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Peanut Shell as a Natural Adsorbent for the Removal of Acid Blue 25 from Aqueous Solution

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Apeanut shell was used as a low-cost agricultural waste to eliminateacid blue 25 dye from an aqueous solution. Contact time, sorbate concentration, particle size, and sorbent mass were all investigated in batch sorption tests. The sorption process was investigated in terms of equilibrium and kinetics models. The sorption process is better in agreement with the pseudo-second-order model, with a greater regression coefficient value of 1 under all experimental conditions, according to adsorption kinetic results. The models of Freundlich, Langmuir and Temkin were used to describe the isotherms of adsorption, and equilibrium data was consistent with Freundlich isotherm with a higher regression coefficient value, R^2. Based on the findings, the peanut shell is much more economical, cheap, viable, and very effective for the removal of acid blue 25 dye from aqueous solution.

Keywords: dye removal, acid blue 25, peanut shell, isotherm models, kinetics models.

Introduction

Many different industries employ dyes, including textile, rubber, paper, cosmetic, pharmaceutical, and many other industries, to give a certain color to their products. Those industries which are discharging wastewater with different dye concentrations to water resources constitute an important source of pollution to aquatic system (Katheresan et al., 2018; Hassan et al., 2021). Many of these dyes, especially organic ones, can be toxic, carcinogenic, mutagenic, and may affect aquatic life (Idan et al., 2017).

Several conventional approaches, including chemical and physical procedures, have been employed to remove color pollution from industrial wastewater (Al-Tohamy et al., 2022). However, these procedures are expensive

and frequently poor at removing colors, as well as are less adaptive to the wastewater with high dye concentrations (Liang et al., 2014; Dutta et al., 2021).

The removal of many kinds of dyes is possible using the adsorption method, which was chosen because it is straightforward, efficient, and easy to use (Shabaan et al., 2020; Shahrin et al., 2022). Many adsorption studies were performed to ascertain the impact of contact time, preliminary dye concentration, temperature, and pH on the treatment processes of various types of dye (Dutta et al., 2021).

Due to the significant economic expense, many researchers are focusing on finding less expensive materials and economical adsorbents for use in wastewater treatment (Kooh et al., 2016; Senthil Kumar et al., 2019). Recently, due to their availability and low cost, agricultural and industrial wastes have been widely used as a natural adsorbent to remove dyes from waste water effectively (Hassan et al., 2021)

Peanut shell powder was discovered to be an economical, natural, and abundantly available adsorbent for removing reactive colors from an aqueous solution (Sakalar et al., 2010; Boumchita et al., 2017). Many studies have been done to examine the capacity of peanut shell powder to remove various reactive colors such as Green 19, Orange 16, and Yellow 14from aqueous solutions (Nadi et al., 2012; Wu et al., 2019; Garget al., 2019). More than 90% of these dyes have been adsorbed from the wastewater by using peanut shell powder (Garget al., 2019; Herbert et al., 2021; Pączkowski et al., 2021; Khiaophong et al., 2022).

To the best of our knowledge, however, employing dried crushed powder made from peanut shells has not yet been studied for the adsorptive removal of acid dyes (acid blue 25) from wastewater. The main objective of this research is to assess the removal of acid blue 25dye from synthetic solutions by using peanut shells as an abundant and low-cost sorbent.

Methods

Preparation of peanut shell

The peanut shells depicted in *Fig. 1* were gathered, rinsed with distilled water, dried for 24 hours at 80°C, crushed, and sieved with a size 50 mesh sieve. The powder was stored in a pot to be used later.

Fig. 1. *Peanut shells*

Adsorbate

Acid blue 25 was chosen for this study. It is used to dye wool, silk, and mixed fabrics and to print them directly. Throughout the production process, the dye is usually used to color paper, leather, and cellulose.

Acid blue 25, IUPAC name – sodium;1-amino-4-anilino-9,10-dioxoanthracene-2-sulfonate, is an anionic dye. Its chemical structure is described in *Fig. 2*, and the physicochemical properties are given in *Table 1* (Idan et al., 2017).

