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Adsorption Study of Rhodamine –B Dye on Plant (Citrus Leaves)

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Abstract:

The current research includes the adsorption of Rhodmine-B Dye on the surface of Citrus Leaves using the technique of UV. Vis spectrophotometer to determine data of quantitative adsorption at various contact time, ionic strength, PH and temperature conditions. As a function of temperatures 25,35,45,55 ^{0}C, the dsorption phenomenon was examined, and the results showed that Rhodamine-B adsorption Citrus leaves rose with increasing temperatures on the surface (endothermic process). Using various NaCl solution concentrations, the effect of ionic strength on adsorption has also been studied. Increasing the importance of ionic strength has been shown to improve the amount of adsorption of Rhodamine-B on citrus leaves at constant temperatures.The quantity of Rh-B dye that was adsorbed on the citrus leaves was increased with increasing the PH of the solution in rang 3-7. Then the results were subjected to the practical results obtained with the use isotherms of the Langmuir, Frendelsh, and Temkin. The results can be shown that the isotherm suitable for adsorption applies to Ferndelsh and Temkin. The thermodynamic functions (the amount of change in enthalpy, the amount of change in entropy and the amount of change in the free energy of Gibbs) were also studied, and it was found that the thermodynamic results of the adsorption process of the Rhodamine-B dye on the powder of citrus leaves are endothermic and an automatic adsorption process.

Keywords: Rhodamine B, Adsorption,Citrus Leaves, Isotherm,Thermodynamic.

Introduction:

Today, all societies suffer from water pollution problems due to the drainage of industrial effluents into surface water contaminated with toxic dyes from a wide range of industries, such as textiles, leather, sheet, printing, food, beauty products, paint, rubber, plastics, pesticides, wood preserving chemicals and pharmaceutical-industries[1]. Water pollution is defined as water contamination and the alteration of water's physical, chemical and biological characteristics. It entails the dumping of any sewage or commercial waste or any other fluid. In water, gaseous or solid compounds are likely to produce a nuisance by means of their physical presence, odor or taste. Such discharge can damage and harm Water for the public as far as domestic hygiene is concerned. They are concerned with commercial, manufacturing and agricultural life.

The discharge of dye effluents also imparts color from the sources for miles downstream to the receiving stream. This color is aesthetically unacceptable and therefore decreases the penetration of light into the water, thus limiting the efficacy of photosynthesis in aquatic organisms and thereby making an adverse impact on their growth[2].

Natural compounds like the toxins, surfactants, some synthetic dyes and their precursors have varying biochemical and morphological influences on plants and animals[3].

A dye is a colored compound that binds chemically to the substrate to which it is added. This separates dyes from pigments that do not bind to the substance they color chemically. The dye is normally added in an aqueous solution and will need a mordant to enhance the dye's intensity on the fiber[4] Dyes can cause skin inflammation, accelerated heartbeat, vomiting, diarrhea, tissue necrosis, and shock[5].

Dyes can be categorized in different ways: (e.g., according to the chemical constitution, application class, and end-use). The Principal categorizations of dyes are based on the natural

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fibers to which they will be applied and the chemical of each dye character. In order to form chemical bonds, reactive dyes react with fiber molecules[6]. Dyes may be categorized as anionic: direct, acid, and reactive dyes; cationic: simple dyes; and non-ionic: disperse dyes[7].

Rhodamine B (RH-B) is a synthesized organic colorant used as biological stain in paper, draw, food, leather, pharmacy, cosmetic, labs, etc. This colorant has a carcinogenic and toxic effect, hence the use in food and cosmetics is currently limited[8].

For the removal of dyes, many methods involving biological, physical, chemical and related technology have been published. Adsorption is the treatment of choice among the many therapies and provides the best outcomes as it can be used to extract various forms of dyes simultaneously[9].

In brief, by physical isolation, chemical methods or biological degradation, dye recovery from waste water can be accomplished. Adsorption, oxidation, biological therapy, electrochemical treatment, membrane filtration, and coagulation flocculation are several major techniques that are commonly used for the removal of dyes[10].

This method of adsorption is used to remove chemical chemicals, hazardous substances, dyes, and other products that conventional techniques do not remove. Adsorption on certain textures, such as natural materials with porous properties such as activated charcoal, zeolite, silica gel, porous clays, some agricultural residues, and plant parts, may largely eliminate these components[11].

In contrast to other processes, adsorption of farm waste has a low cost and high performance benefit [12-15].

In this work, the adsorption of RhB dye from aqueous solutions on Citurs leaves powder, which are considered environmentally friendly and of low-cost. The efficiency and behavior of adsorbents were studied at different concentration and temperatures.

