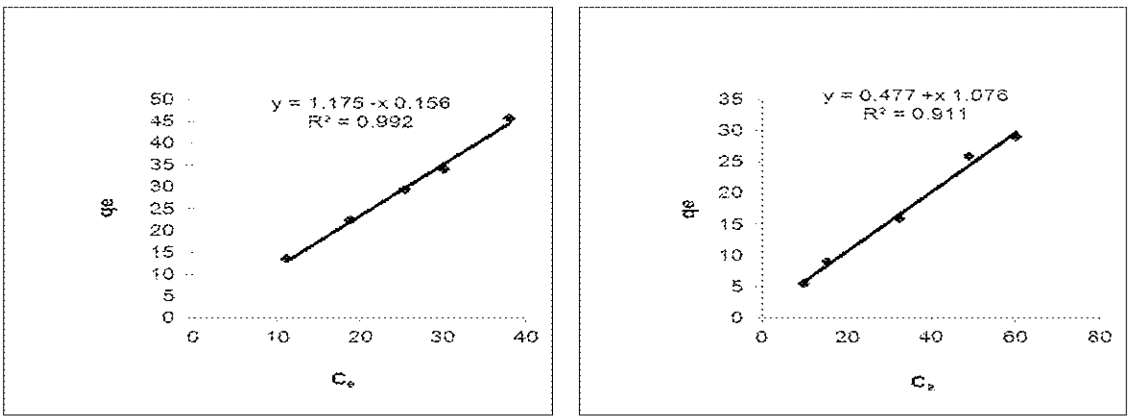



**Figure (8): Langmuir isotherm of *lactoflavin* on Mint at different temperatures.**

In both of Langmuir and Freundlich isotherms, linearity of $\log C_e$ vs. $\log q_e$ or $1/C_e$ vs. $1/q_e$ respectively in figures (7&8) exhibited the heterogeneous adsorption of lactoflavin on active sites of Mint adsorbent [13, 15],and from the intercepts and slope of Langmuir and Freundlich isotherms, it is found that the 1/n and b constant have becomen enhanced, which agree with the theory of adsorption [16].

Table (1): Freundlich and Langmuir constants of lactoflavin adsorption over Mint surface at different temperature.

| Temperature | $30^\circ C$ | $40^\circ C$ | $50^\circ C$ | $60^\circ C$ |
|---|---|---|---|---|
| Langmuir constants $Q^\circ$ (mal/g) | 0.00015 | 0.00019 | 0.00021 | 0.00026 |
| b(× $10^{-3}$) mol/L | 187 | 195 | 235 | 305.5 |
| Temperature | $30^\circ C$ | $40^\circ C$ | $50^\circ C$ | $60^\circ C$ |
| FrenudlichConstants | | | | |
| N | 5.22 | 4.95 | 3.77 | 5.0 |
| $K_f$ | 0.012 | 0.0145 | 0.0219 | 0.0318 |

The thermodynamic data were evaluated from Langmuir isotherms [17], using the following equations (s)

$$\Delta G^\circ = -RT\ln K_{eq} \quad \text{---------------------} \quad (7)$$

$$\Delta H^\circ = \frac{R\,T_2 T_1}{T_2 - T_1} \ln\frac{K_2}{K_1} \quad \text{----------------------} \quad (8)$$

and $$\Delta S^\circ = \frac{\Delta H^\circ . \Delta G^\circ}{T} \quad \text{---------------------} \quad (9)$$

Where $K_1$, $K_2$ and Keq are the equilibrium constants at 30, 40 and $60^\circ C$ respectively, and obtained from slope of adsorption isotherms at different concentrations [18].

Evaluated thermodynamic parameters, change in free energy ($\Delta G^\circ$), change in enthalpy ($\Delta H^\circ$) and change in entropy ($\Delta S^\circ$) are presented in table (2) negative value of $\Delta G^\circ$, investigates the feasibility of adsorption of lactoflavin on Mint, furthermore the decrease in $\Delta G^\circ$ values with increasing of T, confirms the spontaneous of the process at $60^\circ C$ .