Fig. 2. *Chemical structure of acid blue 25 dye*

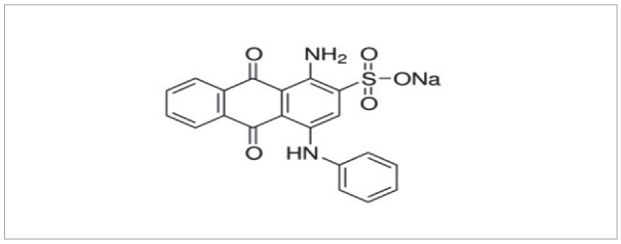


Table 1. *The physiochemical properties of acid blue 25 dye*

Property Name	Property Value
Molecular weight	416.38 g/mol
Molecular formula	$C_{20}H_{13}N_2NaO_5S$
C.I. name	62055
Absorption maxima	602 nm
Form	Powder
Color	Blue

Dye solution preparation

0.1g of dye was diluted in a liter of distilled water to create a stock solution that contained 100mg of dye per liter. The stock solution was diluted to the necessary

concentration to create the working solution. The dye solution concentrations were obtained by taking measurement for the solution absorbance at the characteristic wavelength of acid blue 25 (max = 602 nm) with a double-beam UV-VIS spectrophotometer.

Adsorption experiments

Equilibrium time was determined using equation 1, after that the most important effective variables in adsorption processes were investigated. These parameters included the adsorbent dose, contact time, initial dye concentration, and particle size of the peanut shell. The impact of these variables on the removal effectiveness of the dye utilized was investigated.

Study of the influence of a peanut shell dosage gives an idea of the effectiveness of the peanut shell and the ability of acid blue 25 dye to be adsorbed with a minimum peanut shell powder dosage. The effect of the sorbent dosage was investigated by varying the amount of peanut shell powder from 0.8 to 3 g/100 mL and added to acid blue 25 dye solutions of 100 mg/L. The flasks were shaken for 2 hours and at agitation speed of 250 rpm.

To study the effect of contact time, the dye concentration was fixed at 100 mg/L. The samples were withdrawn at increasing contact time every 15 minutes until 3 hours. The flasks were shaking with agitation speed of 250 rpm.

In order to study the effects of initial dye concentration on the percentage removal of acid blue 25 dye, a series of 250 mL Erlenmeyer flasks containing 100 mL of dye solutions with known initial concentrations (25, 50, 75, 100, 150 and 200 mg/L) were prepared. Each flask received 2.5 g of peanut shell, and it was shaken continuously for three hours at 250 rpm.

In industry, fine particles (less than 0.25 mm) are not preferred as they need a long time to settle. As a result, further, expensive, and time-consuming filtration procedures are required to separate the adsorbent with the fine particle size. On the other hand, adsorbents with high particle sizes (more than 2 mm) produce a small surface area, which lowers the adsorption efficiency (Koay, 2013). Thus, in order to study the effect of the particle size of peanut shells, four ranges of the particle size were selected: more than 4.75 mm, 4.75–2 mm, 2–0.25 mm and less than 0.25 mms. The adsorption experiment was carried out by adding 2.5 g of peanut shells, with different particle size ranges, added to each flask containing 100 mL of dyes solution with an initial dye concentration of 100 mg/L. All flasks were shaken at 250 rpm at 25°C for 3 hours.

For all the experiments, filter paper was used to filter the dye solution before using the UV spectrophotometric measurement to separate the adsorbent. The efficiency of dye acid blue 25 removals was calculated according to equation 2:

$$q_e = \frac{(C_i - C_e) * V}{W} \quad (1)$$

$$\text{Removal } \% = \frac{(C_i - C_e)}{C_i} * 100 \quad (2)$$

Where: C_i – represents the initial concentration of dye (mg/L); C_e – the equilibrium dye concentration (mg/L); q_e – the adsorbed solute quantity at equilibrium per adsorbent unit weight (mg/g); V – the dye solution volume (L); W – the adsorbent weight (g).

