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Adsorption of Titan Yellow Using Walnut Husks: Thermodynamics, Kinetics and Isotherm Studies

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ABSTRACT

The adsorption of Titan Yellow on a natural biosorbent (Walnut Husks) has been investigated. The dye concentration's amount of adsorbent, Ionic strength, touch time and temperature on Titan yellow adsorption activity have been investigated. Under optimal working conditions, walnut husks can remove more than 85.5 % of dye with a 0.06 g dose, with a 15 ppm initial dye concentration and contact time of 20 minutes at 298 K. The surface's appearance was determined using a scanning electron microscope (SEM). Langmuir, Freundlich, Temkin, Jovanovich, and Halsey adsorption isotherm models are used to interpret the experimental results. The following adsorption isotherm models best fit the evidence, according to the results: Freundlich, Halsey> Langmuir> Temkin>Jovanovich. The thermodynamics showed negative (ΔG,ΔH and ΔS) values, suggesting spontaneous , exothermic, and During the process of adsorption, the solid–solution interface has less randomness. According to the findings of this research, walnut husks could be used as a new low-cost, high-efficiency adsorbent for dye removal from wastewater.

Keywords :- Titan Yellow(T.Y); Adsorption; Walnut Husks; isotherm; Kinetic; Thermodynamic.

1-Introduction

Extensive use in many commercial applications of synthetic dyes Large amounts of dye waste water have been formed. Most are of them .It is deemed unsafe and requires thorough removal. Dye waste water is typically described as having a high salt and organic content and a low propensity for biodegradation[(1)].Water contamination is known to alter the environmental, biological and physical properties of the water that may influence the life of organisms. Many of the types of approaches that have been commonly used for the disposal of polluted water can be physical , chemical or biological [(2)] . Since adsorption provides performance, economy, versatility and simplicity of design, ease of production activity without unnecessary side products, it is better than other approaches, such as flocculation and coagulation, Flotation of froth, fermentation, biological method and Separation of membranes . As a result, adsorption has become a common method of dye removal. chemical contaminants and heavy metal ions from waste water [(3,4)]. Adsorption can be described is a major surface effect that typically defines the concentration of a component's position at such an interface with another solution or bulk stage. Adsorption is a natural phenomenon that occurs as the Entropy of the system decreases as Gibbs free changes [(5)]. Consequently, recent research has focused on developing a low-cost, locally available material to replace activated carbon, which is expensive and difficult to regenerate [(6)]. In this article, to remove titan yellow dye(Anionic dyes), walnut husks were used. Water-soluble reactive, because of their vivid hue and acidic qualities, anionic dyes are the most difficult to adsorb. However, there is no literature on anionic dye adsorption. and the anionic charges on the dyes and the anionic charges on the dyes, the adsorption ability dyes that are acidic is usually much lower than that of simple dyes [(7)]. Titan Yellow (T.Y), also known as Thiazol Yellow G and Clayton Yellow, is a sulfonic azo dye that has a negative charge. Azo dyes are a type of organic colored compound that has been used in a variety of industries, including textiles, papers, and leathers [(8)].

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2-Experiments

2.1 - Materials:

Use high-purity products that can be found on the local market. Walnut Husks were used and Titan yellow .

2.2 - Dye preparation

Titan yellow dye solution was made as a concentrated stock solution 100 mg/L by dissolving 0.0250 g of the dye that was used in 250 ml (D.W), Chemical formula $C_{28}H_{19}N_5Na_2O_6S_4$, M.Wt 695.720 g/mol , λmax 400nm , other physical properties of the dye. In figure (1) the structure of titan yellow is shown [9] .

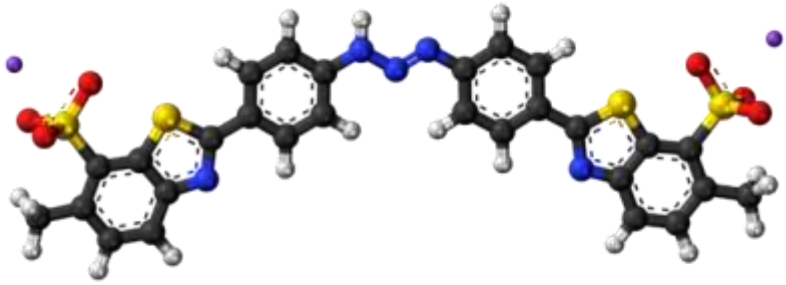

Figure 1. Titan yellow dye structure [10]

2.3-Walnut Husks Preparation

After gathering the walnut husks, they were washed in both tap and deionized water. Walnut husks were washed, ground, and sieved to yield (0.2) mm adsorbent particles using a mechanical sieve. The surface was evaluated with SEM techniques, Figures 3 demonstrate this.

