Al-Rafidain Journal of Engineering Sciences

Journal homepage https://rjes.iq/index.php/rjes

ISSN 3005-3153 (Online)

Comparative Removal of Crystal Violet Dye Using Peanut Hull Powder and Its Modified Forms: Adsorption Mechanisms, Isotherms, and Kinetics

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ARTICLE INFO

Article history:
Received xxxx
Revised xxxx,
Accepted xxxx,
Available online xxxx

Keywords:
Adsorption
Cationic dye
Crystal Violet
Isotherm
Peanut Hull Powder

ABSTRACT

In this work, the removal of cationic dye; Crystal Violet (CV) by (Peanut Hull Powder (PHP), activation of Peanut Hull Powder (PHPAC) with HCl, and activated carbon derived from PHP) from aqueous solution in batch experiments. The adsorbents were characterized using BET for analysis of the specific surface area. The finding showed that the adsorption capacities of PHP, PHPAC, and PHPAC were 95.5 %, 96.8 %, and 98.7 % respectively. Under ideal circumstances, the isotherms of adsorption using the Langmuir, Freundlich, Sips, and Temkin isotherm models were used to validate the experimental data. The maximum adsorption capacity (q_{max}), as determined by isotherm investigations, was 13.25815 mg/g. The Freundlich Model is the better-fitting model with the highest R^2 value in the PHP experiments. According to the kinetic analysis, the pseudo-second-order better describes the adsorption behavior. The study found that adjusting factors like pH, temperature, contact duration, adsorbent dose, adsorbent particle size, and the stirring rate significantly improved adsorption efficiency. The results show much higher dye removal rates under these conditions at the optimum values; 6, 25°C, 60 min, 1.5 g, 150 µm, and 120 rpm for the above-mentioned conditions respectively, and offer a thorough investigation of adsorption kinetics and isotherms. This research provides new insights into the adsorption mechanism and suggests potential applications for industrial wastewater treatment, promoting more sustainable and cost-effective solutions.

1. Introduction

Water is essential for human and animal survival. It is often used in industries and may become polluted due to chemical exposure. Water pollution poses a significant hazard to the ecosystem. Therefore, it is crucial to reduce contaminants in industrial wastewater before it is discharged [1]. The textile industry holds the largest share since it integrates with other economic sectors both locally and globally, and it may generate a wide range of job opportunities. The growing amount of wastewater containing toxic dyes from different industries is still a major environmental and plant public health concern, making it difficult for conventional water treatment plants to remain in operation [2]. Color development in the dye is due to the existence of chromophores. The two major sources from which dyes are mostly generated are natural and man-made. Natural sources comprise, insects, animals, and minerals, on the other hand, synthetic dyes are created by humans utilizing a variety of chemical compounds [3]. It has a wide range of scientific and industrial uses, including dyeing and printing fabrics, paper, leather, and other materials [4]. The introduction of dyes in

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https://doi.org/10.61268/sseesm94

effluents alters the aesthetics, transparency, and gas solubility of water bodies. This reduces the ability of water to renew owing to decreased solar penetration and altered photosynthesis. Synthetic dyes are generated globally at a rate of around 7×10^7 tons per year, with textile industries using over 10,000 tons [5]. The textile industry uses a lot of cationic and direct dyes because of their benefits, which include good color brightness, a large color palette, appropriate substantivizes, and affordability [6]. Tris (4-(dimethylamino) phenyl) methylium chloride), often known as crystal violet (CV) color [7], is a synthetic triaryl methane dye that is used as a pH indicator. CV dye is cancerous, mutagenic, and poisonous to mammalian cells. It can cause serious eye discomfort and light sensitivity. Additionally, it can cause injury by inhalation, ingestion, and interaction with the skin [8]. Adsorption is a popular method for removing pollutants owing to its cost-effectiveness, versatility, and ease of use [9]. Adsorption is an efficient, renewable, and environmentally beneficial approach that relies on the particular surface area and adsorption capacity of interior molecules [10]. In recent years, agro-industrial waste has been identified as a cost-effective, quantity, renewable nature, and plentiful resource for waste management solutions [9]. natural adsorbents are naturally occurring sorbents that are derived from the environment like clays, bacteria, and agricultural wastes. In this research, the focus was on peanut hull powder (PHP) because in many nations, is a leftover agricultural waste product and activated carbon derived from peanut hull powder. Experiments using the one-factor-at-a-time (OFAAT) approach are carried out by changing one variable while holding the other variables constant.

