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Adsorption of Brilliant Scarlet 3r dye onto Corn Silk as Agricultural Waste in Neutral Medium

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Abstract

This study investigates the adsorption of Brilliant Scarlet 3r dye (BS 3r) onto corn silk (CK), an agricultural waste, in a neutral medium. The characteristics of corn silk as an adsorbent were analyzed using Fourier transform infrared spectroscopy (FTIR) and Atomic force microscopy (AFM). Batch adsorption experiments were conducted to examine the effects of corn silk weight, initial BS 3r concentration, adsorption period, adsorption temperature, and pH of the medium on the adsorption process. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms models were used to represented the equilibrium experimental date, the obtained values of correlation coefficient R^2 indicated that the adsorption followed the Langmuir isotherm. The kinetics analysis results showed that the adsorption of Brilliant Scarlet 3r dye (BS 3r) onto corn silk followed the pseudo second-order model (PSOM), indicating its suitability for describing the adsorption kinetics. Thermodynamic parameters, including ΔG°, ΔH°, and ΔS°, indicated that the adsorption process of BS 3r dye onto corn silk was spontaneous and exothermic in nature.

Keywords: Adsorption; Corn silk, Brilliant Scarlet 3r; Kinetic.

امتزاز الصبغة القرمزية اللماعة 3r على حرير الذرة كمخلفات زراعية في وسط متعادل

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الخلاصة

تبحث هذه الدراسة في امتزاز الصبغة القرمزية 3r (BS 3r) على سطح حرير الذرة (CK) وهي مخلفات زراعية, في وسط متعادل . تم تحليل خصائص حرير الذرة كمادة مازة باستخدام طيف الاشعة تحت الحمراء(FTIR) ومجهر القوة الذرية (AFM). اجريت تجارب دفعات الامتزاز لفحص تأثير وزن حرير الذرة, تركيز BS 3r الابتدائي ، فترة الامتزاز, درجة حرارة الامتزاز, درجة حموضة الوسط على عملية الامتزاز. تم استخدام نماذج متساويات درجة حرارة الامتزاز لنكماير, فريندلش, دوبنن رادوش كيفج (D–R) لعرض نتائج تجارب الاتزان وتشير القيم التي تم الحصول عليها لمعامل الارتباط (R^2) الى ان الامتزاز يتبع متساوي درجة الحرارة لنكماير. أظهرت نتائج التحليل الحركي ان امتزاز الصبغة القرمزية 3r (BS 3r) على حرير الذرة يتبع إنموذج المرتبة الثانية الكاذب(PSOM), مما يشير الى ملائمته لوصف حركيات الامتزاز. أشارت المعلمات الدينمية الحرارية، بما في ذلك ΔG°, H° و ΔS° , الى ان عملية امتزاز صبغة BS 3r على سطح حرير الذرة كانت تلقائية وباعثة للحرارة بطبيعتها.

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1. Introduction

The discharge of dyes into wastewater from the textile industry is a significant environmental concern due to its negative impact on the photosynthetic activity of aquatic ecosystems. Additionally, certain dyes can degrade into toxic, carcinogenic, and mutagenic compounds, further exacerbating the environmental risks [1, 2]. Therefore, it is crucial to treat these colored effluents from industrial wastewater before they are released into the environment. Various biological and physicochemical methods have been developed to remove these organic toxic compounds from industrial wastewater, aiming to minimize their environmental consequences. The biological methods include anaerobic and aerobic processes[3], precipitation [4], chemical oxidation [5], Flocculation-coagulation [6], ion-exchange [7], membrane filtration [8], photocatalytic degradation [9], and adsorption [10]. However, the most of organic dyes are difficult to be remove using conventional biological and physicochemical processes since these compounds are stable against the oxide agents, resist biodegradation and light [11]. Therefore, adsorption technique becomes an efficient methods to eliminate these organic dyes from wastewater because of its simplicity, low cost and high efficiency [12].

The use of adsorption techniques has led to the utilization of various natural and synthetic materials, including polymers, clay, activated carbon, industrial by-products, and agricultural waste, as effective adsorbents [13]. Agricultural waste materials, in particular, have gained significant attention due to their abundance and high surface area, which contribute to their remarkable adsorption capacity [14].

Corn silk (Figure 1) is a yellow, silky substance that grows on the top of corn fruits and is considered a major by-product of the corn processing industry. It is commonly discarded as eco-friendly agricultural waste [15]. These materials are utilized to remove various dyes such as methylene blue [16], indigo Carmine [17], reactive Blue 19, reactive Red 218 [18], also it was used for lead removal [19].

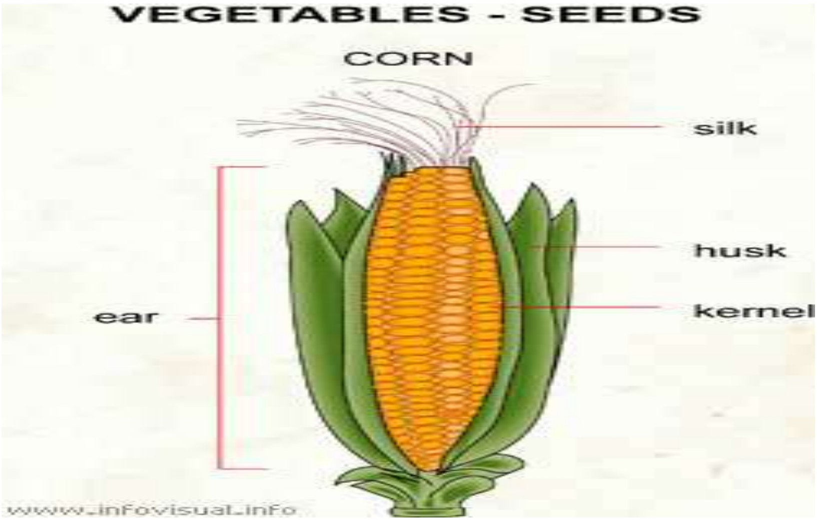

Figure 1: Corn silk as adsorbent.

The objective of this study is to explore the efficacy of corn silk (CK) as a viable adsorbent for the elimination of Brilliant Scarlet 3R dye, a common textile dye, from water-based solutions through the utilization of adsorption techniques. Various adsorption isotherms, namely Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) models, have been employed to elucidate the adsorption data. Additionally, the kinetics and thermodynamics associated with the adsorption process of BS 3R dye onto CK have been thoroughly examined.

2. Experimental

2.1. Adsorbate

Brilliant Scarlet 3r dye is an azo dye with a vibrant strawberry red color, which is synthesized from aromatic hydrocarbons. Its chemical formula is $C_{20}H_{11}N_2O_{10}Na_3S_3$, and its IUPAC name is trisodium(8²)-oxo-8[(4-sulfonatonaphthalen-1-yl)hydrazinylidene]naphthalene-1,3-disulfonate. The dye exhibits maximum absorption at a wavelength of 505 nm, and it has a formula weight of 604.49 g/mol. The chemical structure of the dye is illustrated in Figure 2.