Figure 2. Image of (a)Walnut Husks (b) Walnut Husks powder.

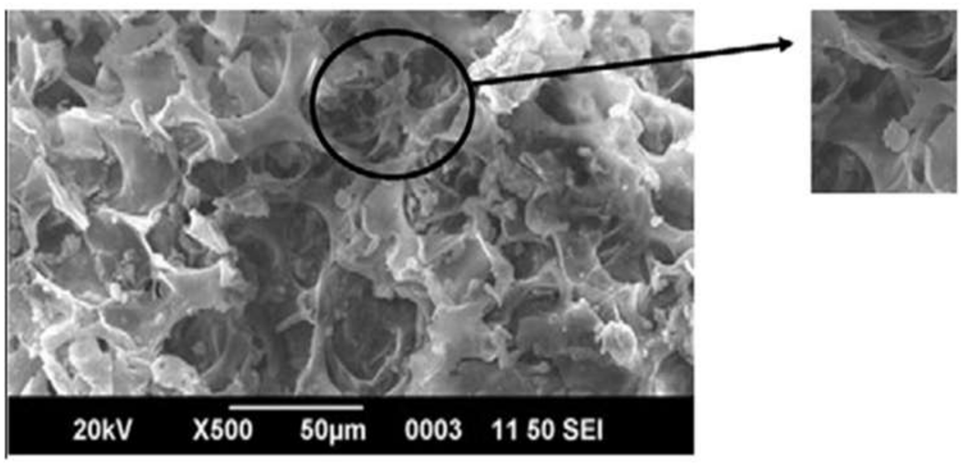

Figure 3. SEM image of Walnut Husks.

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Figure 3 Imagine the surface of the Walnut Husks using an electronic scanning microscope (SEM), Where it comes to form and size, spherical shapes are made up of well-connected units. The surface was flat and rough, resulting in more surface area and hence more effective adsorption positions. [11].

3-Discussion of the Findings (Equilibrium adsorption studies)

3.1- Contact Time Impact

The aim of the analysis was to decide the best time for titan yellow adsorption using walnut husks. By using 0.02g adsorbent material added to (25 mL) of dye solutions 15 ppm titan yellow at 150 rpm for (10-100 min) at 298K. The contact time's impact is shown in Figure (4). The amount of the adsorbed titan yellow increases with increasing time until it levels off after some (50 min). As a result, the total amount of time spent on all other experiments was 20 minutes. Since after 20 minutes, the improvement in the adsorption ratio was less. and after (50 min). it was not noticeable.

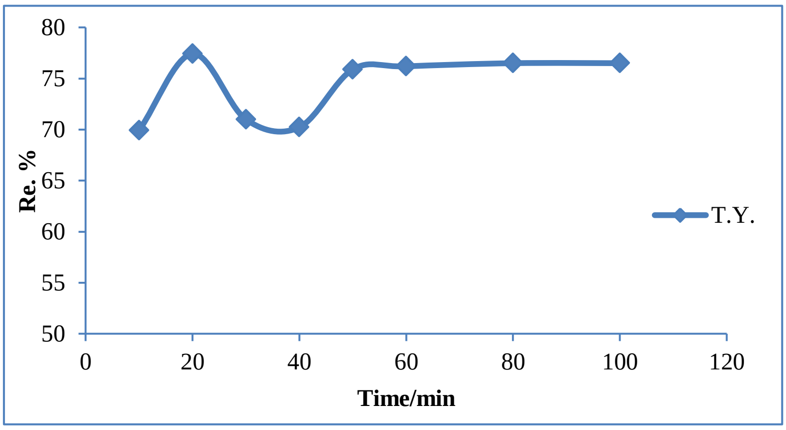

Figure 4. illustrate the contact time Impact

3.2- Adsorbent weight Impact

The adsorbent's weight was calculated to be between (0.01-0.08) g in Figure (5). Offers a simple view that, The dye proportion increased as the adsorbent's significantly influenced elimination from the solution increased the active sites of adsorption improved as the surface region of the adsorbent was increased. [12].With an increase in adsorbent weight up to a limit of 0.6 g, there is an increase in adsorption capacity giving a maximum adsorption ratio 85.51% .The weight of the adsorbent was set at 0.06 g because adsorption was unnoticeable above this weight.