Material and Methods:

Chemicals and Apparatus

Rhodamine B molecular dye formula ($C_{28}H_{31}ClN_2O_3$) and chemical composition Fig.1 is supplied by the HIMEDIA Company while citrus leaves were collected from the University of Baghdad gardens. The leaves of Citrus aurantium contain organic chemicals, including alkanes, alcohols, carboxylic acids, esters, soaps, etc.[16]

Sodium hydroxide was supplied from BDH with purity 99%, Hydrochloric acid was provided from BDH with purity 37%, and Sodium chloride with purity 99.5%. Thermostated Shaker water bath model JEIOTECH (BS-11)-Germany was used to shake the aqueous solutions of dye with adsorbents, while Remi Centrifuge Model R&C. Bombay-India was utilized to separate the adsorbents from the aqueous solution of dye. UV-Vis spectrophotometer model PC1650 Doube beam – Shimadzu was used to record absorbance of Rhodamine B before and after adsorption experiments. pH-mater model Hanna-HI-8417-England was used to adjust the pH of the solutions

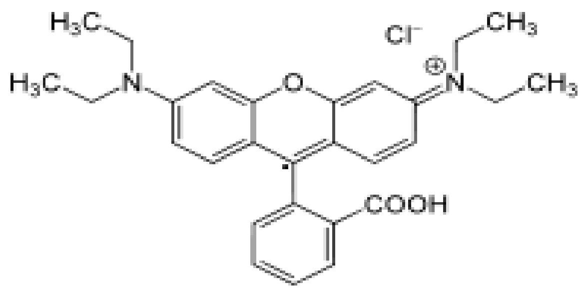

Figure 1. Structure of Rh-B

Absorbed Substance

By dissolving specifically weighted colour in refined water to the centralization of 8 ppm, the rohdamine B dye stock structure was set up, was used without aiding cleaning at λ_{max} 542 nm, Fig.2 indicates the dye absorption spectrum. The arrangements were accomplished by weakening the structure of the color stock to different starting focuses in precise ranges from Fig.3 shows the calibration curve, which was used to convert the absorbance value of dye to concentration according to Beer-Lambert law.

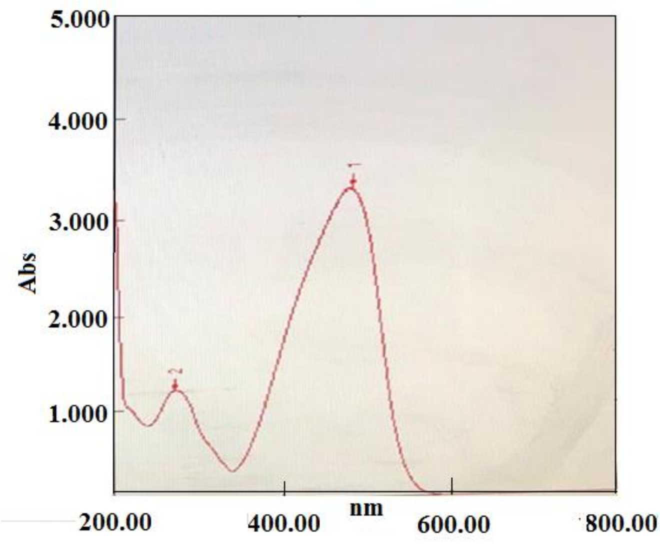

Figure 2. Absorption spectrum of Rhodamine B dye

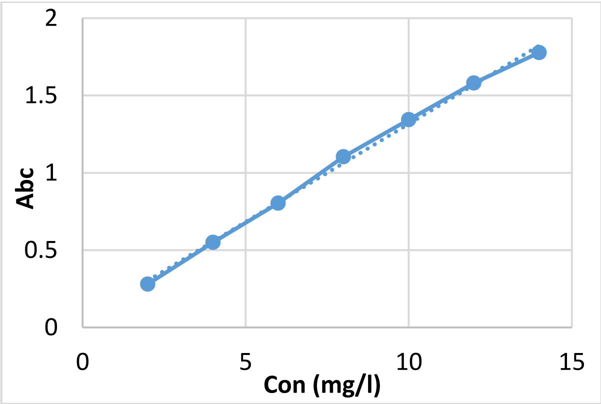

Figure 3. The Calibration Curve of the Rh B Dye

Preparation of Citrus Leaves Powder

After they were picked, citrus leaves were washed and the leaves were cleaned with plain water from the soil clinging to them, then washed with purified water, dried in an oven (Hot Air Oven LTD, LDHAM, England at 90 Co for 30 min, and ground with an electric grinder after drying, sifted with a sieve 75µm and stored away from moisture

Batch Adsorption Experiment

To prepare 100ppm from the dye, 0.1 gm of RhB was dissolved in 1L of distilled water.
Different dye concentrations were prepared for RhB at concentrations of 2-14 ppm.
0.1M of HCl and 0.1M of NaOH solutions were used to adjust the pH according to the media in which the adsorption process was conducted takes place and to reduce the error resulting from changing the acidity of the media on the sample size and prepare NaCl solution 0.1, 0.01, 0.001 M. The adsorption was observed by evaluating the convergence of Rhodamine B in a double bar Visible spectrophotometer configuration, at λmax 542 nm. The percentage of dye expulsion and volume of rhodamine B adsorbed on adsorbent was determined using the following equation to determine the-qyantity of dye adsorbed[17] Eq.1.

$Q_e = (C_0 - C_e)V/W$ ……………1

Where the main and equanimity (mg/l) amounts of dye, respectively, are C_0 and C_e. At the moment of equanimity (mg/g), Q_e is the sum of dye adsorbed on the adsorbent, V is the volume (l) of solution and W is the mass of the adsorbent (g).

Factors Effecting Adsorption System

Dosage of adsorbent. Original dosage of adsorbent 0.1, 0.2 ,0.3, 0.4, and 0.5 g, 8 ppm concentration. Both decanters were put in a water bath fitted with a temperature 25 C^0 shaking system 100 rpm and with a period 25 C^0, 30 min.