Adsorption isotherm studies

Langmuir isotherm

The Langmuir model assumes constant adsorption energy for all of the active binding sites on the adsorbent and deals with the monolayer maximum adsorption capacity of the adsorbent, which means each site can take in only one dye molecule. Equation (3) represents the Langmuir model.

$$q_e = \frac{Q * b * C_e}{(1+b) * C_e} \quad (3)$$

Equation 4 was used to generate the equilibrium parameter (RL), a separation factor, without dimension, that was connected to the Langmuir isotherm and used to further predict whether or not the study adsorption was beneficial (Maneet al., 2007; Pączkowski et al., 2021).

$$RL = \frac{1}{(1+b) * C_o} \quad (4)$$

Where: b – the Langmuir constant; C_o – the initial dye concentration; C_e – the concentration of the dye molecules in an equilibrium solution.

The following RL values show the adsorption type: unfavourable (RL > 1); linear (RL = 1); favourable (0 <RL < 1); and irreversible (RL = 0).

Freundlich isotherm

An exponential distribution of the several active sites' energy serves as the foundation for the Freundlich isotherm. It is observed that the adsorbent's strong binding sites are employed for binding first, and that the binding force decreases as the degree of occupancy increases. The Freundlich equilibrium adsorption curve describing the liquid and solid phase concentration of acid blue 25 at equilibrium are presented in equation (5).

$$q_e = K * C_e^{1/n} \quad (5)$$

Where: C_e – denotes the dye concentration at equilibrium; K – the affinity between the dye and the adsorbent (mg/g); 1/n – denotes the adsorption intensity or surface heterogeneity; q_e – the amount of dye adsorbed on each mass unit of the adsorbent (Freundlich, 1906).

Temkin isotherm

Temkin isotherm is one of the earlier isotherms, which assumes that there is a linear decrease in the adsorption heat with an increase in the coverage because of the interactions between the dye and the adsorbent. The linear form of Temkin isotherm shone in equation (6) (Inyinbor et al., 2016).

$$q_e = B * \ln A + B * \ln C_e \quad (6)$$

Where: B = RT/b (j/mol) refers to the Temkin constant related to the heat of adsorption; A is the equilibrium binding constant (L/g); R equals to 8.314 J/mol K; b is a Temkin isotherm constant (J/mol); T refers to the absolute temperature of the solution (°K).

Adsorption kinetic studies

The progression of dye adsorption to attain equilibrium is predicted using kinetic adsorption studies. The mechanism estimation of adsorption process is essential for design purposes as well (Benjelloun et al., 2021). The diffusion models, pseudo-first order, pseudo-second order, Elovich model and intra-particle diffusion studies were applied to study the adsorption mechanism of the acid blue dye on the peanut shell.

Pseudo-first-order model

The kinetics of dye adsorption have frequently been predicted using the pseudo-first-order kinetic model. Lagergren's initial pseudo-first-order rate statement based on solid capacity is expressed as follows (Azizian, 2004).

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (7)$$

The slope and intercept of the log (q_e-q_t) versus t (time) plot can be used to calculate K_1 and q_e.

Pseudo-second order model

The equation (8) represents the pseudo-second order model (Ho and McKay, 1999; Ho, 2000):

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (8)$$

The slope and intercept of the plot t/q_t vs t can be used to determine q_e and K_2.

Elovich model

Elovich model has been used for the chemisorption removal of dye onto heterogeneous solid surfaces. It makes the assumption that the energy on the solid surface is heterogeneous, but it offers no explanation for how adsorption works. Equation (9) represented the Elovich model's linear version (Ademiluyiand David-West, 2012).

$$q_t = \frac{1}{b} \ln \alpha\, b + \frac{1}{b} \ln t \quad (9)$$

Where: α – the initial rate of dye adsorption (mg/g/min); B is related to the surface coverage and activation energy for chemisorption (g/mg).