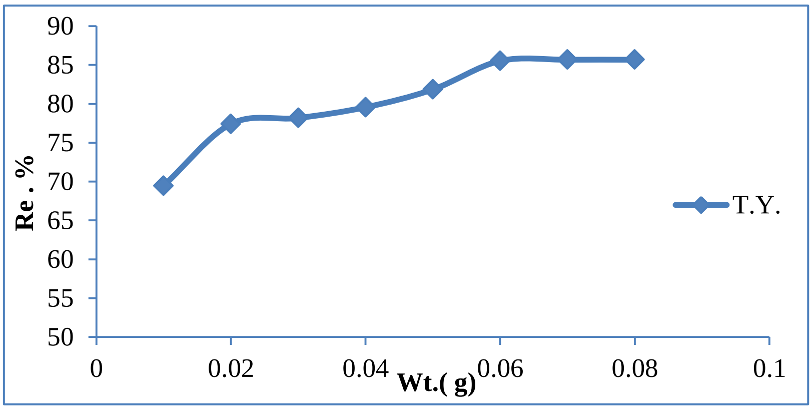

Figure 5. illustrate Adsorbent weight Impact.

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3.3- Ionic Intensity Impact

Various concentrations were used, varying from (0.02-0.07)M for each of the salts, at 298 K, a number of tests were carried out. assess the effect of ionic strength on absorption potential and removal rate (NaCl, $CaCl_2$, $AlCl_3$). The adsorption ratio of aluminum chloride salt was as high as it could be. The ionic strength effect is depicted in Figure (6).

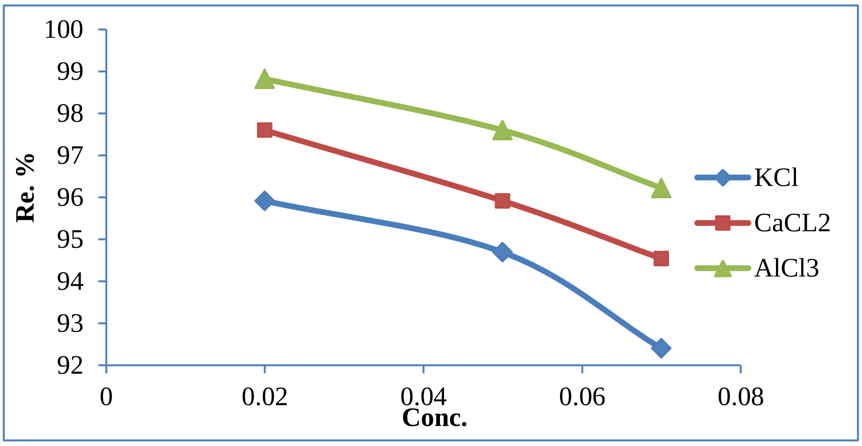

Figure 6. illustrate Ionic Intensity Impact**.**

3.4- Temperature Impact

Walnut husks were used to studied Titan yellow. Under a certain temperature range (298-328 K). Equations 1 to 4 Thermodynamic parameters such as Gibbs free (ΔG) were measured, enthalpy (ΔH) and entropy (ΔS)[(13)] ,which are listed in table (1). Figure (7). Demonstrates a temperature-affecting influence**.**

$K_{eq} = \frac{Q_e \text{ x } m}{C_e \text{ x } V}$ ………..………… (1)

$\Delta G = -RT lnK_{eq}$ ……………...…. (2)

$lnK_{eq} = \frac{-\Delta H}{RT} + con.$ .... (3)

$\Delta S = \frac{\Delta H - \Delta G}{T}$ …………….…….. (4)

Table 1. Parameters in Thermodynamics $\Delta G,\ \Delta H\ and\ \Delta S$ at (298-328)K

adsorbate	Temp. K	**-ΔG** KJ. mol^{-1}	**-ΔH** KJ. mol^{-1}	**-ΔS** J. mol^{-1} . K^{-1}
Titan yellow	**298**	4.3997	18.4596	47.1808
	308	3.96345		47.0653
	318	3.54262		46.9087
	328	3.01329		47.0923

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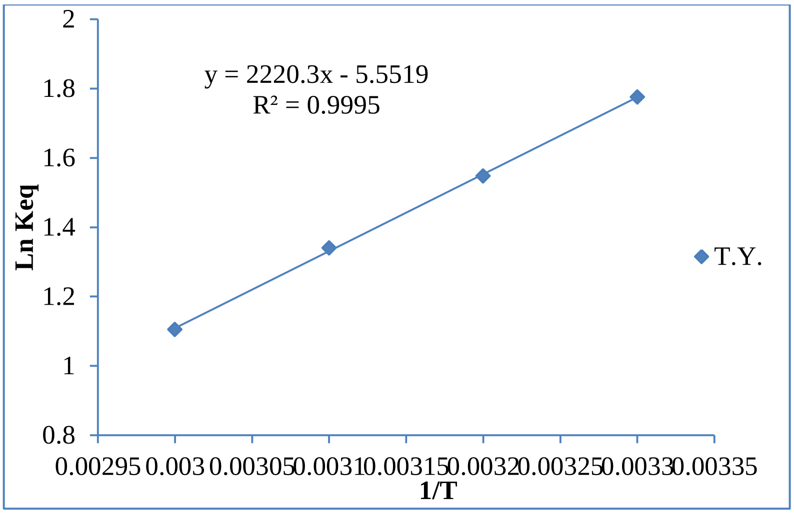

Figure 7. illustrate Temperature Impact.