Contact Time of Adsorption System: Study adsorption process equilibrium at 25˚C for an adsorbent sum of 0.4 g of citrus leaves powder in 25 ml. The sample was withdrawn from the shaker for regular time intervals of 10,20, 30, 40, 50, 60, and 70 min.

Temperature: At temperatures of 25, 35, 45, and 55 ^{0}C in an indoor regulator paired with a shaker, the adsorption process was repeated in the same way. The experiments were carried out by taking 25 ml of Rhodamine B arrangement with different color convergences varying from different beginning convergences.of 2 - 12 ppm.

Ionic strength: The adsorption experiments carried out at various concentrations of NaCl 0.1, 0.01 and 0.001M at 25 °C with 25 ml of dye concentration.

***pH**:* Adsorption experiments were conducted at 25°C at pH 3, 7 and 11 with 25 ml of 8 ppm color focus. Hydrochloric acid 0.1M and sodium hydroxide 0.1M were used to change the acidic and basic pH of the solution.

Results and Discussion:

Adsorbent Dosage: -

The effect of the adsorbent dosage on the removal of RhB dye was explored in different quantities of powdered citrus leaves, while keeping the initial dye concentration 8ppm in 30 min at 25 ^{o}C .Fig.4 shows the effect of dosage of citrus leaves powder on the adsorption percentage removal of rhodamine B dye.

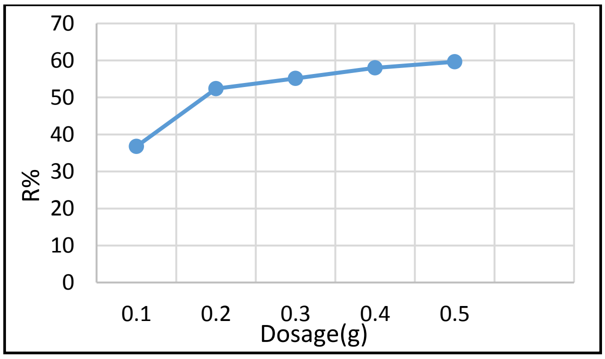

Figure 4. Effect of Adsorbent Dosage on Percentage RB Dye Removal on Citrus leaves powder.

The surface mass that provided the lowest absorbency (highest adsorption value) was picked and was 0.4 gm from the surface of the Citrus aurantium leaf powder.

Although the rise in the weight of the powdery orange leaf powder surface contributes to an increase in the amount of active sites primed for dye adsorption on the adsorbent surface, this means an increase in dye adsorption.removal percentage to increase the surface effectiveness.

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Determine the equilibrium time of adsorption systems (Contact Time)

To evaluate the time necessary for the adsorption of Rohdamine B on the surface of the powdered Citrus leaves to achieve the equilibrium state at temperature 298 k and concentration C_0= 8 ppm for coloring and with a steady adsorbent weight 0.4 g . Fig.5 indicates that the dye (RB) is quickly absorbed when the dye is adsorbed into the powdered citrus leaf in the first 30 minutes. This arises because the active centers on the adsorbent surface are empty, but the adsorption slows down as these active centers are filled with dye particles.

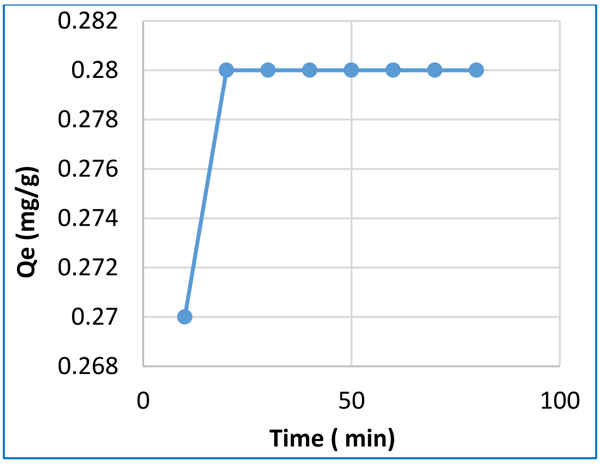

Figure 5. The Effect of Contact Time on the Adsorption Rate of RhB Dye at Citrus Leaves Power Surface .

Effect of Temperature

The effect of the adsorption temperature of the simple rhodamine B dye on the surface of the powder of Citrus aurantium leaves in the thermal range 25, 35, 45, and 55 ^{o}C was analyzed by fixing the adsorbent mass 0,4 g from the surface of the powder of Citrus aurantium leaves and at the concentrations 2,4,6,8,10,12 ppm of the dye Fig.6 .