Intraparticle diffusion studies

To investigate adsorption mechanism, it is vital to recognize the steps that are taken during adsorption. The adsorption procedure is thought to involve a number of steps: the diffusion process of dye via the boundary layer, dye intraparticle diffusion, the dye adsorption on the internal sorbent surface, and dye migration from the bulk of the solution to the sorbent surface. The intraparticle diffusion rate can be expressed by the square root of time. The plot of qt vs t0.5 is defined by a number of linear areas that indicate the transfer of the external mass followed by intra-particle or pore diffusion, if it is assumed that the sorption process is influenced by spherical particle diffusion and convective diffusion in the solution. The intra-particle diffusion model is described as follows (McKay et al., 1987):

$$q_t = k_i t^{0.5} + I \quad (10)$$

Results and Discussion

SEM analysis

The SEM photographs of peanut shell (*Figs. 3a* and *3b*) show SEM images before and after adsorption of peanut shell, respectively. It is evident from *Fig.3a* that the pores of the peanut shell are highly heterogeneous. After dye adsorption, the particles are remarkably covered by dye acid blue 25 molecules, indicating a local adsorption due to heterogeneous surfaces. Furthermore, as noticed in *Fig.3b*, it can be suggested that dye acid blue 25 molecules penetrate to the pores of the peanut shell.

FTIR analysis

Fig. 4 displays the FTIR spectra of the powdered peanut shell before and after adsorption. The chemical analysis of the peanut shell powder reveals wide bands in the range of 3200–3600 cm^{-1}, attributed to the stretching of O-H bonds, C–H stretching region (2800–3000 cm^{-1}), carbonyl group stretching region (1550–1750 cm^{-1}), and fingerprint bands (below1550 cm^{-1}). Because the absorption in the finger print region corresponds to intricately interacting vibration systems, it is difficult to definitively attribute it to any one vibration (Abd El-Latif1, 2010). The broad band at 3351.75 cm^{-1} found on the spectrum of peanut shell shows the presence of the H bonded OH group. The peak at around 1646.79–1623.55 cm^{-1}probably indicates C = C stretching. The region between 1500 and 1800 cm^{-1} is a special range to evaluate the degree of saponification since this represents the carbonyl and double bond region (Yuvaraja et al., 2020). Whereas the medium peak located at 1029.55 cm^{-1} band is assigned to the C-N medium amines.

Fig. 3. *SEM photographs of peanut shell: (a) before adsorption; (b) after adsorption*

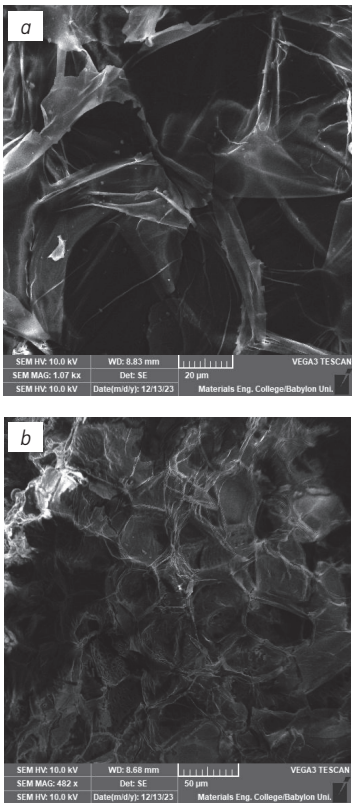
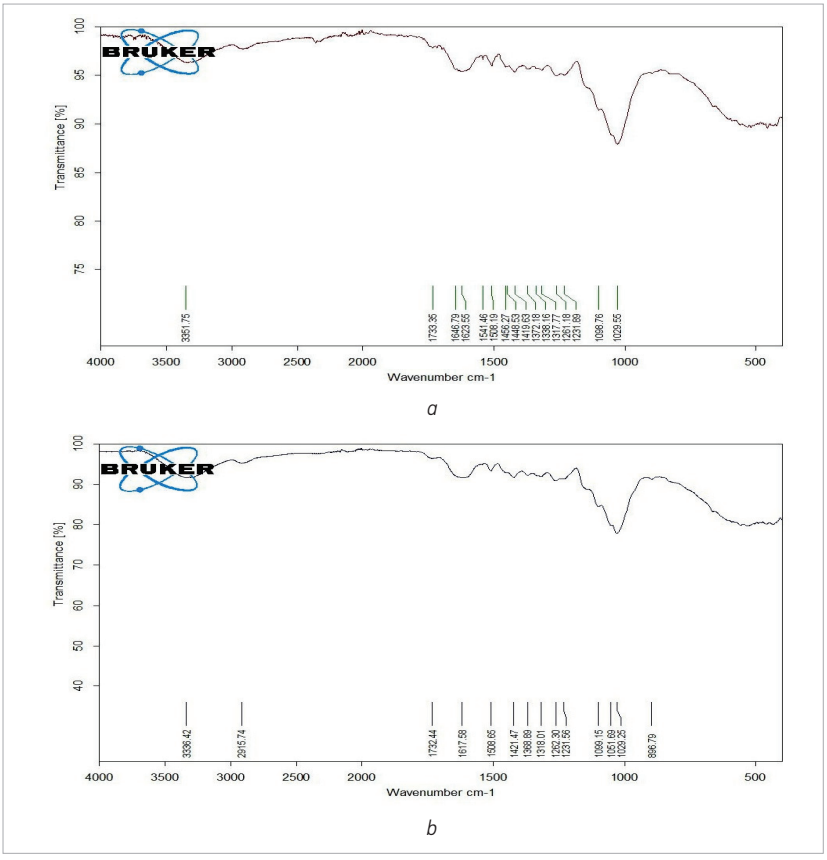