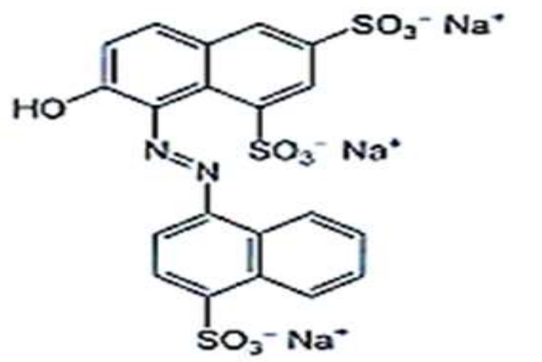

Figure 2: The chemical structure of BS 3r dye [20].

A stock solution of Brilliant Scarlet 3r (BS 3r) dye was prepared by dissolving 1000 mg/L of the dye in water. From the stock solution, various concentrations ranging from 20 to 100 ppm were prepared by dilution.

2.2. Adsorbent

Corn silk (CK) samples were obtained from local fruit and vegetable markets. The collected CK was thoroughly washed with distilled water to remove any impurities and dust particles. Subsequently, it was dried in an oven at 105°C overnight to ensure complete drying. The dried CK was then ground using a mechanical grinder (Silver Crest, YT-4689A, Germany) and stored in a dry location. The CK powder is known to contain various important compounds such as carbohydrates, vitamins, proteins, volatile oils, steroids, flavonoids, and polyphenols [21].

2.3. Adsorption experiment

The adsorption of BS 3r dye onto the surfaces of CK was conducted using the batch method. In this method, various concentrations of the working solutions were brought into contact with 0.2 g of CK as the adsorbent in 50 mL round bottom flasks. The experiments were carried out at a temperature range of 298-318 K and a pH of 7, with an adsorption period of one hour. The solutions were agitated using a mechanical shaker at 250 rpm. After the designated adsorption period, the suspensions were filtered, and the initial and equilibrium concentrations of the BS 3r dye were determined using a UV-Vis spectrophotometer at a wavelength of 505 nm, corresponding to its maximum absorption. The amount of adsorbate adsorbed onto the CK sorbent, qe (mg/g), was estimated using the following equation [22]:

$$q_e = \frac{(C_s - C_e)\mathrm{V}}{Wt} \quad (1)$$

The ability of removal (removal percentage) was obtained as:

$$\mathrm{R\%} = \frac{C_s - C_e}{C_s} \times 100 \quad (2)$$

where Cs and Ce is the starting BS 3r dye and equilibrium concentration for BS 3r dye (mg.L^{-1}) respectively, V is the volume (mL) of dye solution and Wt is the weight of CK (g).The characterization of corn silk was carried out using Fourier transforms infrared spectroscopy (FTIR) is measure using a Shimadzu IR affinity (Japan) in the 4000-400 cm^{-1} region. Average diameter and average particles volume were measured by atomic force microscopy (AFM) type (NaioAFM-2022-Switzerland**)** technique. UV-Vis spectrophotometer model(Schematize 1800-Japan) was used to determine the absorption wavelength for the dye.

3. Results and Discussion

3.1. Characterization

3.1.1. *Fourier transforms infrared spectroscopy (FTIR)*

Figure 3 illustrates the functional groups identified in the CK powder. The broad band observed at 3421.48 cm-1 can be attributed to the N-H stretching vibration. The peak at 2923.88 cm-1 corresponds to the C-H stretching vibration [23]. Additionally, the presence of a peak at 1649.02 cm-1 indicates the presence of an N-H bond, which suggests the presence of proteins in the CK powder [24]. The peaks observed at 1257.50 cm-1 and 1245.93 cm-1 can be attributed to carbonyl stretching. Furthermore, the broad band observed at 1037.63 cm-1 indicates the presence of sugars in the pyranose form [25] .

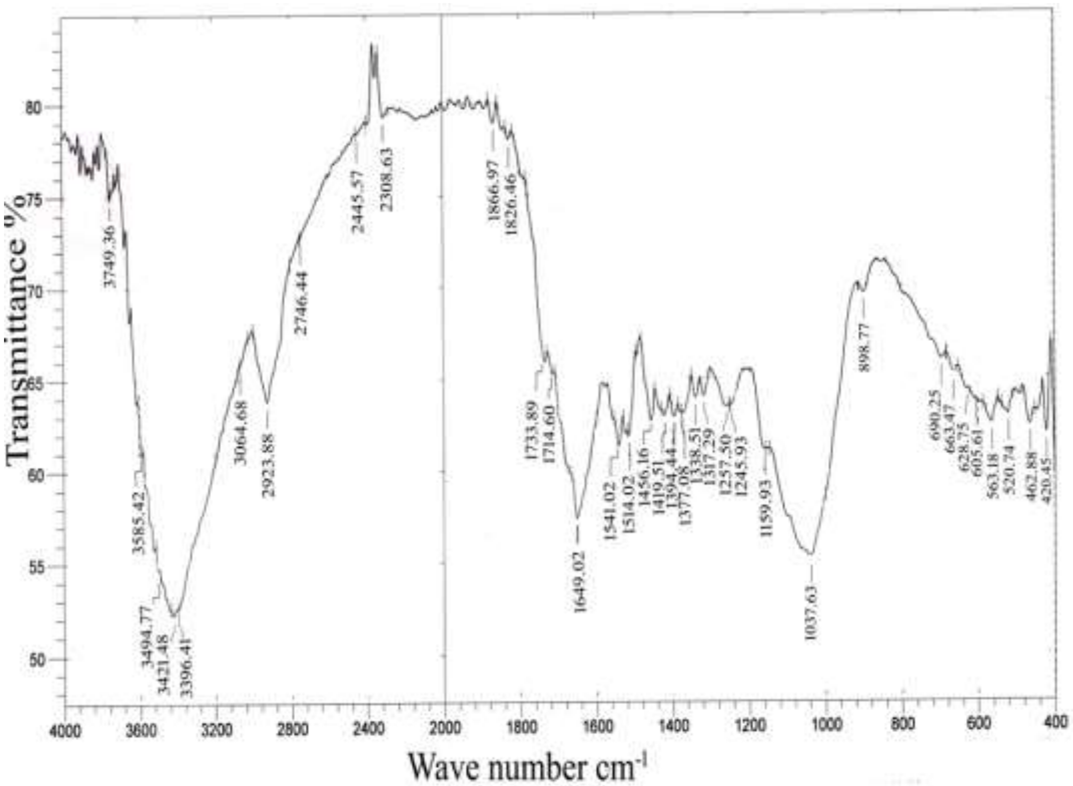

Figure 3: FTIR transmission for CK sample.

3.1.2. *Atomic Force Microscopy (AFM)*

An information about the volume, 3D pictures, and about average grain diameter were obtained using AFM technique. Figure 4 shows a typical surface and the granularity cumulating distribution for the CK sample. The obtained results show that the average diameters of CK sample is 197.1 nm, and the average volume of the particles is 1.119 nm^3.