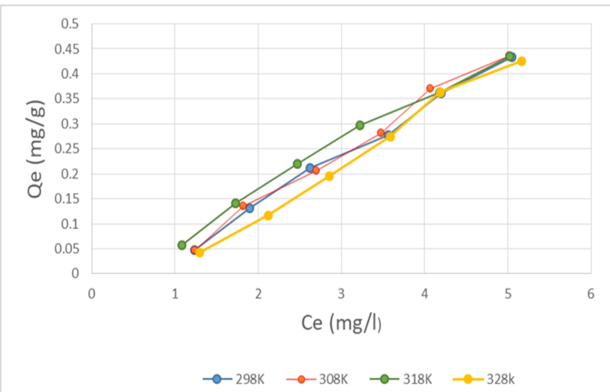

Figure 6. Adsorption Isotherm of Rh-B on Citrus plant leaves powder at Different Temperatures

Effect of PH

PH has a major effect on the removal of dye from aqueous solutions, as it influences the adsorbent's superficial charge, the degree of dye ionization, the isolation of the groups added to the adsorbent's active site and the molecular structure of the dye[18] Fig.7

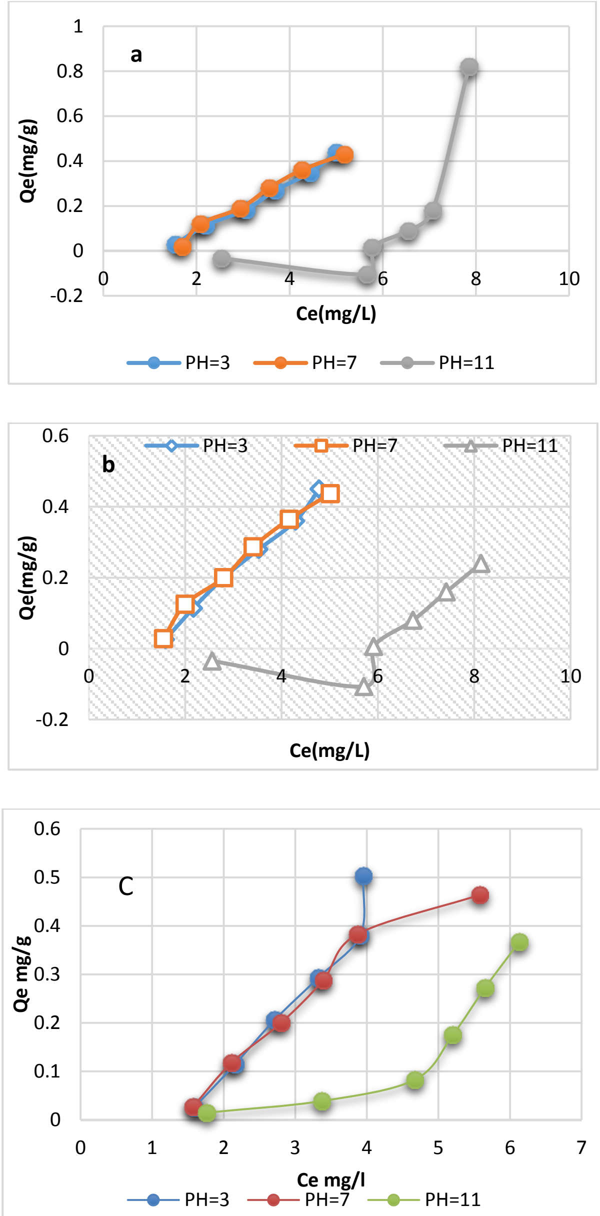

Figure 7. Effect of PH on the removal of Rh-B dye on citrus leaves powder in temperatures (a) 298 K(b) 308 K (c) 318 K

Effect of Ionic Strength

The effect of ionic strength of adsorption of rhodamine B dye Fig.8-10 on the surface of Citrus leaves powder 0.4 g was studied by adding 0.1, 0.01, and 0.001M salt in a temperature range 298-318 K contact time: 30 min. It can be clarified that the cationic sodium ions enhance the potential of the dye to interact on the surface of the adsorbents, bearing in mind the overarching objective of how the additional set of sodium chloride courses of action triggers increased rivalry at first glance between rhodamine B particles and electrolyte particles over the expulsion aims[19].

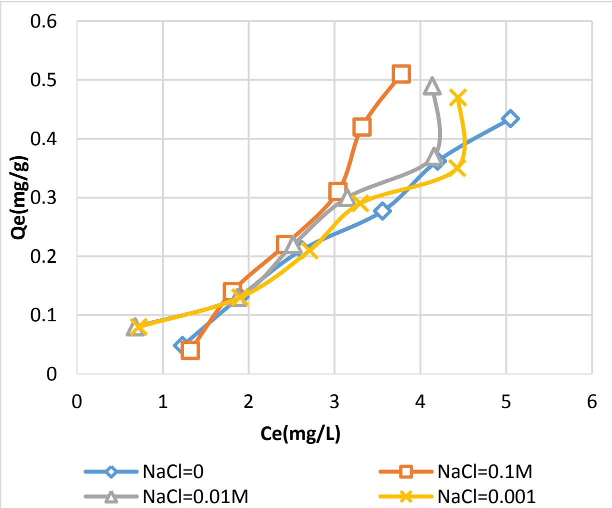

Figure 8. The effect of Ionic strength on the Adsorption of Rhodamine B Dye at a Temperature (298 K)

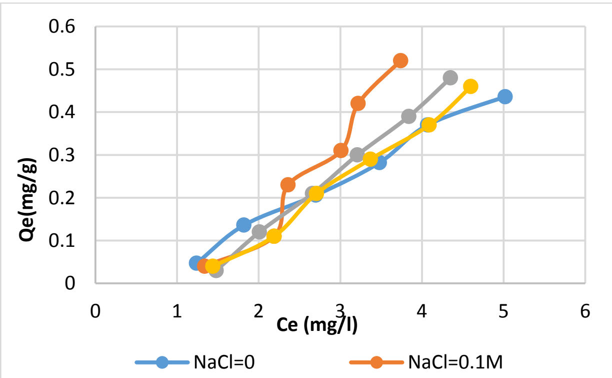

Figure 9. The effect of Ionic strength on the Adsorption of Rhodamine B Dye at a Temperature(308K)