Fig. 4. *FTIR spectra of peanut shell: (a) before adsorption; (b) after adsorption*



Effect of adsorbent dosage

The adsorbent dosage effect on the adsorption of a fixed concentration of acid blue is demonstrated in *Fig.5*. As the dose of peanut shell powder was increased over the range of 0.8–3 g/ 100mL, the dye removal rate increased from 47.8 to 91.3%.

As the amount of adsorbent is increased, more accessible adsorption sites become available, enhancing the removal efficiency (Al-Ghoutiand Al-Absi, 2020; Hassan et al., 2021).

Also, adsorption process improvement as sorbent dose increases may possibly be ascribed to enhanced surface area and more adsorption sites could be increased.

Effect of contact time

The contact time effect on the acid blue 25 adsorptions on the peanut shell is presented in *Fig.6*. It can be seen that the amount of adoration is fast in the first stages. The equilibrium in 180 min is the result of active site saturation, which prevents additional adsorption from occurring, as reported by Parimelazhagan et al. (2023). The graph is a single line that is smooth and continuous before reaching saturation, which suggests that acid blue dye may be covered in a monolayer on the surface of the adsorbent (Balarak et al., 2019; Samat et al., 2021).

Influence of initial dye concentration

The initial concentration's influence on the adsorption of the dye on peanut shells is shown in *Fig.7*. The removal percentage increased within 90–91.6% as the initial concentration varied within 25–100 mg/L. The driving power to overcome the resistance of the mass transfer of dye between the solution and the adsorbent surface increases as the initial dye concentrations rise (Srisamai, 2021). Similar findings were made by Wu et al. (2019).

Effect of adsorbent particle size

The particle size effect is shown in *Fig.8*. The removal increased from 65.4% to 93.2% when particle size decreased from 4.75 to 0.25 mm. Because adsorption is only possible on the adsorbent's external surface area as small particles have a larger external surface area, an increase in the removal efficiency with the decreasing particle size can be attributed to these results (Srisamai, 2021).