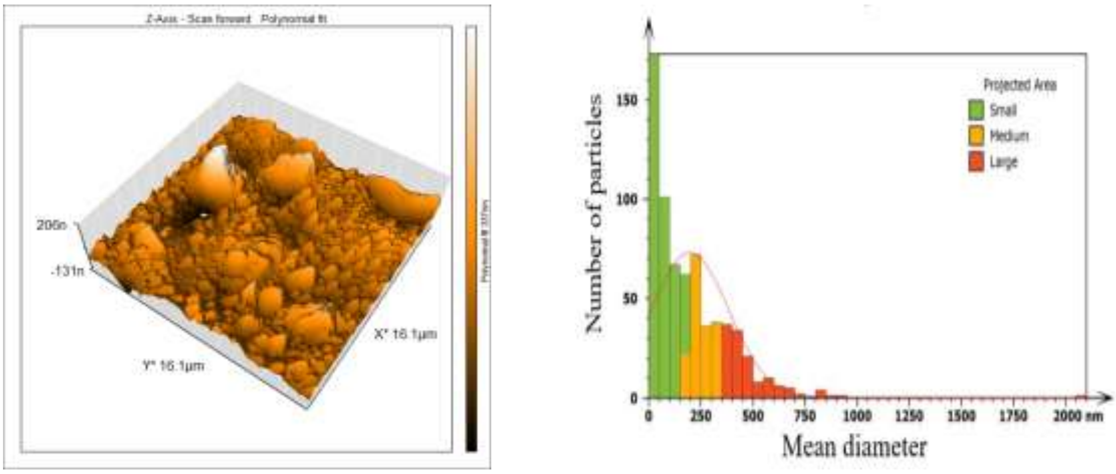

Figure 4: 3D AFM image and average mean diameter for CK sample

3.2. Adsorption of BS 3r dye onto corn silk

3.2.1. Spectrophotometric determination BS 3r dye

The absorption spectra of BS 3r dye were recorded using a UV-Visible spectrophotometer at a wavelength of 505 nm. The absorbance value is 0.079. Figure 5 illustrate the UV-visible spectrum for BS 3r dye.

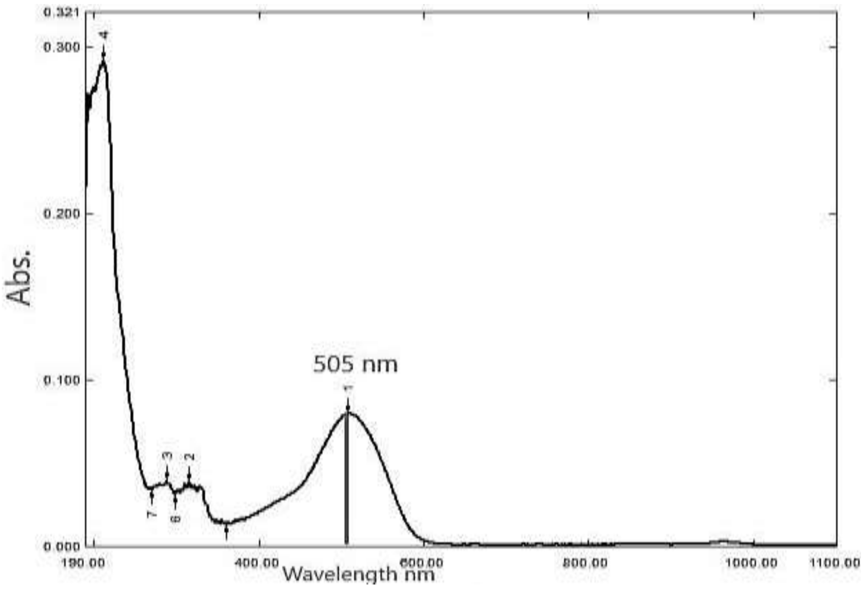

Figure 5: UV-Visible absorption spectrum for (20 mg/L) BS 3r dye

3.2.2. The impact of operating conditions

3.2.2.1. The impact of corn silk weight

In Figure 6, the effect of CK weight on the removal percentage (R%) of BS 3r dye is demonstrated. The initial concentration of the dye was set at 20 mg/L, at a temperature of 298 K and an initial pH of 7. Various weights of CK ranging from 0.1 to 0.4 g were used in a 50 mL dye solution. The results indicate that the maximum removal percentage was achieved when the CK weight was 0.2 g. Beyond this point, further increases in CK weight did not significantly affect the removal efficiency of BS 3r dye. Therefore, the optimum CK weight of 0.2 g was selected for subsequent experiments.

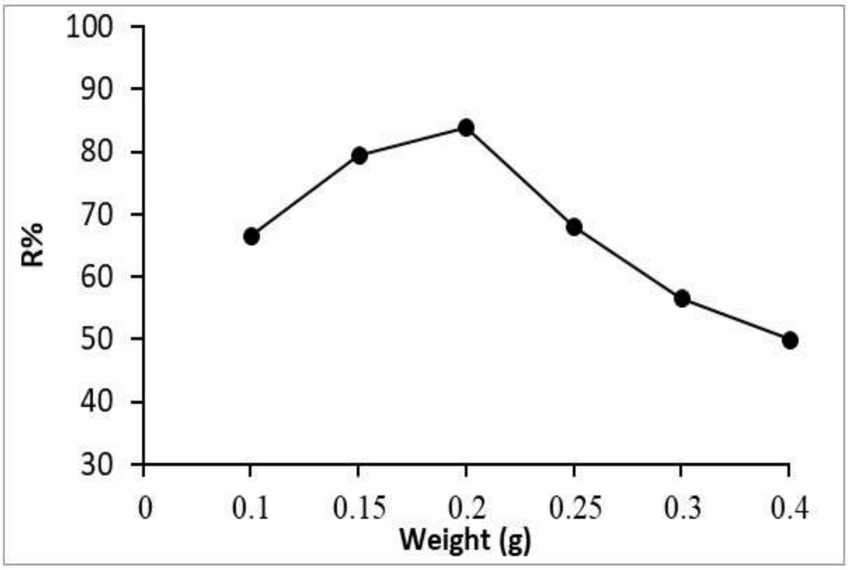

Figure 6: The impact of corn silk weight on the removal percentage of BS 3r dye.

3.2.2.2. The impact of starting BS 3r concentration

In Figure 7, the relationship between the removal percentage and the starting concentrations of BS 3r dye is presented. The starting concentrations of the dye were varied from 20 to 100 ppm, while maintaining a temperature of 298 K, pH of 7, and CK weight of 0.2 g in a 50 ml dye solution. The results indicate that the highest removal percentage of 83.03% was achieved at a starting concentration of 20 mg/L. However, as the BS 3r concentration increased beyond this point, the removal percentage gradually decreased. This observation suggests that as the concentration of BS 3r dye increases, the available adsorption sites become saturated, leading to a reduction in the overall removal percentage [26].