- The adsorption mechanism is random, so negative free energy values apply; the values of the free energy declined as the temperature rose, meaning that adsorption was physical [14,15].
- The exothermic function is shown by a negative value of ΔH. [16].
- The reduction in freedom randomness is expressed by negative values of ΔS[17] .

Adsorption isotherm

To illustrate the equilibrium data from this study, the Langmuir, Freundlich, Temkin, Jovanovich, and Halsey adsorption isotherms were used. Values of the correlation coefficients r^2 calculated using linear regression were used to determine the isotherm equation's acceptability and validity for equilibrium data. 25 mL conical flasks were used in the adsorption tests, which were carried out at temperatures ranging from (298-328) K. At ideal conditions, the equilibrium state was found (adsorbent materials of 0.06 g , dye concentration of 15 ppm , 298 k and 20 min at 150 rpm. From the equation (6) the amount of the adsorbed substance was computed .

$$\% = [(C_0 - Ce)/C_0] \times 100 \quad \ldots\ldots\ldots\ldots (5)$$

$$Qe = V(Co - Ce)/\, m \quad \ldots\ldots\ldots (6)$$

Where:-

$Qe = x/m$: is the quantity of adsorbed substance in (mg/g) adsorbend, V: is the size of pesticide solution L used C_0: is the concentration at the initial (mg/L), Ce: is the equilibrium state's concentration (mg/L), m: is the mass of the adsorbent material in (g) [18].

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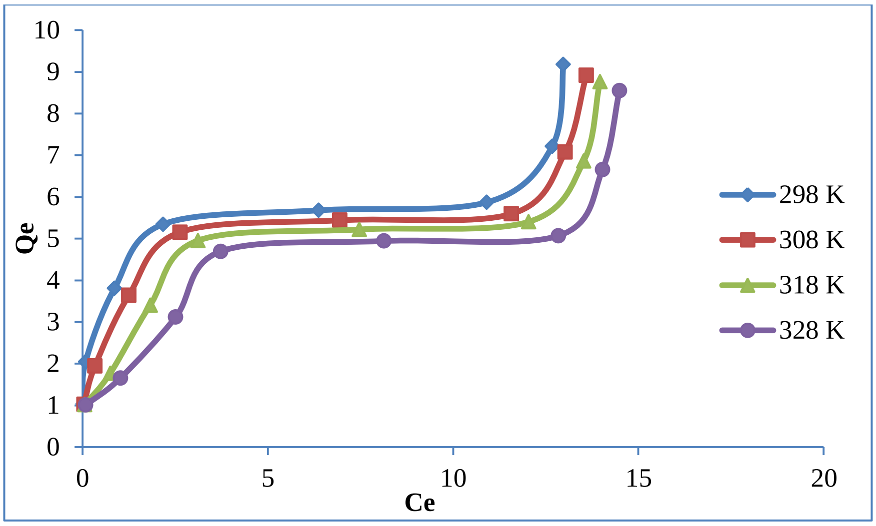

Figure 8. Isotherm of adsorption at various temperatures.

The experimental findings were used to determine the form of the isotherms, which were found to be similar according to the Giles rating (L- curve) [19] .

- **Langmuir isotherm** : -

The isotherms of the Langmuir model were estimated using the equation below.

$$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{C_e}{a} \dots\dots\dots\dots(7)$$

Where:-

a: $(mg\ /\ g)$maximum absorption capacity (Langmuir constant).

b: $(mg\ /\ L)$ The Langmuir constant has everything to do with adsorption affinity and free energy. [20] .

A linear plot was obtained when Ce/Qe vs. Ce as shown in Figure(9).

The adsorption operation's feasibility is determined using the separation factor R_L, which is defined by equation (8).

$$R_L = \frac{1}{(1 + b\ C_o)} \dots\dots\dots\dots\dots(8)$$

The R_L meaning denotes the isotherm's beneficial or unfavorable group ($R_L > 1$), linear $R_L = 1$, irreversible $R_L = 0$ or favorable $0 < R_L < 1$ [21] .