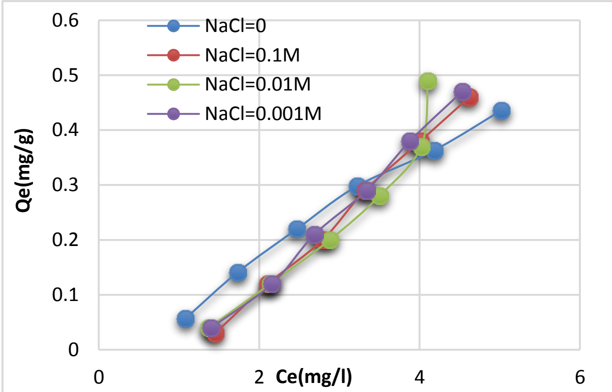

Figure 10. The effect of Ionic strength on the Adsorption of Rhodamine B Dye at a Temperature (318K)

Adsorption Isotherm

The adsorption on the surface of Citrus aurantium leaf powder of rhodamine B dye from its aqueous solution was tested at varying amounts and at different temperatures 298, 308, 318, 328K .
The findings demonstrate that Ferndelsh and Temkin are protected by an isotherm appropriate for adsorption.
-Langmuir Adsorption Isotherm
The Langmuir isotherm was calculated by the following Eq.2

$$C_e / Q_e = 1/q_{max} K_L + (1/q_{max})\, C_e \text{………………. 2}$$

If C_e is the adsorbate equilibrium concentration (mg/L),Q_e is the sum of adsorbed per gram of equilibrium adsorbent (mg/g),q_{max} is the overall adsorption power (mg/g) and K_L is Langmuir is the adsorption energy constant Fig.11 .

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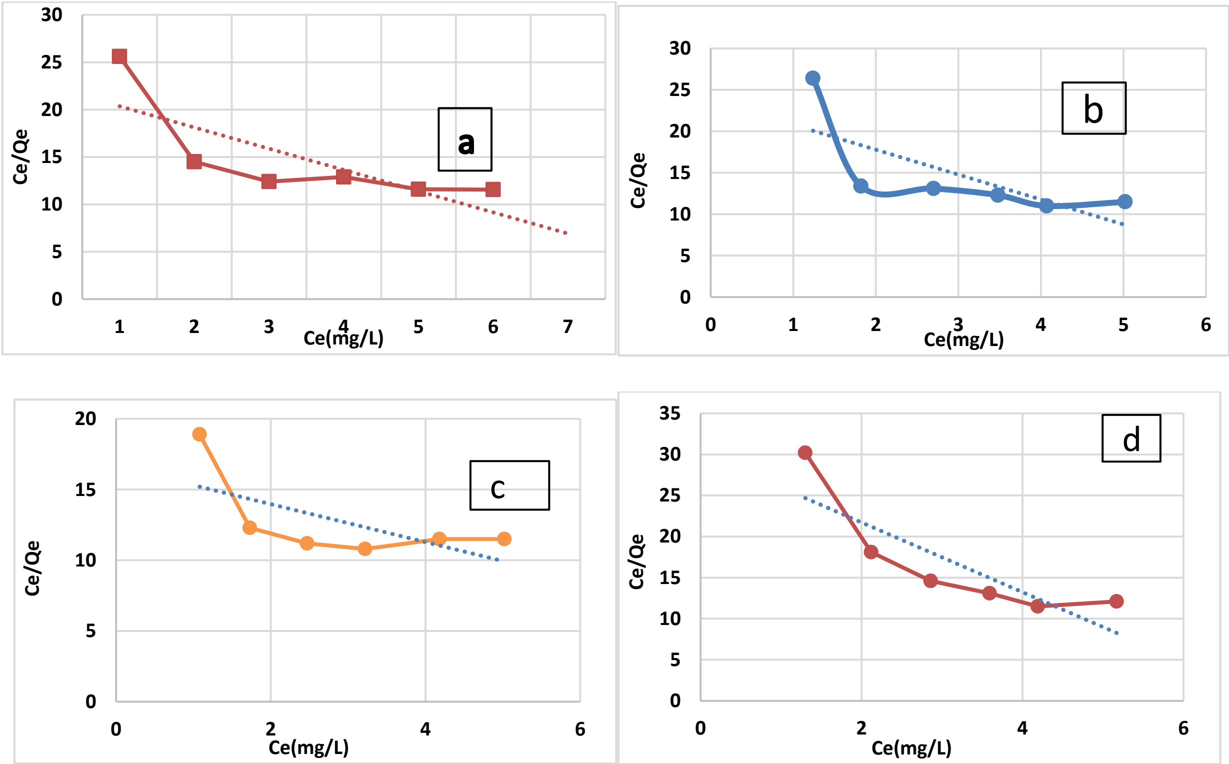

Figure 11. Langmuir linear relationship between Ce/Qe and Ce for Rhodamine B dye on Citrus leaf powder at a temperature range a) 298 b)308 c) 318 d) 328 K.