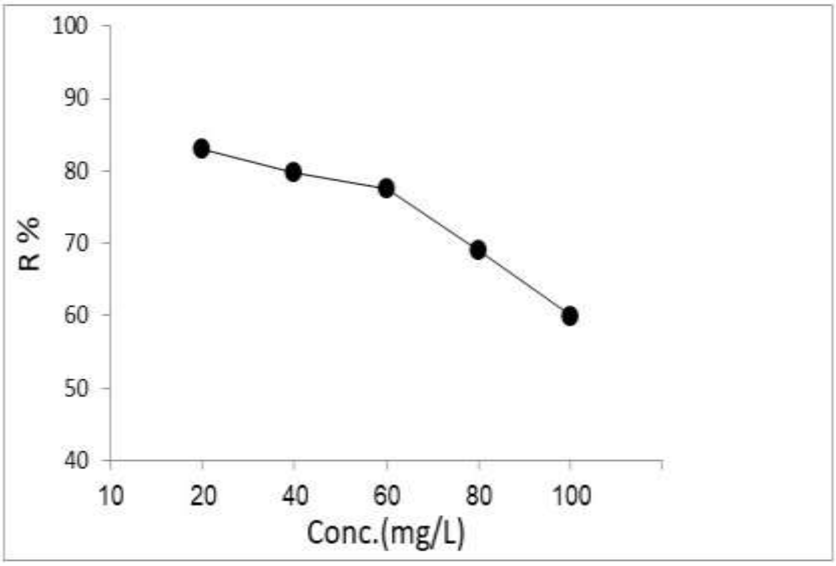

Figure 7: The impact of starting BS 3r concentration on the removal percentage.

3.2.2.3. The impact of adsorption period

Figure 8 shows the impact of adsorption period on the adsorption of BS 3r onto CK surface. The adsorption period changed from 15-120 min with keeping other operating parameters constant. It can be seen from this Figure that the values of R% increase from 65.45% to 84.03% after one hour then when the period of the adsorption increase the removal decrease and remained almost constant, this may be related to that a large number of the BS 3r molecular accumulated on the surface of CK after one hour because of the high availability of active surface sites on it, after that there is no vacant surface that was available for adsorption. So optimum adsorption period was selected one hour for the further experiments [27].

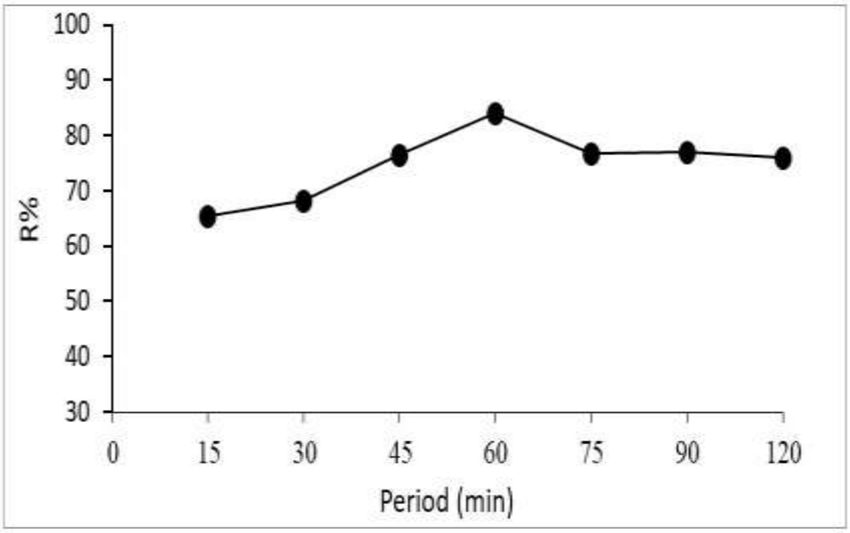

Figure 8: Impact of the adsorption period on the removal percentage for BS 3r dye.

3.2.2.4. The impact of adsorption temperature

The influence of temperature on the removal percentage was investigated within the range of 298-318 K, while maintaining a constant concentration of 20 mg/L of the dye and keeping other parameters unchanged. The findings are presented in Figure 9. It can be observed that as the temperature increased from 298 to 318 K, the removal of the dye decreased. This trend suggests that the adsorption of BS 3r dye onto corn silk is classified as an exothermic process. The significant decrease in the removal percentage with the rise in temperature may be attributed to the weakening of the adsorption forces between the BS 3r dye molecules and the active sites on the surface of the corn silk [28].

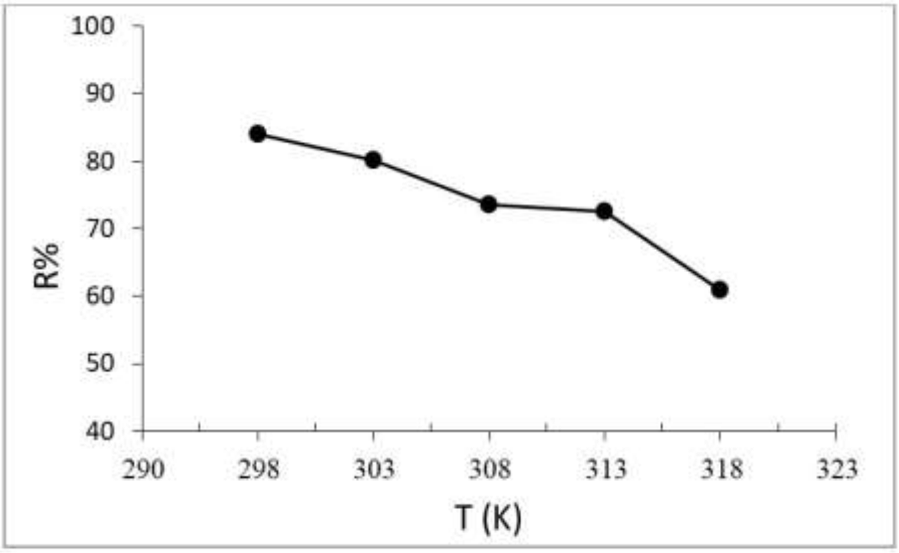

Figure 9: Impact of temperature on the removal percentage for the adsorption of BS 3r onto CK surface.

3.2.2.5. The impact of pH

The influence of pH on the removal percentage of BS 3r dye was investigated within the pH range of 2.1-10.2 at a temperature of 298 K. The experiments were conducted using a starting BS 3r concentration of 20 mg/L, 0.2 g of adsorbent weight, and a one-hour adsorption period. The pH of the solution was adjusted to the desired values by adding small amounts of either 0.1 M HCl or NaOH solutions. As shown in Figure 10, the values of R% decrease from 87.4% to 33.5% as the pH value increases from 2 to 10.2. This can be explained by the following mechanism: At lower pH values, an increased concentration of H+ ions on the adsorbent surface results in a positive charge, leading to enhanced adsorption of the anionic BS 3r dye. This is attributed to the electrostatic attraction between the dye and the CK surface, which facilitates maximum removal of the dye. On the other hand, when pH value increased there are increasing in the number of negatively charged sites caused an electrostatic repulsion between the dye and the CK surface [29]. Since this study established at neutral medium so the pH was installed at 7.