- **Freundlich isotherm**

For multilayer sorption on a heterogeneous surface, the Freundlich isotherm is expected. The Freundlich equation has the following linear form:

$$Log\ Q_e = Log\ K_f + \frac{1}{n} Log\ C_e \dots\dots\dots\dots\dots(9)$$

where :-

Qe and Ce are similar to the definitions given above. K_f (L/mg) and (n) are constants in the Freundlich equation that are dependent on capacity of adsorption and the intensity of adsorption respectively [22] . A linear plot was obtained when logQe vs. logCe as shown in Figure.9.

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- **Temkin isotherm**

The adsorbent relationships and adsorbing species are demonstrated by the Temkin isotherm . According to this theory, Because of the existence of adsorbent-adsorbate interactions, the heat of adsorption for all molecules in the adsorption layer drops linearly with increasing surface coverage. The Temkin equation takes the following linear form:

$$Q_e = Bln\, A_t + B\, ln\mathrm{C_e} \dots\dots\dots\dots\dots\dots (10)$$

where: -
A_t : is the binding at balance that corresponds to the maximum binding energy.
B :is a constant that is related to adsorption heat. [23] . When you have a linear plot, Qe vs. $ln\ Ce$ as shown in Figure(9).

- **Jovanovich isotherm**

This model is based on the assumptions found in the Langmuir model and the probability of such mechanical interactions (adsorbent-adsorbate) is taken into account [24] .

$$LnQ_e = ln\, Q_{max} - K_J\mathrm{C_e} \dots\dots\dots\dots\dots\dots . (11)$$

Where Q_{max} and K_J The Jovanovich isotherm constants can be calculated using the intercept and slope, respectively. A linear plot was obtained when $lnQe$ vs. Ce as shown in Figure(9).

- **Halsey isothermal**

In multilayer adsorption, the Halsey isothermal model is optimal. The heterogonous existence of the adsorbent. The Halsey equation has the following linear form: [25]

$$LnQ_e = \frac{1}{n_H} ln\, K_H - \frac{1}{n_H} ln\mathrm{C_e} \dots\dots\dots\dots . (12)$$

Where:-

K_H and n_H are the Halsey isotherm constants. A linear plot was obtained when lnQe vs. lnCe as shown in Figure(9).

Table 2. The adsorption reaction Langmuir, Freundlich, Temkin, Jovanovich, and Halsey acts at (298–328) K.

Temp. K	Langmuir isotherm				Freundlich isotherm			Isotherm Temkin		
	a mg/g	b Mg/L	R^2	R_L	K_f	n	R^2	B	A_T	R^2
298	7.6982	1.2118	0.9268	0.0521	3.7222	3.5599	0.9617	0.9818	109.158	0.8659
308	7.6687	0.7813	0.9131	0.0786	3.0874	2.9717	0.9594	1.1368	31.8742	0.8434
318	7.8431	0.4750	0.8911	0.1230	2.6187	2.6730	0.9370	1.2176	16.2419	0.7954
328	7.8247	0.3378	0.8515	0.1648	2.2882	2.5464	0.9195	1.2294	11.1106	0.7529

Temp. K	Jovanovich isotherm			Halsey isotherm		
	K_J	Q_{max}	R^2	n_H	K_H	R^2
298	0.1007	2.3473	0.6346	3.5599	107.64	0.9617
308	0.1001	2.1812	0.6638	2.9717	28.511	0.9594
318	0.1028	1.9697	0.7032	2.6730	13.113	0.9370
328	0.1033	1.7728	0.7450	2.5464	8.2292	0.9195