The goal was to investigate the possibility of using PHP in different modifications as an adsorbent to remove harmful CV color from a water medium and to correlate the adsorption kinetics data of CV onto produced peanut hull powder. Equilibrium adsorption isotherm investigations have been carried out to comprehend the procedures involved in the removal of the chosen color from PHP. To assess the synthesized adsorbent's viability, a variety of spectroscopic methods were used to characterize it.

2. Methodology

2.1 Materials

The crystal violet dye (CV), which was purchased from Sinopharm Chemical Testing Co., Lt, has a molecular formula of $C_{25}H_{30}ClN_3$ as shown in Figure 1, color indexed number of C.I.42555, a maximum wavelength of 590 nm and molecular weight of 407.979 g. mol^{-1} and its solubility in water is 16 g/l at 25°C. The dye was purchased with a purity of 99% and used without further purification. Waste peanut hull was collected after separating and utilizing the fruit from the plant shell at a market located nearby. Adjustment of dye solution pH before adsorption was conducted with NaOH or HCl.

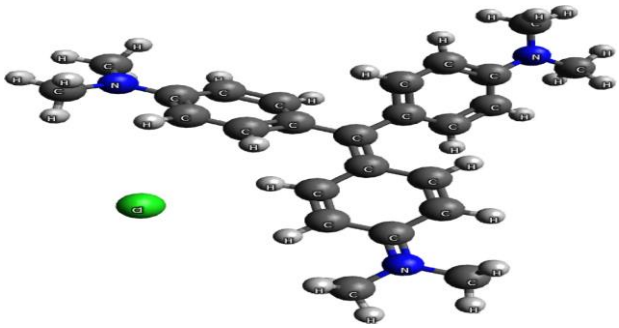

Figure 1. Crystal violet dye's molecular structure in three dimensions. Colors: green is chloride, blue is nitrogen, white is hydrogen, and gray is carbons [11].

2.2 Adsorbent preparation

2.2.1 Preparation of Peanut Hull Powder (PHP)

Waste peanut hull was collected after separating and utilizing the fruit from the plant shell at a market located nearby. The peanut hull (PH) comprising of dirt, dust, and other particles was thoroughly washed with tap water, then washed many times with distilled water followed by sun-drying for five days. After that, a drying process was in an oven (60 °C) for 5 h then ground into a fine powder using an electrical grinder and sieved by conventional sieves to obtain desired particle sizes from (150 µm - 1.18 mm) was accumulated and stored in

cans for use in the adsorption investigations. Figure 2 displays some stages of preparation of PHP.

Figure 2. Peanut hull powder preparation

2.2.2 Activation of the peanut hull powder (PHPA)

Prepared HCl (0.5 M) with volume of 7.5 ml was added to 1.5 g of (150 µm) PHP before washing then stirred on magnetic stir for 30 min at 80°C and 120 rpm to obtain a homogenous solution. The solution was then filtered and washed with distilled water to remove excess HCl until the washing solution reached neutral, as shown in Figure 3. The product was dried a 110°C in a drying oven. To employ the dried PHP in the testing at optimum condition, it was lastly put in flasks with stoppers.