The endothermic nature was also supported and proved from positive value of $\Delta H^\circ$, while good affinity of lactoflavin dye towards the adsorbent active sites, is revealed by the positive value of entropy $\Delta S^\circ$.[16,17].

Table (2): Effect at temperature on the maximum adsorbed quantity of lactoflavin. at $C_e$ =4.11 , $PH$ =9.0

| T °C | TK | $(\frac{1}{T})K^{-1} \times 10^3$ | $Q_e \frac{mg}{g}$ | $\ln q_e$ |
|---|---|---|---|---|
| 30 | 303.15 | 3.2986 | 39.5 | 3.676 |
| 40 | 313.15 | 3.1933 | 30.05 | 3.41 |
| 50 | 323.15 | 3.0445 | 29.71 | 3.37 |
| 60 | 333.15 | 3.0016 | 20 | 2.995 |

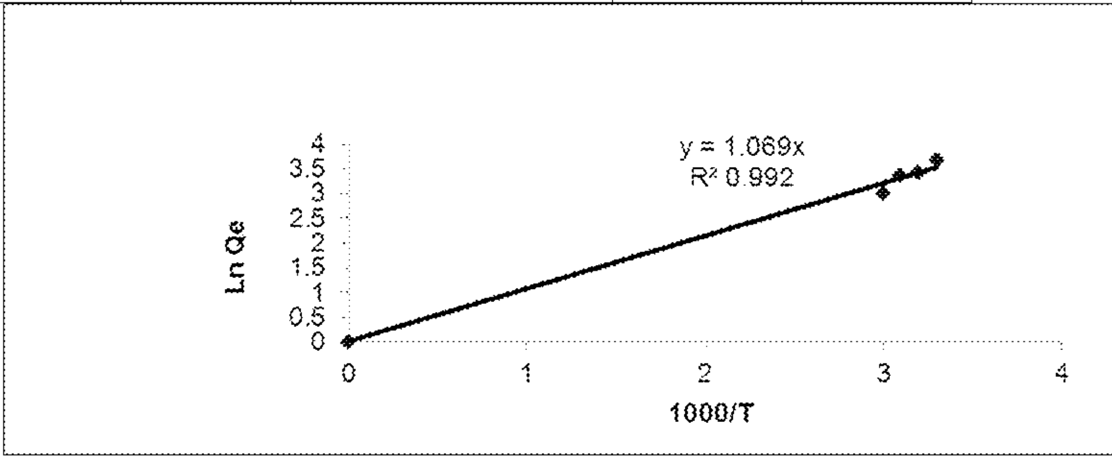



**Figure (9): Plot of Ln Qe against 1/T for adsorption of l*actoflavin* on Mint**

From the plotting of $\ln x_m$ or $\ln q_e$ versus $\frac{1}{T}$ yields straight line to afford ($K_d$) equilibrium constant for adsorption of lactoflavin on Mint adsorbent as well as the applications of vant Hoff:

Equations in the following figure (10) has to evaluate $\Delta H^{\circ}, \Delta S^{\circ}$ and $\Delta G^{\circ}$