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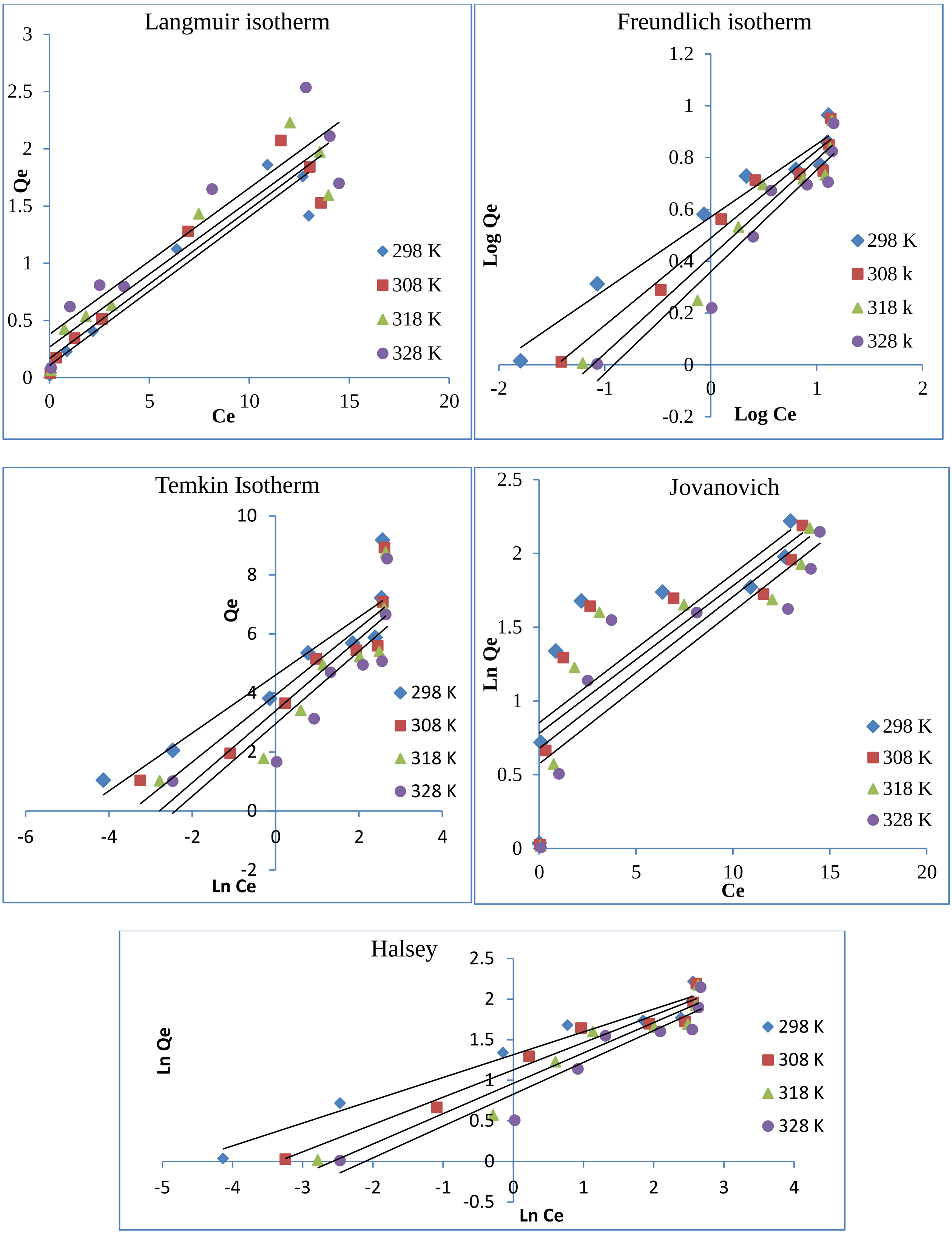

Figure 9. Isotherms for titan yellow dye at different temperatures.

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The Freundlich and Halsey isotherm are more applicable, as seen by the correlation coefficient (R^2) in table 2. This indicates that titan yellow adsorption on walnut husks is multilayer sorption on a heterogeneous surface.

Kinetics study:

Equations (14) and (15) were used to measure the formulas pseudo first order kinetic and pseudo second order kinetic models. And Q_t can be calculate from equation (13)[26,27]

$$Q_t = \frac{(C_0 - C_t)V}{m} \ldots \ldots \ldots (13)$$

$$\text{Log}\,(Qe - Qt) = \log Qe - \frac{K_1 t}{2.303} \ldots \ldots \ldots \ldots (14)$$

$$\frac{1}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \ldots \ldots \ldots \ldots (15)$$

where Qe and Qt (mg/g) are the equilibrium and time t (min) adsorption capacities, respectively. The pseudo-first-order rate constant is K_1 (min^{-1}), The pseudo-second-orderv is K_2 (g mg^{-1} min^{-1})

Table 3. Adsorption Kinetics Model

Pseudo − first − order	***K_1***	***Qe***	***R^2***
	0.7093	579.1619	**0.6647**
Pseudo − second − order	***K_2***	***Qe***	**R^2**
	0.0447	15.3374	**0.9970**