Fig. 5. *Adsorbentdose, g/100 mL*

Fig. 6. *Contact time (min)*

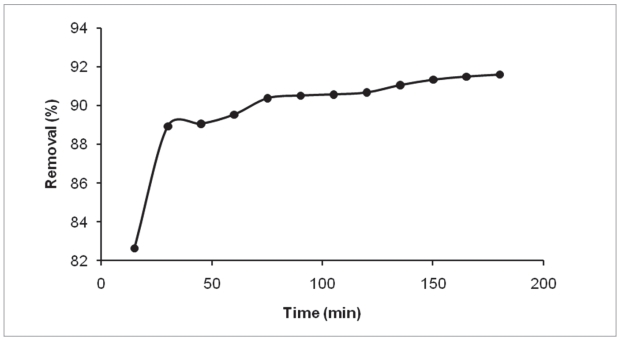


Fig. 7. *Initial concentration of dye, mg/L*

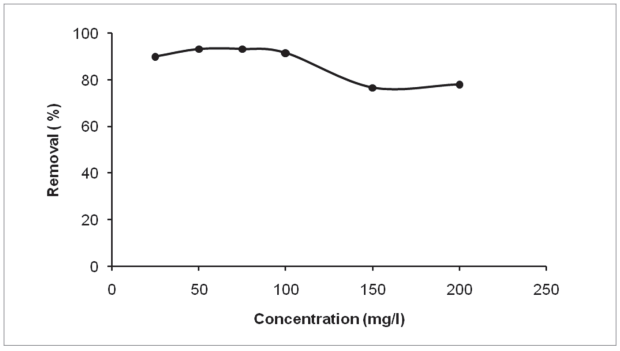
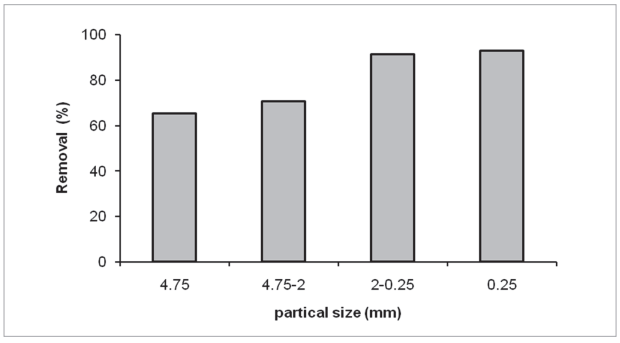


Fig. 8. *Particle size of adsorbent(mm)*



Prior research on the removal of color by silica (McKay et al., 1987) and the utilization of sago waste for the sorption of copper and lead both observed the improved removal by smaller particles (Khan et al., 2009; Balarak et al., 2019).

Isotherm analysis

Basic prerequisites for the adsorption system design include equilibrium data, also referred to as an adsorption isotherm (Benjelloun et al., 2021). In this study, the equilibrium data for acid blue onto peanut shells were modeled with the Langmuir, Freundlich and Temkin models. The plots of a linearized form of Langmuir, Freundlich and Temkin are described in *Figs. 9,10* and *11*, respectively, the adsorption isotherm constants and correlation coefficients for all models are shown in *Table 2*.

Fig. 9. *Adsorption isotherm of the Langmuir model for acid blue 25 ontopeanut shell*

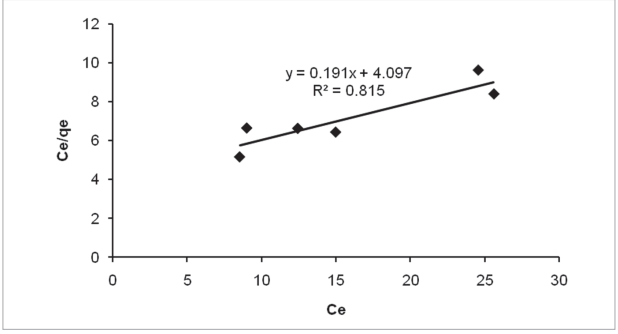


Fig. 10. *Adsorption isotherm of the Freundlich model for acid blue 25 onto peanut shell*

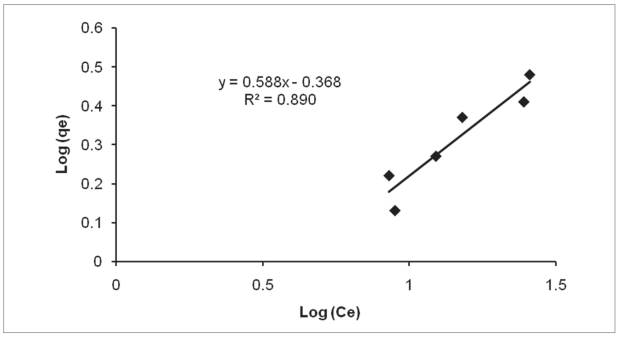


Fig. 11. *Adsorption isotherm of the Temkin model for acid blue 25 onto peanut shell*