Figure 3. Activation of peanut hull powder with HCl (0.5M)

2.2.3 Carbonization and activation of peanut hull powder (PHPAC)

To carbonize the PHP powder by chemical method, ten grams of peanut hull powder (150 µm) was added to a ceramic crucible and burned at 600°C for 30 minutes in a furnace, the powdered peanut hull underwent carbonization.

1.5 g of the carbonization peanut hull powder was immersed in a 7.5 ml HCl (0.5 M) solution at a mass ratio of 1:5 (peanut: HCl), then stirred on a magnetic stirrer for 30 min at 80°C and 120 rpm to obtain a homogenous solution, then left the solution for 24 hours, after that, the solution was washed with distilled water until it became neutral. Ultimately, a drying oven was used to dry the substance and obtain dried activated carbon as seen in Figure 4.

Figure 4. Activated carbon preparation of PHP

2.3 Batch experimental work

2.3.1 The factors that were studied

All factors were varied while maintaining the same values for the other factors in each experiment. The factors studied in the One-factor-at-a-time approach (OFAAT), included the following:

2.3.1.1 pH

Experiments were conducted with pH levels ranging from 2 to 10. The pH of the CV dye solution was adjusted using 0.1 M HCl or 0.1 M NaOH solution, accordingly.

2.3.1.2 The contact time

To examine the effect of contact time on CV dye adsorption, contact times were adjusted from 10 to 90 minutes.

2.3.1.3 Temperature

The removal of CV dye from an aqueous solution was studied at different temperatures (15–40°C).

2.3.1.4 The adsorbent dosage

Different adsorbent doses from (0.5–3 g) were tested.

2.3.1.5 The Adsorbent particle size

The influence of particle size on CV removal was investigated using varied PHP particle sizes ranging from 150 µm to 1.18 mm.

2.3.1.6 The Initial Dye Concentration

The impact of initial CV dye concentration on adsorption was examined by varying it from (2-250) mg/l.

2.3.1.7 The stirring rate

The impact of shaking speeds utilized were 50,85, 120, 155,190, and 225 rpm.

2.3.2 Adsorption Experimental procedure

Using PHP as an adsorbent, CV was adsorbed from an aqueous solution in a batch mode setup. 0.5 g of dye and 1000 ml of distilled water were combined to create a dye stock solution, which was then diluted to various concentrations between 2 and 250 mg/l. 0.1 M of either HCl or NaOH was added to the solutions to bring their pH level down to the desired level. With a pH meter (OAKTON, HANNA (HI 1131- B), Romania), the pH value was measured. A digital orbital shaker (Dai-Han, SHO-2D, England) was used to agitate the sample volume of 150 ml of dye solution in serial conical flasks (250 ml) during batch mode adsorption testing. Repeat the experiment every time for each parameter by changing the

parameter levels and fixing other parameters. The shaker was run at a specific rpm until equilibrium was reached. Following different time intervals, the aqueous phase was separated by using a centrifuge (Shengji, KA-1000, Germany) for 5 min at 5000 rpm and via filtering, then the concentrations of the leftover CV dye were measured at the maximum wavelength (λ max = 590 nm) using a UV/Visible spectrophotometer (Labomed, lnc., UVD-3000, USA). The following formula was used to get the percent removal (R) of dye [12]

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

Where C_o and C_e are the initial and final concentrations of the desired dye in terms of mg. l^{-1}, respectively.

Using the following formula, the amount of Crystal Violet dye adsorbed per unit mass of the adsorbent (q_e) (mg/g) was determined [13]:

$$q_e = \frac{(C_o - C_e)v}{M} \quad (2)$$

Where M is the weight of the adsorbent used (g), and v is the volume of the solution applied (L).

Figure 5 shows samples of CV dye with different dosages of PHP on shaker.