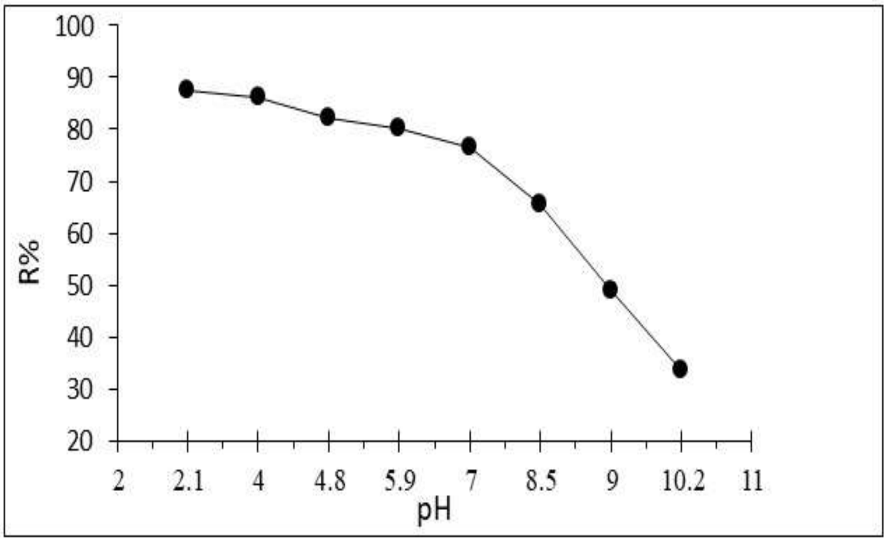

Figure 10: Impact of pH on the removal percentage for BS 3r dye.

3.3 Adsorption isotherm

The adsorption isotherms were applied to describe the mechanism of the adsorption of BS 3r dye onto CK surface. Three models including Langmuir, Freundlich and Dubinin-Radushkevich isotherm (D-R) were studied by changing the concentration in a range of 20-100 mg/L, at different temperatures 298-318 K, pH 7, adsorbent weight 0.2 g for one hour as adsorption period.

The Langmuir isotherm is represented as [30] :

$$\frac{C_e}{q_e} = \frac{1}{K_L} \cdot Q_m + \frac{C_e}{Q_m} \quad (3)$$

where C_e is the BS 3r concentration at equilibrium mg/L, q_e is to the amount adsorbed at equilibrium mg/g, Q_m maximum adsorption capacity and K_L is Langmuir constant (L /mg). The values of K_L and Q_m calculated from the linear plot between C_e/q_e against C_e (Figure 11-a). The obtained results are listed in Table 1. A significant property related to Langmuir equation is the equilibrium coefficient, or separation factor Rs, it was estimated using the following equation:

$$R_s = \frac{1}{1 + K_L \cdot C_s} \quad (4)$$

When values Rs between (0,1) indicate that the adsorption is adequate. Linear (Rs=1) , favorable (0 < Rs < 1), Irreversible (Rs = 0) and unfavorable (Rs > 1) [31]. Table 1 shows that the values of 1 > R_s >0 which indicated that the adsorption of BS 3r dye onto CK surface is favorable.

The Freundlich isotherm is written as [32]:

$$\ln q_e = \ln k_{Fr} + \frac{1}{n_f} \ln C_e \quad (5)$$

Where K_{Fr} (mg/g) and 1/n the Freundlich constant refers to the adsorption capacity and adsorption intensity respectively. These data were obtain from the intercept and slope of the relation between In q_e and ln C_e (Figure 11-b). The calculated results are represented in Table 1.

In this Table the values of $1/n_f$ > 1 indicated that the adsorption of BS 3r dye onto CK surface favorable [33].

The Dubinin-Radushkevich (D-R) isotherm model is a common way to represent the energy distribution during adsorption onto heterogeneous surfaces. The linear form of D-R isotherm written as [34]:

$$\ln q_e = \ln K_{D-R} - B\,\varepsilon^2 \quad (6)$$

Where q_e: is the equilibrium quantity (mg/g) of dye in the surface of adsorbent, K_{D-R}: the equilibrium binding constant for the hypothesized adsorption saturation capacity ($mg.g^{-1}$), B: is Dubinin isotherm constant (mol^2/kJ^2) and ε: is Polanyi potential which described as[35] :

$$\boldsymbol{\varepsilon} = R\,T \ln \left[1 + \frac{1}{C_e}\right] \quad (7)$$

The adsorption means free energy (E) can be estimated from the following equation :

$$E = -\frac{1}{(2B)^{0.5}} \quad (8)$$

Where T (K) absolute temperature, R is the gas constant (8.314 J/mol.K) and C_e: (mg/L) is the equilibrium concentration of adsorbate. Figure 10-c point to the plot of ln q_e against polani potential ($\mathcal{E}^2$) for the adsorption of BS 3r dye onto CK sample. Table 1 shows the D-R isotherm data for the adsorption of BS 3r dye onto CK sample at various temperatures. The adsorption process may be classified as physical adsorption if the values of E are less than 8 kJ/mol, while it considered as a chemical adsorption if the values of E is between 8-16 kJ/mol [36].

The values of E in Table 1 were found to be less than 8 kJ/mol which suggested that the adsorption of BS 3r dye onto CK surface occurs by physical adsorption mechanism.

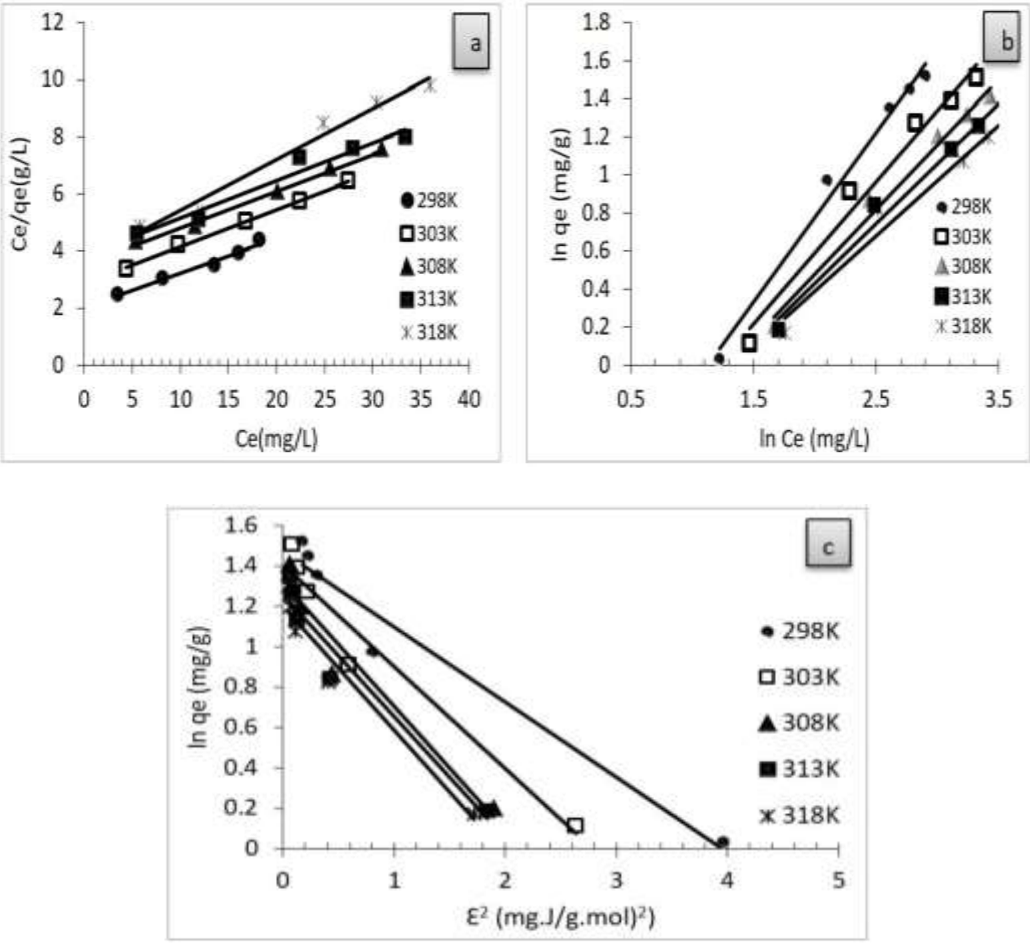

Figure 11: Adsorption isotherm plots for (a) Langmuir (b) Freundlich and (c) D-R models at different temperatures

Table 1: Adsorption isotherm models constants.