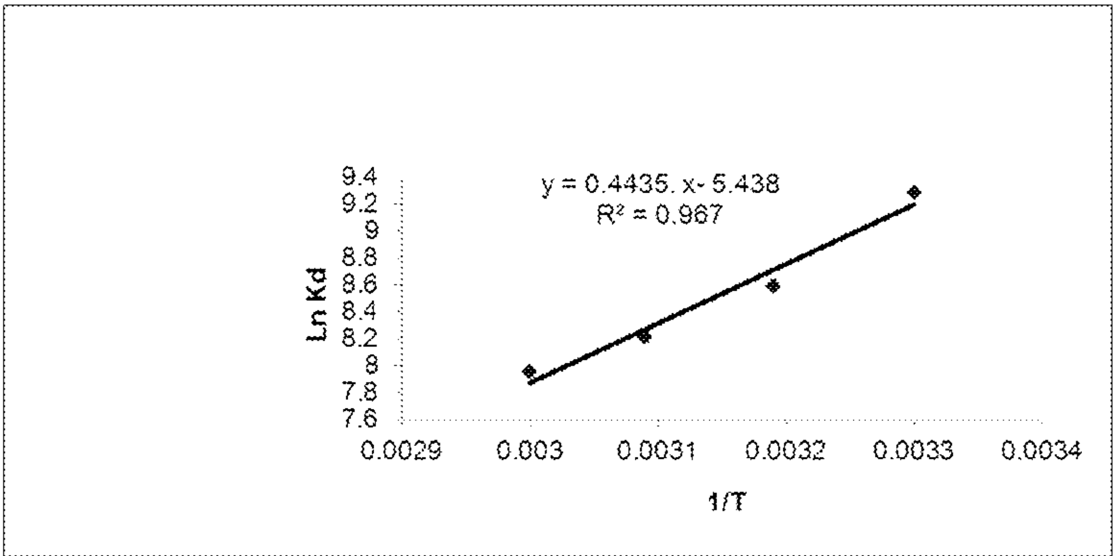



**Figure (10): Vant Hoff's equation for adsorption process with Mint (0.30gm) as adsorbent ($PH$ =9.0)**

Table (3): thermodynamic parameters for the adsorption *lactoflavin* on Mint adsorbent.

| T◦C | $\Delta G^\circ$ (KJ.$mol^{-1}$) |
|---|---|
| 30°c | 29.55 |
| 40°c | 31.56 |
| 50°c | 35.71 |
| 60°c | 37.91 |
| $\Delta H^\circ$ (KJ$mol^{-1}$) | 9.511 |
| $\Delta S^\circ$ (KJ$mol^{-1}$) | 66.91 |

From tables(2&3) it is observed that calculation of thermodynamic parameters by plotting of Freundlich isotherms $\ln x_m$ or $\ln Q_e$ vs $\frac{1}{T}$ (on-x-ais), yield a straight line of slope $\Delta H^\circ$ and then $\Delta S^\circ$ and $\Delta G^\circ$ were calculated from equations (7,8,9), thus the adsorption of lactoflavin on Mint adsorbent at optimum conditions of time contact and *PH* =9.0, showed endothermic behavior of $\Delta H^\circ$=+9.511 KJ/mole and spontaneously of $\Delta G^\circ$=-37.91 KJ/mole.[18,19].
From the Vant Hoff's calculations (equations7, 8, and 9), the thermodynamic parameters of $\Delta G^\circ$, $\Delta S^\circ$, and $\Delta H^\circ$ supports the physio chemical adsorption[20,21] rather than ion-exchange, due to high available of functional groups, and the adsorption isotherms were obeyed to Freundlich and Langmuir models of endothermic process ($\Delta H^\circ$=+9.511KJ/mole), thus, its process agrees well with absorption of retiming, polysaccharides on natural resins and adsorbents[22-24].

## Conclusions:

The present work suggest economic method to purify Iraqi water from high levels of lactoflavin pigment . As well as, the adsorption study was depending mainly on the dose of Iraqi Mint speeded in Iraq soils . Furthermore, the endothermic-heterogeneous process of adsorption have good benefits in enhancement the development of green analytical chemistry.

## Reference:

1- V.K. Gorg, R.Gupta, A.Yadar"Dye removal from aqueous solution by adsorption on treated dust", *Bioresour* Technol. *89*, (2003), pp.1211-124.
2- T.Robinson,G.Mc.Mullan,R.Marchant,P.Nigam,*BioresourTechnol77*, (2001),pp.247-255.
3- M.Raftullah, O.Sulaiman, R.Hashim, A.Ahmed, *J.Hazard.Meter,177*, (2010), pp.70-80.
4- I.M.Bant, P.Niggam, D.Singh, R.Marchant, *Bioresour Technol. 58*,(1996), pp.217-227.
5- I.M.Maal, V.C. Virstava, N.R.Agrawa, I.M.Mishra "*Comprehensive Chemosphere*" 61,(2005), pp.492-501.
6- N.Nashua, H.Z.Zurainan, H.I.Maarof, N.A.Zubir and N.Amiri, *Int.J.of Environ of Engi. 8*, (2011),pp. 50-55.
7- R.Gong, Y.sum, J.Chen and C.Yang, *Dyes and Pigments 67,* (2005), pp.175-181.
8- Langmuir, I.*J.Am.Chem.Soc.* 38, (1911),pp. 2221-2295.
9- Frenudlich H.M.F,Zeit, Polym. C*hen.Research*57A, (1906),pp. 385-470.