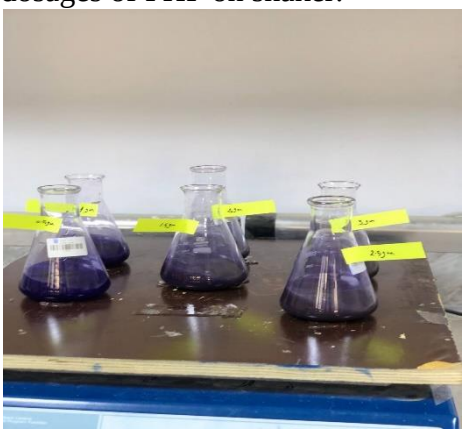

Figure 5. Samples of CV dye with different PHP dosages

2.3.3 Optimum condition for all parameters

After finishing each experiment for all parameters, the results showed that the optimum conditions were pH = 6, contact time = 60 min, temperature =25°C, the adsorbent dosage =1.5 g, the adsorbent particle size = 150 µm, the initial dye concentration =20 mg/l, and the stirring rate =120 rpm. All the experiments were repeated at optimum conditions to obtain the optimal removal efficiency for PHP = 95.5 %,

and under the optimum conditions, crystal violet dye adsorption on PHPA and PHPAC were 96.8 % and 98.7 %. as shown in Figure (6).

Figure 6. Photos of removal efficiencies of PHP, PHPA and PHPAC at optimum condition

2.3.4 Isotherms of adsorption

Regarding the possibilities of interaction, coverage, and heterogeneity or homogeneity, a set of isotherm model assumptions are developed. Langmuir, Freundlich, Sips and Temkin isotherms. The adsorption of peanut hull powder in an aqueous solution was investigated using the linear Langmuir equation model, the Freundlich equation, Sips equation, and the Temkin equation at a range of varied concentrations (5, 10, 15, 20, 25, 30, 50, 75) mg/L, the linear equation of the Langmuir model is given by Eq. (3):

$$q_e = \frac{q_m b_1 c_e}{1+b_1 c_e} \quad (3)$$

where C_e, q_e, q_m, and b_l represent the pollutant concentrations at equilibrium (mg. l^{-1}), the adsorption capacity at equilibrium (mg. g^{-1}), and the maximum adsorption capacity (mg. g^{-1}) about the Langmuir equilibrium constant, respectively. It also quantitatively illustrates the convergence between pollutants and flocs (l. mg^{-1}) [14]. Because of the equilibrium form, the Langmuir isotherm might not be sufficient to relate the single-layer adsorption formation. concerning the several adsorption processes. The Langmuir formula's fundamental operation was based on the dimensionless differentiation factor (R_L), as displayed in Eq. (4) [15-17]:

$$R_L = \frac{1}{1+bC_0} \quad (4)$$

where C_o denotes the initial concentration (mg/l) and b is the Langmuir isotherm constant indicating the adsorbent's active sites' affinity (l/mg)

The following is the expression for the Freundlich non-linear model [18]:

$$\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e \quad (5)$$

Where K_f = Freundlich constant (the intercept of the Freundlich plots), n = slope, qe (mg. g^{-1}) = amount of dye adsorbed per gram of an adsorbent. K_f and n are temperature-dependent, with $\frac{1}{n}$ denoting the adsorption intensity. As soon as $\left(0 < \frac{1}{n} < 1\right)$ the adsorption is desirable, it is undesirable if $1 < \frac{1}{n}$, and it is irreversible if $\left(\frac{1}{n} = 1\right)$ [19]. Additionally, the slope and intercept indicate the adsorption and correspondingly, the adsorption intensity [20].

This is the equation for the Sips model [21]:

$$q_e = \frac{K_S C_e B_S}{1+a_S C_e B_S} \quad (6)$$

Where KS, βs, and a_s are Sips constants, K_S, a_s are measured in (l/mg) and βs is dimensionless.