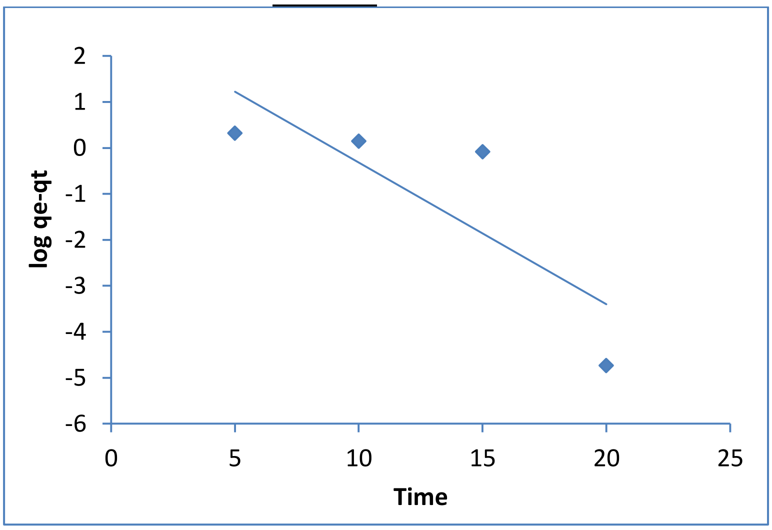

Figure 10. Pseudo-first-order

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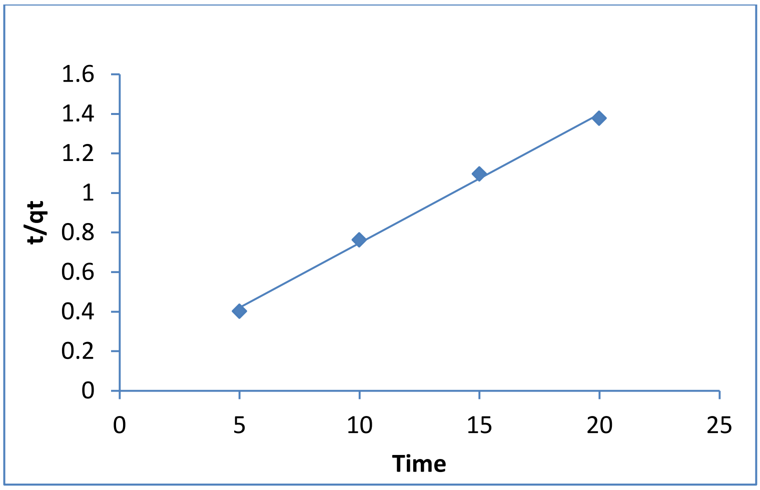

Figure 11. pseudo-second-order

R^2 indicates that the parameters in the linear plot have a similar relationship, indicating that the adsorption mechanism follws a pseudo second order kinetic model (Fig.10,11).

4-Conclusions:-

- This research showed that walnut husks can be used as an important adsorbent material for withdrawing titan yellow dye from aqueous solutions.
- At optimum conditions (15 ppm dye concentration, absorbent content weight 0,06 g and contact time 20 min.) at 298 K, the removal ratio was 85.5 %.
- It was discovered that the equilibrium results match the Freundlich and Halsey isotherm model very well.
- Thermodynamic experiments show that the adsorption mechanism was exothermic and spontaneous, and that it reduced randomness at the solid-solution interface.
- Titan yellow adsorption on walnut husks follows a pseudo second-order kinetic model, according to a kinetics study.

References

[1] Vimonses, V., Lei, S., Jin, B., Chow, C. W., & Saint, C. (2009). Adsorption of congo red by three Australian kaolins. *Applied clay science,* 43(3-4), 465-472.

[2] Al-Taweel, S. S., Jabbar, N. K., Al-Taweel, R. S., & Auda, A. J. (2016). Local wheat peel as a solid surface to remove Azure B dye from aqueous solution: Equilibrium isotherms and thermodynamic study. *Baghdad Science Journal*, 13(2).

[3] Xu, Z., Li, W., Xiong, Z., Fang, J., Li, Y., Wang, Q., & Zeng, Q. (2016). Removal of anionic dyes from aqueous solution by adsorption onto amino-functionalized magnetic nanoadsorbent. *Desalination and Water Treatment,* 57(15), 7054-7065.

[4] Xu, L., Zheng, X., Cui, H., Zhu, Z., Liang, J., & Zhou, J. (2017). Equilibrium, kinetic, and thermodynamic studies on the adsorption of cadmium from aqueous solution by modified biomass ash. *Bioinorganic chemistry and applications, 2017.*

[5] Jaism, L., Radhy, N., & Kmal, R. (2015). A study of Adsorption of Azure B and C from Aqueous Solutions on Poly (Acrylamide-co-Crotonic acid) Hydrogels Surface. *Chem. and Pro. Eng. Research,* 32, 62-69.

[6] Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal: *a review. Bioresource technology,* 97(9), 1061-1085.

[7] Bulut, E., Özacar, M., & Şengil, İ. A. (2008). Equilibrium and kinetic data and process design for adsorption of Congo Red onto bentonite. *Journal of hazardous materials,* 154(1-3), 613-622.

[8] Shi, Q. X., Li, Y., Wang, L., Wang, J., & Cao, Y. L. (2020). Preparation of supported chitosan adsorbent with high adsorption capacity for Titan Yellow removal. *International journal of biological macromolecules,* 152, 449-455.