Freunddlich Isotherm

The isothermal equation was determined as follows

$\log Q_e = \log K_f + 1/n \log C_e$……… 3

Where Q_e is adsorbed dye (mg/g) is the indicator of Rh B, C_e is the equilibrium grouping of in the structure, color (mg/l), K_f and 1/n are constants that integrate the elements influencing the adsorption cap and the force of adsorption, individually, separately Fig.12.

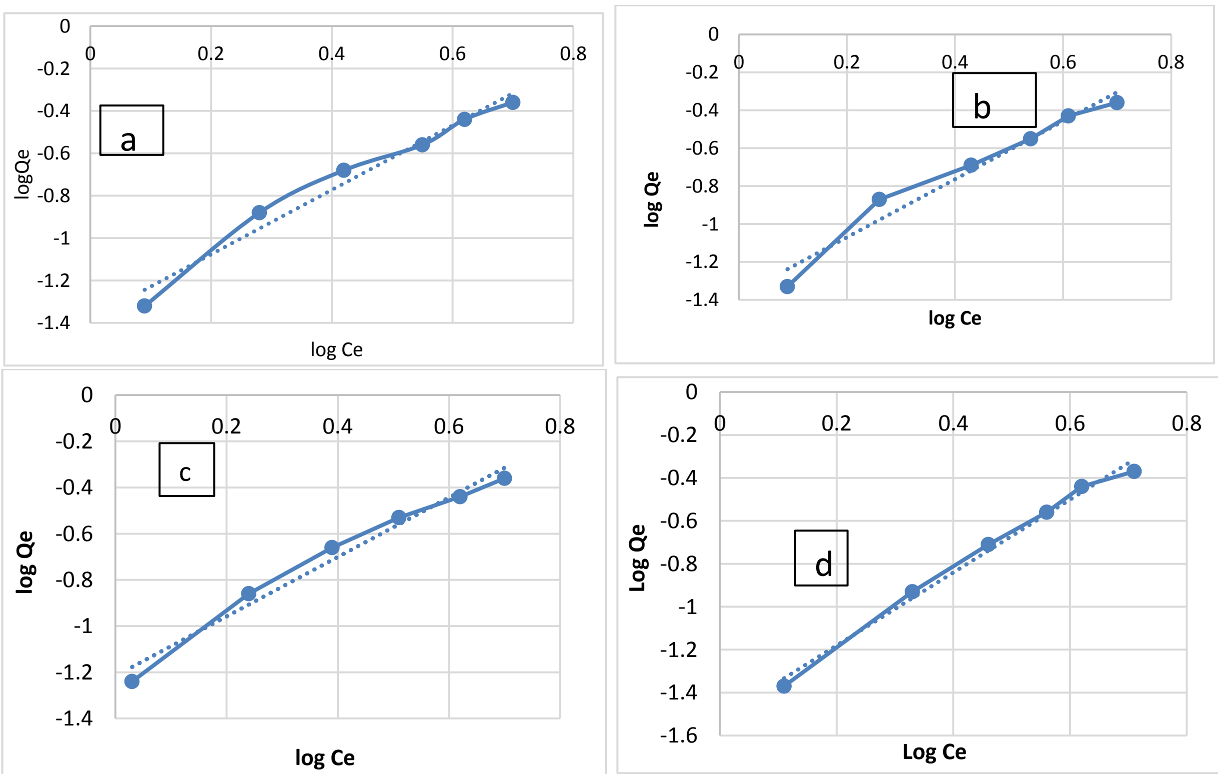

Figure 12. Freundlich Linear relationship between log Qe and log Ce for rhodamine B dye on citrus leaves powder at a temperature range: a) 298 b) 308, c) 318 and d) 328 K.

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Temkin Isotherm

Temkin discovered the impacts of certain circuitous sorbate/adsorbate relationships on adsorption isotherms and proposed that the warmth of adsorption of a large number of particles with scope decreases directly in the sheet in view of these relations. The Temkin isotherm was used after the Eq.4 Fig.13.

$Q_e = B_T \ln K_T + B_T \ln C_e$ ……………… 4

Where.

B_T, K_T = the equilibrium binding constant (1/g)