The following are the linear and nonlinear models for the Temkin model: [22]

$$q_e = B\, ln\, A_T + B\, ln\, C_e \quad (7)$$

$$B = \frac{RT}{b_t} \quad (8)$$

Where AT is the maximum binding power (1/g), B is continuously connected to the adsorption heat (J/mol). R stands for molar gas constant (8.314 kJ/mol), the dye solution's temperature in Kelvin (K), and the Temkin isotherm constant, or bt [22].

2.3.5 Adsorption kinetics

The empirical data were used to calculate the intraparticle diffusion, pseudo-second-order, and pseudo-first-order Lagergren models.

Several time intervals (0, 10, 20, 30, 40, 50, 60, 70,80, and 90) min, 1.5 g of the peanut hull powder at a temperature of 25 °C and an initial concentration of 20 mg/l with the values of the kinetic coefficients of dye adsorption on the PHP surface were studied to examine the useful results of the dye adsorption investigation. The pseudo-first-order expression is provided as follows [19]:

$$\frac{dq_t}{d_t} = K_1(q_e - q_t) \quad (9)$$

Where k_1 is the pseudo constant rate for the adsorption process and q_e and q_t are the amounts of metal adsorbed at equilibrium and at time t. The kinetic expression's integration with the starting condition, qt equals is provided by:

$$\int_0^{q_t} \frac{dq_t}{q_e - q_t} = \int_0^t k_1 \, d_t \quad (10)$$

The linear form is given by:

$$ln\, q_e - q_t = ln\, q_e - k_1 t \quad (11)$$

The graph ln (qe − qt) shows the intercept and slope against time t, providing a linear relationship between the pseudo-first-order adsorption constant, k_1 (1/min), and the adsorption capacity at equilibrium, q_e (mg/g). The adsorption capacity at time t is represented by q_t (mg/g) [23]. Additionally, the nonlinear model is:

$$q_{t=} q_e\left(1 - e^{-k_1 t}\right) \quad (12)$$

Equation (13) provides a pseudo-second-order mathematical expression [24]:

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \quad (13)$$

Where amount of adsorbate adsorbed at time 't' is represented by q_t(mg. g^{-1}), q_e(mg. g^{-1}) is the quantity of adsorbate adsorbed at equilibrium, while the pseudo-second-order rate constant is represented by k_2 (g.mg^{-1}.min^{-1}). This equation's linear form is provided in Equation (14) [25]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (14)$$

Additionally, k_2 (g/mg min) is the rate constant for the pseudo-second-order adsorption, and q_e (mg/g) is the equilibrium adsorption capacity. A graph showing t/qt against t was used to calculate k_2 and q_e.

The following is an expression for the intra-particle diffusion model:

$$q_t = k_p t^{\frac{1}{2}} + C \quad (15)$$

The intercept value is denoted by C (mg/g), while the intraparticle diffusion rate constant is represented by k_p(mg/g. $min^{1/2}$).

3. Results and Discussion

3.1 Characterization of Adsorbent

The surface area of PHP and PHPAC was examined using the BET test, which used nitrogen adsorption-degassing conditions at 303 K and a ramp rate of 10 K/min for ten minutes. Micrometric (Horiba, SA - 9600). The surface area was determined to be 22.00 m^2/g for raw PHP and the prepared PHPAC has a large surface area of 56.00 m^2/g. Indicating that the surface of the activated carbon under study contained several sorption sites.

3.2 The removal efficiency of PHP, PHPA, and PHPAC

Crystal Violet dye adsorption on PHP, PHPA, and PHPAC under optimized conditions led to the results that showed nearly 95.5 %, 96.8 %, and 98.7 % of dye was removed respectively as shown in Figure 7. The PHPAC exterior's morphological features are beneficial since they guarantee an active site and a sizable surface area for dye molecule sorption. Before dye adsorption, these adsorption sites were empty, which were then fully occupied by dye molecules after dye uptake. These claims were matched with other results such as [26].