Temp (K)	Langmuir model					Freundlich model		
	K_L (L/mg)	Q_m (mg/g)	Rs	R^2	$1/n_f$	n_f	K_{Fr} (mg/g)	R^2
298	0.06103	8.1201	0.4503	0.9944	0.8915	1.1217	0.3670	0.9870
303	0.04526	7.7033	0.5249	0.9991	0.7510	1.3314	0.4021	0.9775
308	0.03694	7.6942	0.5751	0.9931	0.6830	1.4639	0.4116	0.9861
313	0.03456	7.5532	0.5913	0.9679	0.6308	1.5851	0.4362	0.9820
318	0.04905	5.5912	0.5048	0.9727	0.5856	1.7076	0.4572	0.9686

D-R model				
Temp (K)	B ($mol^2.kJ^2$)	E ($kJ.mol^{-1}$)	K_{D-R} (mg.g-1)	R^2
298	0.3717	1.1596	4.3498	0.9613
303	0.5049	0.9950	4.0808	0.9493
308	0.6109	0.9046	3.7368	0.9459
313	0.6023	0.9110	3.5174	0.9417
318	0.6156	0.9012	3.3324	0.9527

From the values of correlation coefficients it was noticed that the Langmuir coefficients R^2 are higher than those the other models suggesting that the Langmuir model is the best model to fit the experimental data.

3.4 Kinetic study

To investigate the adsorption mechanism of BS 3r onto the CK surface, two kinetic models were employed: pseudo-first-order (PFOM) and pseudo-second-order (PSOM) models. The experiments were conducted at a temperature of 298 K, starting BS 3r concentration of 20 mg/L, CK weight of 0.2 g, pH of 7, and an adsorption period of one hour. The pseudo-first-order model can be represented by the following linear equation [37]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t \tag{9}$$

Where q_e and q_t are the amount of BS 3r dye that adsorbed at equilibrium and at time (min) mg/g respectively and k_1 is PFOM rate constant for the adsorption process in min^{-1}. The values of q_e and k_1 were estimated from the intercept and slope of the straight line between $\log(q_e - q_t)$ and t.(Figure 12-a). These values were listed in Table 2. The pseudo second order PSOM written as [38]:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{10}$$

Where k_2 is the rate constant for PSOM (g/mg.min). The values of q_e and k_2 were estimate from the slope and intercept of the straight line between t/q_t and t (Figure 12-b)these values are listed in Table 2. As shown in this Table the values of adsorption capacity $q_{e\ cal}$, were close to experimental values $q_{e\ exp}$ for PSOM and the values of R^2 were higher than those for PFOM which indicated a better suitability of this model to explain the adsorption process.

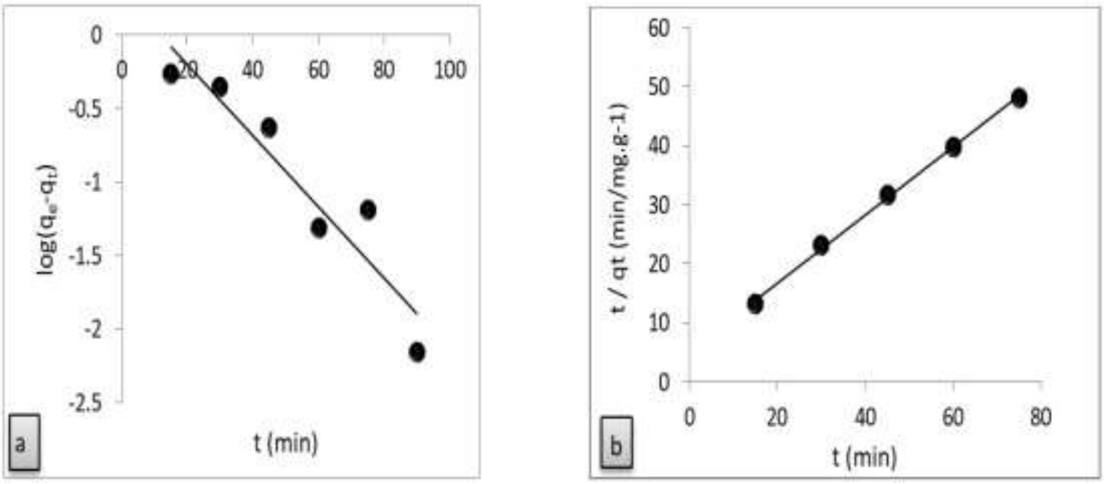

Figure 12: Adsorption kinetic plots for (a) PFOM (b) PSOM at 298 K

Table 2: PFOM and PSOM kinetics data for the adsorption of BS 3r dye onto CK sample.

PFOM				PSOM			
$q_{e\ exp}$ ($mg.g^{-1}$)	k_1 (1/min)	$q_{e\ cal}$ ($mg.g^{-1}$)	R^2	$q_{e\ exp}$ ($mg.g^{-1}$)	k_2 (g/mg.min)	$q_{e\ cal}$ ($mg.g^{-1}$)	R^2
1.567	0.0233	1.2333	0.8923	1.567	2.0050	1.701	0.9792

3.5 Adsorption thermodynamic

Thermodynamic study was established to reveal the behavior of the adsorption of BS 3r dye onto CK surface. The thermodynamic data included the Gibbs free energy ΔG°, enthalpy change ΔH° and entropy change ΔS° were calculated using the following relations [39]:

$$\Delta G° = -RT \ln K_{eq} \quad (11)$$

$$K_{eq} = {q_e}/{C_e} \quad (12)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (13)$$

The values of ΔH° and ΔS˚ were estimate from the slope and intercept of the straight line between ln K_{eq} against I/T (Figure 13) according to the following Van't Hoff relation [40]:

$$\ln K_{eq} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \quad (14)$$

These data are shown in Table(3). In this Table the negative values of ΔG˚ confirm the spontaneous characteristic for the adsorption of BS 3r dye onto CK surface and the negative values of ΔH˚ indicated that this process exothermic in nature. Moreover, the negative values of ΔS˚ revealed that there is a decrease in randomness at the solid-solution interface during the adsorption process.