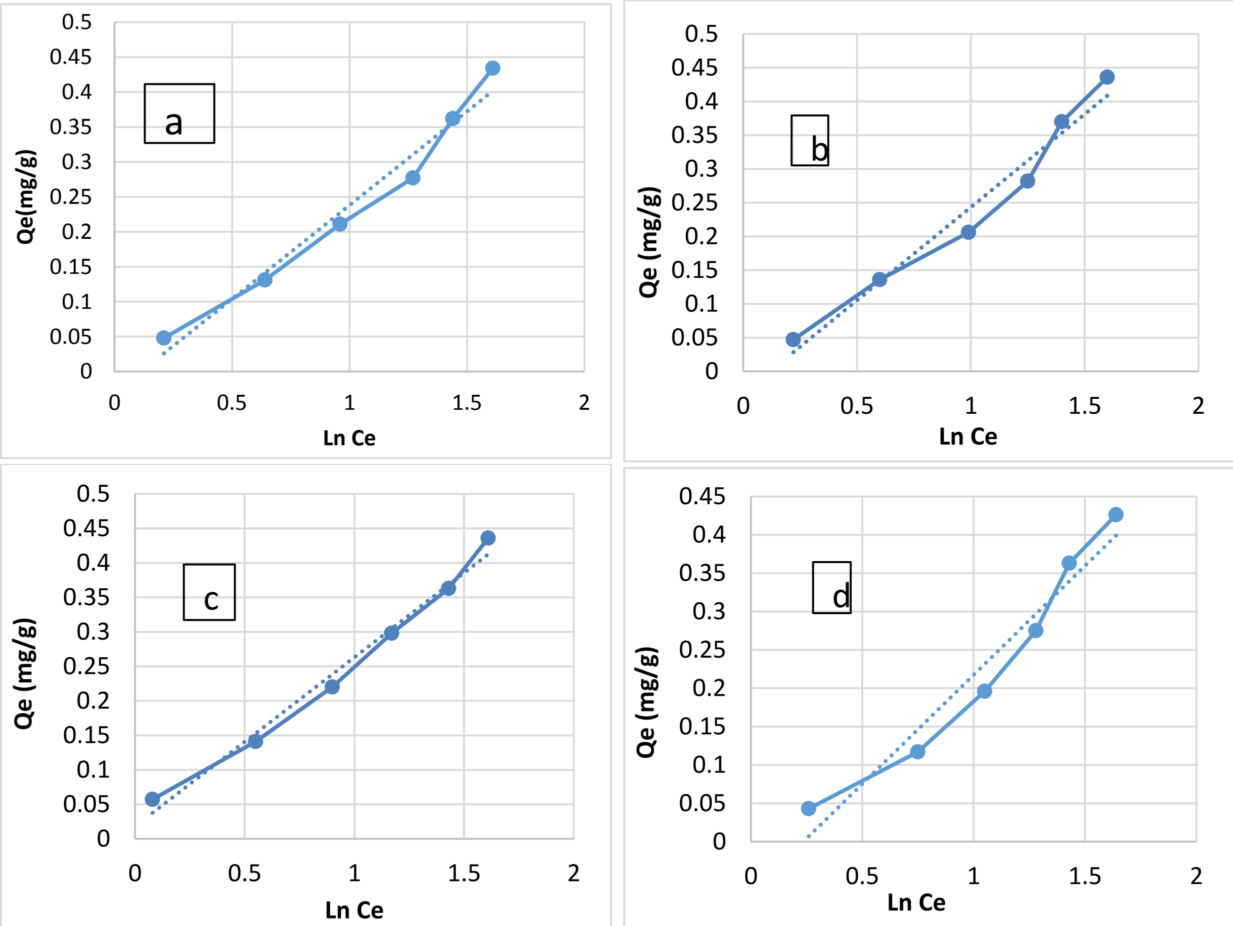

Figure 13. Temkin Isotherm relationship between Qe and lnCe for Rhodamine B dye on Citrus aurantium leaf powder at a temperature range: a) 298 b) 308, c) 318 and d) 328 K

As can be seen from the calculated results in the Tab.1 the R coefficient figures were akin to 1, and for all isotherms, which means that a reasonable one is available in the relationship between Qe and lnn, the corresponding Ce at various temperatures that suggest the useful calculations of the constants. Adsorption of the Freundlich and Temkinin have better explained isothermal for isotherm shows.

Table 1. The factors of langmuir, Freundlich and Temkin condition for the adsorption of Rhodamine B dye on Citrus aurantium leaf powder

Dye	Tem. (K)	Langmuir Constants				Freundlich Constants			Temkin Constants		
		q_{max}	K_L	R_L	R^2	n	K_F	R^2	K_T	b	R^2
Rohdamine B	298	0.4467	0.0991	0.558	0.5975	0.667	24.027	0.9719	1.12	9224.02	0.9705
	308	0.3325	0.1263	0.497	0.5305	0.653	23.768	0.9622	1.124	9291.41	0.9672
	318	0.746	0.08	0.61	0.4207	0.777	16.436	0.9765	1.076	10782.43	0.9851
	328	0.2355	0.141	0,4699	0.7152	0.5884	33.136	0.9899	1.266	9595.33	0.9516

Thermodynamic of Adsorption Process

The effect of thermodynamic factors on the adsorption of rhodamine B on the surface of Citrus aurantium leaf powder at the temperature range 298-318K was studied. Where the study of the effect of temperature on the adsorption process enables us to specify the values of the thermodynamic functions (enthalpy, entropy, free energy) for all adsorption forms, as shown by the Van't Hoff equation, the adsorption equilibrium constant (K_{eq}) was calculated as (ln Q_e/C_e) against the temperature as (1/T) by means of plotting)[20]. The outcomes are recorded in Tab.2 and Fig.14 for the importance of these functions in understanding the adsorption phase system.