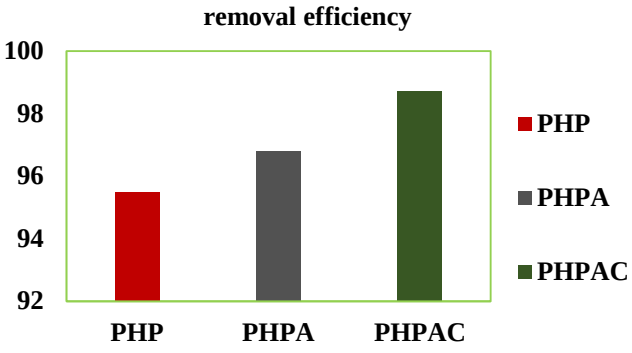

Figure 7. PHP, PHPA, and PHPAC at optimum conditions

3.3 Isotherms of adsorption

Regarding the possibilities of interaction, coverage, and heterogeneity or homogeneity, a set of isotherm model assumptions is developed. Langmuir, Freundlich, Sips, and Temkin isotherms looked for the equilibrium data that would explain the interaction between the adsorbate molecules and the adsorbent surface. To provide a thorough grasp of the nature of interaction. The adsorption of peanut hull powder in an aqueous solution was investigated using the linear Langmuir equation model, Freundlich equation, Sips equation, and Temkin equation at a range of varied concentrations (5, 10, 15, 20, 25, 30, 50, 75) mg/l, The isotherms for the PHP-based adsorption of the CV dye (q_{exp}versus C_e) as seen in Table 1 and Figure 8 and also shows the values of the parameter and correlation coefficient (R^2) for each of the isothermal models. The dimensionless constant separation factor (R_L) values of the Langmuir model, ranged from 0.077057 to 0.556022.

Table 1: Isotherm model parameters for the adsorption of CV onto PHP

Isotherm model	Parameters	Parameter value
Langmuir	q_{max} (mg/g)	13.25815
	b_1 (l/mg)	0.159698
	R_L	0.077057 - 0.556022
	R^2	0.938588
Freundlich	Kf (mg/g (mg/l)$^{-1/n}$)	2.119075
	n	1.621118
	R^2	0.971515
Sips	Ks (l/gm)	2.119072
	β_s	0.6168576
	a_s(l/mg)	0.00012
	R^2	0.971515
Temkin	B	0.929077
	A_T	28.16812
	R^2	0.727619

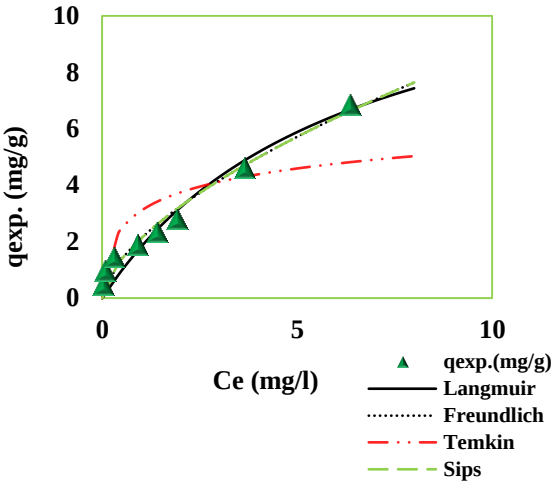

Figure 8. The adsorption isotherms of CV on PHP with experimental conditions: PHP dosage 1.5 g/150 ml dye solution, initial CV concentration 5−75 mg/l, pH = 6, agitation speed = 120 rpm, contact time = 60 min, and temperature = 25 °C

The adsorption of the CV dye on the PHP correlated with the Freundlich isotherm model, with a correlation factor (R^2) of 0.971515 that was very close to one, according to the experimental results shown. Moreover, the Sips isotherm correlation factor (R^2) was identical with Freundlich isotherm (R^2). According to the findings, the data fits best to the Freundlich isotherm model (multilayer adsorption), indicating that the adsorption of CV takes place on the heterogeneous surface of the PHP, according to the values of the Langmuir and Temkin isotherm models, which are 0.938588 and 0.727619 respectively (smaller than the Freundlich isotherm). Additionally, the fact that n is larger than 1 and $\frac{1}{n}$ (i.e., Freundlich intensity) was found to be 0.62 for the adsorption of CV using Peanut hull powder, the value was ($0 < \frac{1}{n} < 1$) knowing that the adsorption is desirable [19, 27-29].