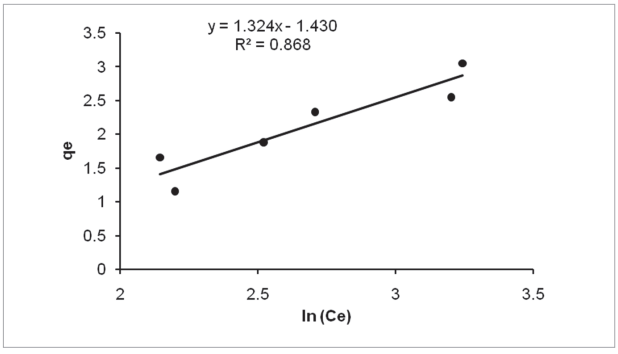


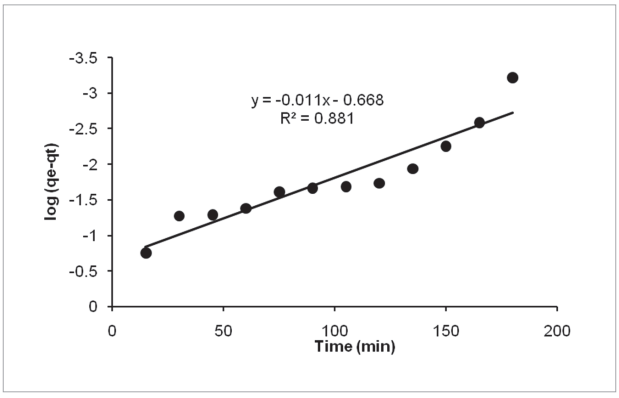
Table 2. *Langmuir, Freundlich and Temkin constants for adsorption of acid blue 25 on peanut shell kinetics study*

Model constants	Parameters	Acid blue 25
Langmuir	*q* max (mg/g)	5.2
	b (L/mg)	0.047
	RL	0.298
	R^2	0.815
Freundlich	K	0.428
	1/n	0.588
	R^2	0.891
Temkin	A (L/g)	2.942
	B (J/mol)	1.325
	R^2	0.868

Adsorption kinetic studies

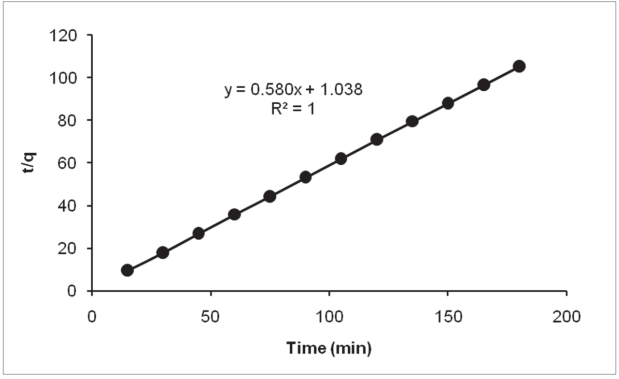
There was no correlation between the experimental results and the pseudo-first-order model. R2 was 0.881, as depicted in *Fig.12*.

Fig. 12. *Kinetic study for adsorption of acid blue 25 on peanut shell by usingthe pseudo-first-order kinetic model*



The linearized plot of second order kinetics is shown in *Fig. 13.* Plots of t/qt vs time were completely linear, and an R2 value equal to 1 indicated that the data were found to suit the second order model fairly well. The second-order nature of the adsorption of acid blue 25 onto peanut shell was consistent with the experimental data. The sorption of methylene blue onto wheat shell has been reported to exhibit similar behaviors (Blue et al., 2012). For numerous sorbent-sorbate systems, Ho and McKay (1998) updated and critiqued the published kinetic data and demonstrated that, in most instances, the pseudo-second-order model is preferable to the pseudo-first-order model.

Fig. 13. *Kinetic study for adsorption of acid blue 25 on peanut shell by using the pseudo-second-order kinetic model*



The linearized plot of the Elovich kinetic model showed a good fit to the experimental data with R^2equal to 0.977 as shown in *Fig. 14.* The plot of qt against ln t yields a straight line with α and b determined using the intercept and slope, respectively. It is seen that the Elovich equation was able to describe properly the kinetics of adsorption acid blue 25 onto peanut shell.