$\Delta G = -RT\ln K_{eq}$ ………………… 5

$\ln K_{eq} = -\ \Delta H/RT + \Delta S/R$……………….6

$\Delta G = \Delta H - T\Delta S$ ……………………..7

where K_{eq} is adsorption equilibrium constant and R is the gas constant

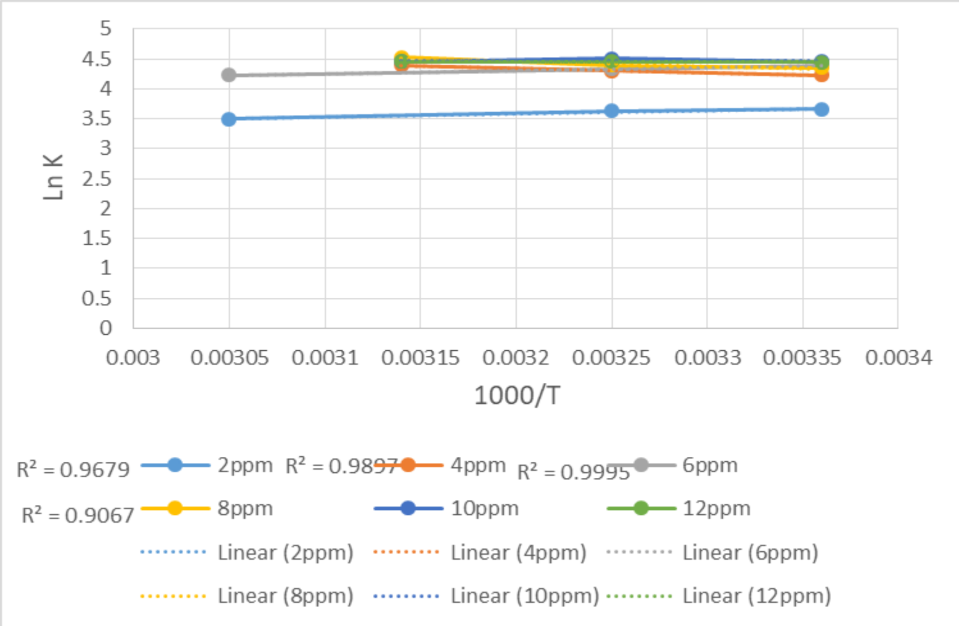

Figure 14. Van`t Hoff plot adsorption of Rh-B dye on citurs leaves powder

Table 2. Thermodynamic parameters of Rh-B dye on citurs leaves powder

C_o	T (K)	ΔH	ΔG	ΔS
	298		-10.877	65.7
6ppm	308	+8.703	-11.088	64.26
	318		-11.6065	63.87
	298		-10.877	89.07
8ppm	308	+15.666	-11.088	86.864
	318		-11.977	86.928

Conclusion:

The adsorption of Rhodamine B dye by citrus leaves powder has been determined. The adsorption was measurement that the dose of adsorbents was 0.4g. The amount adsorption of Rhodamine B dye increasing in PH = 3,7 but decreased with increasing PH. The best contact time within of 30 min for citrus leaves powder. The ionic strength was increasing with an increasing concentration of Sodium chloride. The adsorption process supplied Freundlich and Temkin isotherm models. The thermodynamic factors: ΔG spontaneous, ΔH was endothermic in nature, in addition, the values of ΔS were positive (higher).

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors' contributions:

A M.: Preparation, analysis, curation of data, Study, Writing- main draft.

A M. Far.: Conceptualization, analysis, Resources, Visualization, Editing Writing. The final paper was read and authorized by all writers.

H. I.: Resources, Visualization, Editing Writing.

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دراسة الامتزاز لصبغة رودامين ب على النبات (أوراق الحمضيات)

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[2] قسم الكيمياء، كلية العلوم، جامعة المستنصرية، بغداد، العراق.

الخلاصة:

تتضمن الدراسة الحالية امتزاز صبغة الرودامين B على سطح اوراق النارنج باستخدام تقنية مقياس الأشعة الفوق البنفسجية حيث تم تحديد البيانات الكمية للامتزاز (زمن التلامس، القوة الأيونية، درجة الحموضة، ودرجة الحرارة). تمت دراسة تأثير درجة الحرارة على عملية الامتزاز عند النطاق (25، 35، 45، و55) درجة مئوية حيث أظهرت النتائج بأن عملية امتزاز الرودامين B على مسحوق اوراق النارنج تزداد بزيادة درجة الحرارة مما يدل على أن عملية الأمتزاز عملية ماصة للحرارة. وبأستخدام تراكيز مختلفة من محلول كلوريد الصوديوم تم دراسة تأثير القوة الأيونية على عملية الأمتزاز.فقد ثبت أن زيادة القوة الأيونية تعمل على تحسين كمية أمتزاز رودامين B على أوراق النارنج عند درجات حرارة ثابتة. وأعطت النتائج أن كمية أمتزاز صبغة الرودامين B تزداد بزيادة PH للمحلول في المدى (3-7). ثم خضعت نتائج دراسة الامتزاز لنماذج متساوي الحرارة Langmuir , Freundlich و Temkin ، حيث تم تحديد معاملات كلا من Langmuir و Freundlich و Temkin ، ووجد أن متساوي الامتزازيخضع إلى متساوي الحرارة . Freundlich, Temkin تمت أيضًا دراسة المعاملات الديناميكية الحرارية (مقدار التغيير في المحتوى الحراري ، ومقدار التغيير في الانتروبيا ومقدار التغيير في الطاقة الحرة لـ Gibbs) ووجد أن النتائج الديناميكية الحرارية لعملية امتزاز صبغة Rhodamine-B على مسحوق أوراق النارنج ماصة للحرارة وعملية الأمتزازعملية تلقائية.

الكلمات المفتاحية: الامتزاز، أوراق الحمضيات، الأيزوثرم ، رودامين ب ، الديناميكا الحرارية .