3.4 Adsorption kinetics

A kinetic model could be used to quantify the sorption method's mechanisms, such as chemical reaction, mass transfer, and diffusion control [30]. This highlights how crucial it is to precisely model and fit real-world kinetic data with necessary kinetic models to create an effective treatment system [31]. The kinetic

data of dye adsorption were computed using three different kinetic models: The Pseudo-First-Order equation, the Pseudo-Second-Order equation, and the Intraparticle Diffusion model. Several time intervals (0, 10, 20, 30, 40, 50, 60,70, 80 and 90) were used in the experiment of adsorption. Results in Table 2 demonstrated that the adsorption effectiveness decreased after the maximum adsorption happened, which happened within 60 minutes. The initial fast reaction was caused by open adsorption sites outside the adsorbent. Because dye molecules are poorly held on the adsorbent surface

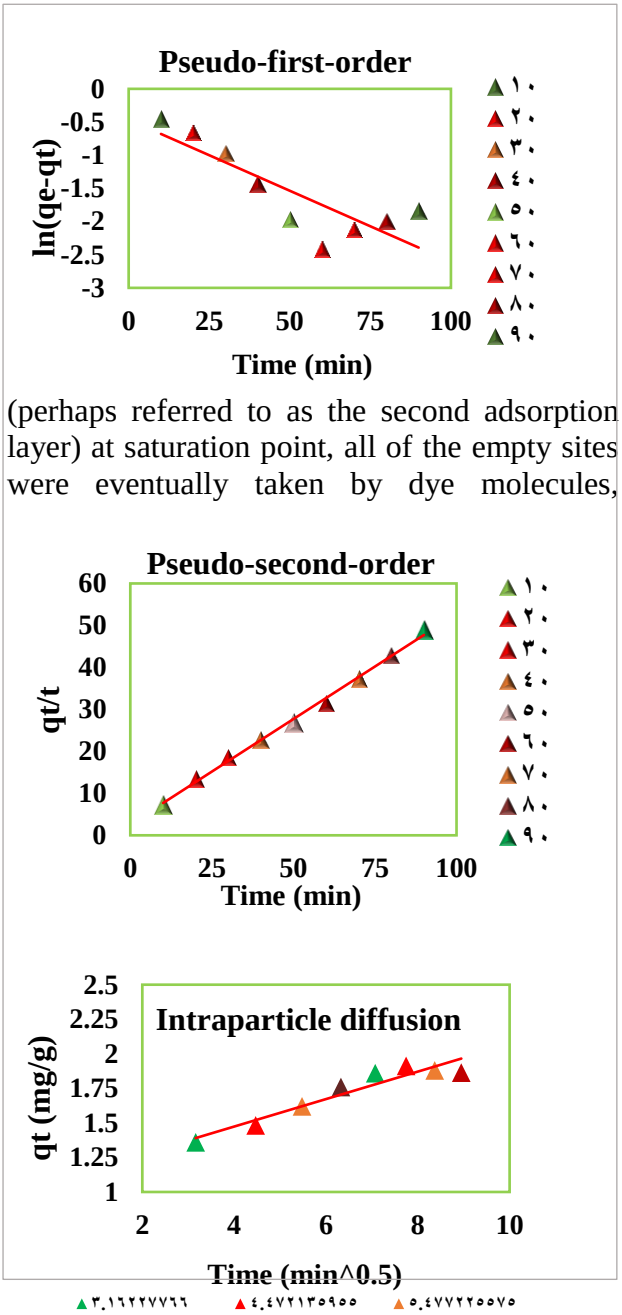

Figure 9. Three kinetic models for adsorption of CV on PHP at 20 mg/l

(perhaps referred to as the second adsorption layer) at saturation point, all of the empty sites were eventually taken by dye molecules, resulting in a lessening of the increase in dye abstraction [32]. Stated differently, dye molecules were incorporated into the adsorbent's active sites at the saturation point [33].