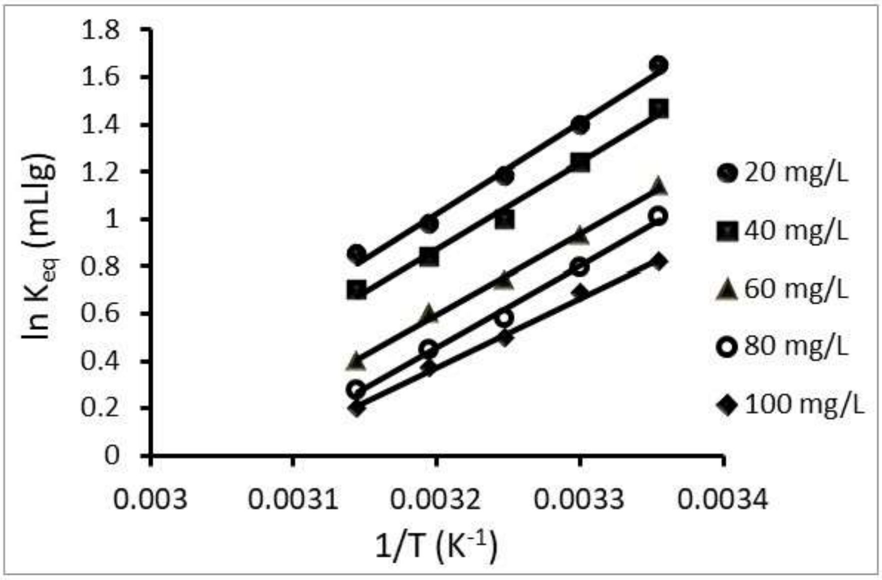

Figure 13: Van't Hoff plots adsorption of BS 3r dye onto CK sample.

Table 3: Thermodynamic parameters for the adsorption of BS 3r dye onto CK sample.

C_s mg/L	(-)ΔH° (kJ/mol)	(-)ΔS˚ (J/mol.K)	(-)ΔG° (kJ/mol)				
			298 K	303 K	308 K	313 K	318 K
20	31.916	93.607	4.0937	3.5167	3.0222	2.5502	2.2106
40	30.442	90.158	3.6376	3.1237	2.5574	2.1859	1.8325
60	28.485	86.209	2.8153	2.3428	1.8916	1.5616	1.0349
80	28.750	88.197	2.5172	2.0153	1.4852	1.1710	0.7286
100	24.634	75.735	2.0341	1.7382	1.2829	0.9576	0.5205

4. Conclusions

In conclusion, this study focused on the adsorption of Brilliant Scarlet 3r dye onto corn silk using batch experiments under various operating conditions. The findings revealed that the maximum removal of the dye occurred after one hour of adsorption, with a CK weight of 0.2 g, a starting dye concentration of 20 mg/L, and a neutral medium (pH 7). The experimental data fit well with the Langmuir model, indicating monolayer adsorption. The pseudo second-order kinetic model accurately described the adsorption process. Thermodynamic analysis indicated that the adsorption of BS 3r dye onto corn silk was a spontaneous and exothermic process. These results highlight the potential of corn silk as an effective adsorbent for the removal of Brilliant Scarlet 3r dye from aqueous solutions.

References

[1] G. Patra, R. Barnwal, S. K. Behera, B.C. Meikap, "Removal of dyes from aqueous solution by sorption with fly ash using a hydrocyclone," *Journal of environmental chemical engineering,* vol. 6, no. 4, pp. 5204-5211, 2018.

[2] Z. Eren and F. N. Acar, "Adsorption of Reactive Black 5 from an aqueous solution: equilibrium and kinetic studies," *Desalination,* vol. 194, no. 1-3, pp. 1-10, 2006.

[3] T. Watari *et al.*, "Anaerobic biological treatment of EG/PG water-soluble copolymer coupled with down-flow hanging sponge reactor," *Environmental Technology & Innovation,* vol. 21, p. 101325, 2021.

[4] Z. Yang, M. Li, M. Yu, J. Huang, H. Xu, Y. Zhou, "A novel approach for methylene blue removal by calcium dodecyl sulfate enhanced precipitation and microbial flocculant GA1 flocculation," *Chemical Engineering Journal,* vol. 303, pp. 1-13, 2016.

[5] L. Malaeb and G. M. Ayoub, "Reverse osmosis technology for water treatment: State of the art review," *Desalination,* vol. 267, no. 1, pp. 1-8, 2011.

[6] M. Lapointe, J. M. Farner, L. M. Hernandez, and N. Tufenkji, "Understanding and improving microplastic removal during water treatment: impact of coagulation and flocculation," *Environmental Science & Technology,* vol. 54, no. 14, pp. 8719-8727, 2020.

[7] M. Wawrzkiewicz, "Anion-exchange resins for CI Direct Blue 71 removal from aqueous solutions and wastewaters: Effects of basicity and matrix composition and structure," *Industrial & Engineering Chemistry Research,* vol. 53, no. 29, pp. 11838-11849, 2014.

[8] S. S. Shenvi, A. M. Isloor, and A. Ismail, "A review on RO membrane technology: Developments and challenges," *Desalination,* vol. 368, pp. 10-26, 2015.

[9] Z. Goodarzvand Chegini, H. Hassani, A. Torabian, and S. M. Borghei, "Enhancement of PMS activation in an UV/ozone process for cyanide degradation: A comprehensive study," *Pigment & Resin Technology,* vol. 49, no. 5, pp. 409-414, 2020.

[10] E. V. Liakos, M. Mone, D. A. Lambropoulou, D. N. Bikiaris, and G. Z. Kyzas, "Adsorption evaluation for the removal of nickel, mercury, and barium ions from single-component and mixtures of aqueous solutions by using an optimized biobased chitosan derivative," *Polymers,* vol. 13, no. 2, p. 232, 2021.

[11] C. Lizama, J. Freer, J. Baeza, and H. D. Mansilla, "Optimized photodegradation of Reactive Blue 19 on TiO_2 and ZnO suspensions," *Catalysis Today,* vol. 76, no. 2-4, pp. 235-246, 2002.

[12] N. H. AL-Shammari and D. E. AL-Mammar, "Equilibrium and kinetic modeling studies for the adsorption-desorption of methyl violet 10B onto leather waste," *Eurasian Chemical Communications,* vol. 4, no. 2, pp. 175-189, 2022.

[13] Y. Kuang, X. Zhang, and S. Zhou, "Adsorption of methylene blue in water onto activated carbon by surfactant modification," *Water,* vol. 12, no. 2, p. 587, 2020.

[14] W. Konicki, I. Pełech, E. Mijowska, and I. Jasińska, "Adsorption Kinetics of Acid Dye Acid Red 88 onto Magnetic Multi-W alled Carbon Nanotubes-Fe_3C Nanocomposite," *CLEAN–Soil, Air, Water,* vol. 42, no. 3, pp. 284-294, 2014.

[15] M. M. Naeem, "Protective effect of Corn silk (Zea mays L.) on kidney and liver functions of rats," *Bulletin of the National Nutrition Institute of the Arab Republic of Egypt,* vol. 60, no. 2, pp. 122-153, 2022.