10- A.Mihal, *J.Hozard Mater*, *128*, (2006),pp. 233-239.
11- A.I.Vogel.*A text Book of Quantitative Inorganic Analysis*,3rd.edition.Longmans Green and Co.Ltd.,London (1961).
12- A.H.Mohamedin, *Int.Biodeteriot.43*, (1999),pp. 13-21.
13- F.Banat, S.Al-Ashech, *Environ.Eng.Policy2*, (2000),pp. 85-90.
14- D.L.Paria, G.M.Lampman, G.K.Kriz*Jr., "Introduction to Spectroscopy*" Saunders Golden Sunburst series (1974).
15- Longzhe, C.W.Guiping and J.Taeseop, *Cand. J.Chem.Eng. 88(1*), (2010),pp. 109-115.
16- I.M. El.Naggar, E.I.Shaloanon and M.I.El-Dessouky, *Advances in Chemical Engineering and Scienc*e, 2, (2012),pp. 180-188.
17- Coskun, R., C.Soykan and M.Sack, *Separation and Purification Technology* (2006), *49*, pp.107-144.
18- Haung, R.,Wang B., Yang B., Zheng D. and Zhang Z., *J.Desalination* 280, (2011), pp.297-304.
19- Sharma, A. and Bhahacharyya KG., *J.Hazard Mater*. B125, (2005), pp.102- 122.
20- Stephen, I.B., and Sulochana, N.*Biores Technol.* 94, (2004), pp.49-52.
21- Ivan A., Nasser T. and Thuraja M.A, *J.Chem.Pharm.Res.* 4(12), (2012), pp.4961-4468.
22- S.Knaebel K. "Adsorbent Selection"*Adsorption Research, Inc.Dubhin*Ohiv, 43, (2011), pp. 1-23.
23- P.Somasundran,S., Shroti and L.Huang, ***"Thermodynamic of adsorption Surfactants at solid-liquid interfaces***" p*ure and appl.Chem.* 70,(1998), pp.621.626.
24- Al-Sharify A.N. &A.H.Rhman,*IraqiJ.Nat.Chem.* 45,(2012), pp.1-10

## أيزوثيرمات أمتزاز اللاكتوفلافين على سطح النعناع العراقي في المحاليل المائية

رشا منعم دعدوش

وحدة ابحاث البوليمر، كلية العلوم، الجامعة المستنصرية

**الخلاصة:**

تتضمن هذه الدراسة ازالة صبغة اللاكتوفلافين من المياه من خلال امتزازه على سطح النعناع العراقي المتوافر بكثرة في الاتربة العراقية .تم الحصول على الظروف المثالية من دالة حامضية ،درجة الحرارة،كمية الممتز والماز ووقت الامتزاز وذلك للوصول الى اعلى نسبة امتزاز بالاعتماد على متابعة التغير بتركيز صبغة اللاكتوفلافين في المحلول بواسطة مطيافية الاشعة فوق البنفسجية والمرئية . لقد وجد ان زمن 60 دقيقة ،درجة حرارة 60 مئوي ، دالة حامضية 9 والتركيز الابتدائي للصبغة يساوي 30 جزء لكل مليون هي الظروف الامثل للحصول على كفائة عالية على سطح النعناع . لقد وجد ان طبيعة عملية امتزاز الصبغة على السطح هي ماصة للحرارة من خلال قياس الدوال الثرموديناميكية لطاقة كبس الحرة ، التغير في الانتروبي والانثالبية . كما درست ايزوثيرمات لانكماير وفريندلج لصبغة اللاكتوفلافين في المحلول على سطح النعناع في مدى من درجات الحرارة (30-60 مئوي) واستنتج ان عملية الامتزاز غير متجانسة – ماصة للحرارة .