[9] Ghaemi, M., Absalan, G., & Sheikhian, L. (2014). Adsorption characteristics of Titan yellow and Congo red on CoFe 2 O 4 magnetic nanoparticles. *Journal of the Iranian Chemical Society,* 11(6), 1759-1766.

[10] Salem, M. A., Salem, I. A., Hanfy, M. G., & Zaki, A. B. (2016). Removal of titan yellow dye from aqueous solution by polyaniline/Fe3O4 nanocomposite. Eur. *Chem. Bull,* 5(3), 113-118.

[11] Popoola, L. T., Aderibigbe, T. A., Yusuff, A. S., & Munir, M. M. (2018). Brilliant green dye adsorption onto composite snail shell–rice husk: Adsorption isotherm, kinetic, mechanistic, and thermodynamics analysis. *Environmental Quality Management,* 28(2), 63-78.

[12] Ibrahim, H. K., Allah, M. A. A. H., Al-Da'amy, M. A., Kareem, E. T., & Abdulridha, A. A. (2020, June). Adsorption of Basic Dye Using Environmental friendly adsorbent. In IOP Conference Series: *Materials Science and Engineering* (Vol. 871, No. 1, p. 012027). IOP Publishing.

[13] Ibrahim, H. K., Al-Da Amy, M. A., & Kreem, E. T. (2019). Decolorization of Coomassie brilliant blue G-250 dye using snail shell powder by action of adsorption processes. *Research Journal of Pharmacy and Technology,* 12(10), 4921-4925.

[14] Bayramoglu, G., Altintas, B., & Arica, M. Y. (2012). Synthesis and characterization of magnetic beads containing aminated fibrous surfaces for removal of Reactive Green 19 dye: kinetics and thermodynamic parameters. *Journal of Chemical Technology & Biotechnology,* 87(5), 705-713.

[15] Liu, J., Wan, L., Zhang, L., & Zhou, Q. (2011). Effect of pH, ionic strength, and temperature on the phosphate adsorption onto lanthanum-doped activated carbon fiber. *Journal of colloid and interface science,* 364(2), 490-496.

[16] Rashwan, W. E., & Shouman, M. A. (2015). Sorption Isotherm Studies for the Removal of Brilliant Blue Dye from Aqueous Solution by Modified Egyptian Kaolin. *Asian Journal of Applied Sciences,* 3(6).

[17] Ata, S., Imran Din, M., Rasool, A., Qasim, I., & Ul Mohsin, I. (2012). Equilibrium, thermodynamics, and kinetic sorption studies for the removal of coomassie brilliant blue on wheat bran as a low-cost adsorbent. *Journal of analytical methods in chemistry,* 2012.

[18] Kibrahim, H., Muneer, A. A., & TKreem, E. (2018). Effective Adsorption of Azure B Dye from Aqueous Solution Using Snail Shell Powder. *Journal of Biochemical Technology,* 9(3), 39-44.

[19] Giles C.H., Smith D., and Huitson A., (1974). A general treatment and classification of the solute adsorption isotherm. I. Theoretical. *Journal of colloid and interface science,* 47 pp.755-765.

[20] Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. Part I. Solids. *Journal of the American chemical society,* 38(11), 2221-2295.

[21] AL-Shemary, R. Q., Ibrahim, H. K., Muneer, A., Kareem, E. T., & Allah, M. A. A. H. (2020, November). Study the Azure A dye adsorption on the surface of the Snail shell modification. In IOP Conference Series: *Materials Science and Engineering* (Vol. 928, No. 5, p. 052021). IOP Publishing.

[22] Freundlich, H. (1907). Über die adsorption in lösungen. *Zeitschrift für physikalische Chemie*, 57(1), 385-470.

[23] Temkin, M. I. (1940). Kinetics of ammonia synthesis on promoted iron catalysts. *Acta physiochim.* URSS, 12, 327-356.

[24] Misra, D. N. (1973). Jovanovich adsorption isotherm for heterogeneous surfaces. *Journal of Colloid and Interface Science,* 43(1), 85-88.

[25] Halsey, G. (1948). Physical adsorption on non- uniform surfaces. *The Journal of chemical physics*, 16(10), 931-937.

[26] Farouq, R., & Yousef, N. S. (2015). Equilibrium and kinetics studies of adsorption of copper (II) ions on natural biosorbent. *International Journal of Chemical Engineering and Applications*, 6(5), 319.

[27] Awala, H. A., & El Jamal, M. M. (2011). Equilibrium and kinetics study of adsorption of some dyes onto feldspar. *Journal of the University of Chemical Technology & Metallurgy*, 46(1).