Table 2: kinetic parameters of three models and regression coefficients, that is, pseudo-first-order, pseudo-second-order, and intraparticle diffusion model

Kinetic model	Parameters	Parameter value
Pseudo-first order	q_e (mg/g)	0.628781
	K_1 (1/min)	0.021425
	R^2	0.708759
Pseudo-second order	q_e(mg/g)	1.99619
	k_2(g/mg min)	0.093937
	R^2	0.996357
Intraparticle diffusion model	C	1.147401
	K_p (mg/g $min^{1/2}$)	0.085951
	R^2	0.843121

as displayed in Table 2 and Figure 9, the findings indicate that the adsorption kinetics of this investigation have nothing to do with the pseudo-first order and intraparticle diffusion models with R^2 values 0.708759 and 0.843121 respectively. The pseudo-second-order model's higher R^2 value supported its position as the best fitted model for CV dye adsorption by PHP with a value is 0.996357. A similar pattern was noted while using different adsorbents [34]. The pseudo-second-order model demonstrates the involvement of chemisorption in the process. For several dye adsorptions from a different adsorbent, comparable outcomes were found [35-37].

4. Conclusions

According to the study's findings, Peanut Hull Powder (PHP), PHPA, and PHPAC have substantial promise as ecologically acceptable

adsorbents for the decolorization of crystal violet dye, with removal efficiencies of 95.5%, 96.8%, and 98.7%, respectively. These findings demonstrate the efficacy of these materials in treating dye-contaminated water. Batch experiments using peanut hull powder to remove crystal violet (CV) dye revealed that the optimal conditions were as follows: a dye concentration of 20 mg/L, pH of 6, particle size of 150 µm, adsorbent dosage of 1.5 g, temperature of 25°C, contact time of 60 minutes, and a stirring rate of 120 rpm. These settings were shown to enhance removal efficiency, demonstrating PHP's practical relevance under these precise conditions. BET study showed that the surface area of PHP was 22.00 m^2/g, whereas the produced PHPAC had a much higher surface area of 56.00 m^2/g. The increase in surface area following HCl treatment suggests that the adsorption capacity has been successfully enhanced. The visible effect of this change on removal efficiency adds to the surface modification's efficacy. The Freundlich isotherm model, with a better correlation coefficient of 0.971515, was found to be the best standard model for the experimental results. This implies that CV adsorption takes place on a heterogeneous PHP surface. The value of Freundlich intensity ($n>1$) suggests favorable adsorption, and the value of RL ($0<RL<1$) verifies this. The pseudo-second-order model, with an R^2 value of 0.996357, was chosen as the best-fitting model for CV dye adsorption via PHP. The significant R^2 value suggests chemisorption, which involves a chemical interaction between dye molecules and the adsorbent. Overall, this study reveals PHP, PHPA, and PHPAC's significant potential as dye removal adsorbents that are both cost-effective and ecologically acceptable. The appropriate adsorption conditions and effective surface modification demonstrate the practicality and scalability of employing peanut hull-derived materials for water treatment. Future research should focus on improving adsorption capacity and investigating the regeneration and reuse of these adsorbents to guarantee sustainability in wastewater treatment procedures.

5. Acknowledgements

First of all, the authors expressed gratitude to Allah for granting them the perseverance to finish this research. Next, they would like to express their gratitude to the environmental engineering department of Tikrit University in Iraq for their technical support during this effort.

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