[16] S. M. Miraboutalebi, S. K. Nikouzad, M. Peydayesh, N. Allahgholi, L. Vafajoo, and G. McKay, "Methylene blue adsorption via maize silk powder: Kinetic, equilibrium, thermodynamic studies and residual error analysis," *Process Safety and Environmental Protection,* vol. 106, pp. 191-202, 2017.

[17] F. Mbarki, A. Kesraoui, M. Seffen, and P. Ayrault, "Kinetic, thermodynamic, and adsorption behavior of cationic and anionic dyes onto corn stigmata: nonlinear and stochastic analyses," *Water, Air, & Soil Pollution,* vol. 229, pp. 1-17, 2018.

[18] G. D. Değermenci, N. Değermenci, V. Ayvaoğlu, E. Durmaz, D. Çakır, and E. Akan, "Adsorption of reactive dyes on lignocellulosic waste; characterization, equilibrium, kinetic and thermodynamic studies," *Journal of Cleaner Production*, vol. 225, pp. 1220-1229, 2019.
[19] M. Petrović, T. Šoštarić, M. Stojanović, J. Milojković, M. Mihajlović, M. Stanojević, "Removal of Pb^{2+} ions by raw corn silk (Zea mays L.) as a novel biosorbent," *Journal of the Taiwan Institute of Chemical Engineers,* vol. 58, pp. 407-416, 2016.
[20] F. Sheng, X. Zhu, W. Wang, H. Bai, J. Liu, P. Wang, "Synthesis of novel polyoxometalate $K_6ZrW_{11}O_{39}Sn\cdot 12H_2O$ and photocatalytic degradation aqueous azo dye solutions with solar irradiation," *Journal of Molecular Catalysis A: Chemical,* vol. 393, pp. 232-239, 2014.
[21] J. Singh, B. S. Inbaraj, S. Kaur, P. Rasane, and V. Nanda, "Phytochemical analysis and characterization of corn silk (Zea mays, G5417)," *Agronomy,* vol. 12, no. 4, p. 777, 2022.
[22] N. H. Al-Shammari and D. E. Al-Mammar, "Adsorption of Biebrich Scarlet Dye into Remains Chromium and Vegetable Tanned Leather as Adsorbents," *Iraqi Journal of Science,* vol. 63, no. 7, pp. 2814-2826, 2022.
[23] A. M. Al-Wadi, D. E. Al-Mammar, "Green Synthesis by Zygophyllum Coccineum Leaves Extract for Preparing ZnO Nanoparticles, and Characteristics Study," *Egypt. J. Chem.* Vol. 65, No. 5pp. 363-369, 2022.
[24] V. Cardenia, M. T. Rodriguez-Estrada, E. Boselli, and G. Lercker, "Cholesterol photosensitized oxidation in food and biological systems," *Biochimie,* vol. 95, no. 3, pp. 473-481, 2013.
[25] G. Sanahuja, G. Farré, L. Bassie, C. Zhu, P. Christou, and T. Capell, "Ascorbic acid synthesis and metabolism in maize are subject to complex and genotype-dependent feedback regulation during endosperm development", Biotechnology Journal, vol. 8, no. 10, pp. 1221-1230, 2013.
[26] R. A. Mohammed and D. E. Al-Mammar, "Using tobacco leaves as adsorbent for the orange-G dye removal from its aqueous solutions," *J. Glob. Pharma Technol*, vol. 11, pp. 273-280, 2019.
[27] T. N. Ramesh, D. V. Kirana, A. Ashwini, and T. Manasa, "Calcium hydroxide as low cost adsorbent for the effective removal of indigo carmine dye in water," *Journal of Saudi Chemical Society,* vol. 21, no. 2, pp. 165-171, 2017.
[28] R. A. Mohammed and D. E. Al-Mammar, "Using natural materials as corrosion inhibitors for carbon-steel on phosphoric acid medium," *Iraqi Journal of Science,* Vol.60, Special Issue, pp. 40-45, 2019.
[29] N. Masoudian, M. Rajabi, M. Ghaedi, and A. Asghari, "Highly efficient adsorption of Naphthol Green B and Phenol Red dye by Combination of Ultrasound wave and Copper-Doped Zinc Sulfide Nanoparticles Loaded on Pistachio-Nut Shell," *Applied Organometallic Chemistry,* vol. 32, no. 8, p. e4369, 2018.
[30] H. H. Kadhim and K. A. Saleh, "Removing Cobalt ions from Industrial Wastewater Using Chitosan," *Iraqi Journal of Science,* vol. 63, no. 8, pp. 3251-3263, 2022.
[31] K. P. Kuśmierek, L. Dąbek, and A. Świątkowski, "Comparative study on the adsorption kinetics and equilibrium of common water contaminants onto bentonite", Desalination and Water Treatment, vol. 186, pp. 373-381, 2020.
[32] K. A. Al-Saade, D. E. AL-Mammar, and H. N. AL-Ani, "Using Phragmites australis(Iraqi plant) to remove the Lead (II) Ions form Aqueous solution," *Baghdad Sci.J,* vol. 14, no. 1, p. 0148, 2017.
[33] A. Dada, A. Olalekan, A. Olatunya, and O. Dada, "Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk," *IOSR Journal of applied chemistry*, vol. 3, no. 1, pp. 38-45, 2012.
[34] C. C. Nnaji, A. E. Agim, C. N. Mama, P. C. Emenike, and N. M. Ogarekpe, "Equilibrium and thermodynamic investigation of biosorption of nickel from water by activated carbon made from palm kernel chaff," *Scientific Reports,* vol. 11, no. 1, pp. 1-20, 2021.
[35] M. Geszke-Moritz and M. Moritz, "APTES-modified mesoporous silicas as the carriers for poorly water-soluble drug. Modeling of diflunisal adsorption and release," *Applied Surface Science,* vol. 368, pp. 348-359, 2016.
[36] L. Liu, X.-B. Luo, L. Ding, and S.-L. Luo, "Application of nanotechnology in the removal of heavy metal from water", in Nanomaterials for the removal of pollutants and resource reutilization: Elsevier, pp. 83-147, 2019.
[37] A. K. Abaas, D. E. Al-Mammar, and H. A. Abbas, "Equilibrium, Thermodynamic and Kinetic Study of the Adsorption of a New Mono Azo dye onto Natural Iraq Clay," *Journal of Global Pharma Technology* , vol. 10(5), pp. 102-109, 2018.

[38] S. A. Saed and D. E. AL-Mammar, “Influence of Acid Activation of a Mixture of Illite, Koalinite, and Chlorite Clays on the Adsorption of Methyl Violet 6B Dye," *Iraqi Journal of Science*, vol. 62, no. 6, pp. 1761–1778, 2021.
[39] A. M. Abbas, Y. I. Mohammed, and T. A. Himdan, "Adsorption Kinetic and Thermodynamic Study of Congo Red Dye on Synthetic Zeolite and Modified Synthetic Zeolite," *Ibn AL-Haitham Journal For Pure and Applied Sciences*, vol. 28, no.1, pp.54-72, 2017.
[40] A.S. Negi, S.C. Anand: A Textbook of physical chemistry, *India: New Age International publishers*, 2008, p. 364.