Fig. 14. *Kinetic study for adsorption of acid blue 25 on peanut shell by using the Elovich kinetic model*

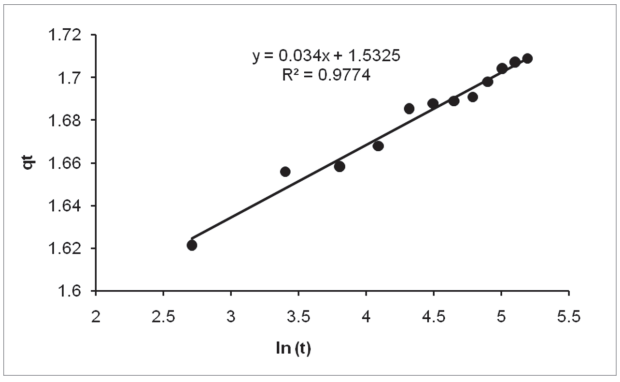


Table 3 provides a summary of the results for adsorption kinetic parameters of acid blue 25 onto peanut shell and the related linear regression coefficient R^2.

Table 3. *Adsorption kinetic parameters of acid blue 25 onto peanut shell (rpm = 200, dosage = 2.5 g/100 mL, pH 5)*

Model constants	Parameters	Acid blue 25 dye
First order model	q_e	0.215
	K_1	0.026
	R^2	0.881
Second order model	q_e	1.722
	K_2	0.324
	R^2	1
Elovich kinetic model	b	29.42
	α	$1.29*10^{18}$
	R^2	0.977
Intra particulate diffusion model	I	0.0083
	K_i	1.6025
	R^2	0.939

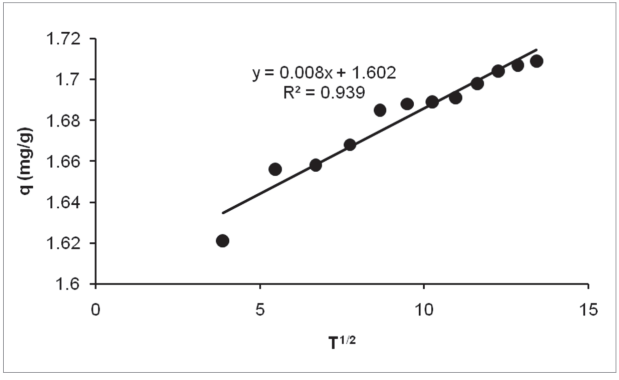
Intraparticle diffusion

Intraparticle diffusion mechanism was researched to better investigate the workings of the adsorption process. A plot of q against $t^{0.5}$ by Weber et al. was utilized to look at the intraparticle diffusion process. In the region where the rate-limiting factor is pore diffusion, the slope of the linear component of the plot was identified as a rate parameter that describes the rate of adsorption. The boundary layer effect's magnitude is indicated by the plot's intercept. The bigger the intercept, the greater the impact of the boundary layer (Wu et al., 2009). The variations in adsorption rates between the first and end stages may be the cause of departure from the origin. *Table 3* lists the values of Ki and I. It was discovered that the value of Ki rose as the dye solution's initial concentration was raised. Mane et al. found a similar finding regarding the adsorption of brilliant green onto fly ash (Mane et al., 2007).

The linear lines for the acid blue dye do not cross through the origin, as can be seen in *Fig. 15.* This indicates that there are other mechanisms that are involved in the

adsorption process, which are rate-limiting, in addition to pore diffusion. Along with intraparticle diffusion, another mechanism might be involved during the entire adsorption process (Giannoulia et al., 2023)

Fig. 15. *Intraparticle diffusion plot for the removal of acid blue 25 from an aqueous solution*



Conclusions

The results of adsorption acid blue 25 dye from an aqueous solution showed that peanut shell powder can be effectively used as a bio-adsorbent for the removal of anionic acid blue 25 dye. The peanut shell bio-adsorbent shows a maximum percentage removal of 93.2%. The kinetic studies stated that the adsorption kinetics of dyes on peanut shell followed the pseudo-second order model. According to the present study, one could conclude that the peanut shell is an effective adsorbent for anionic dyes removal from colored textile wastewater.

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