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Application of NaOH-activated peanut shells as a low-cost adsorbent for the removal of cationic dyes

Farida Hamdache[1]*, Farid Halet[1,2], Saida Bekhti[1], Abdelmalek Chergui[1,3], Ahmed Réda Yeddou[1] and Boubekeur Nadjemi[1].
[1]Laboratory of Study and Development of Techniques of Treatment and Water Treatment and Environmental Management L.E.D.T.E.G.E, Department of Chemistry, E.N.S Kouba, BP 92 Kouba 16308, Algiers, Algeria.
[2]Department of Biology, University M'Hamed Bougara Boumerdes, Avenue de l'indépendance, Boumerdes 35000, Algeria
[3]Laboratoire des Sciences et Techniques de l'Environnement, Département Génie de l'Environnement, National School of Engineering. E.N.P, 10 Rue des Frères OUDEK, El-Harrach 16200, Algiers, Algeria.
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*to whom all correspondence should be addressed: e-mail: farida.halet@g.ens-kouba.dz
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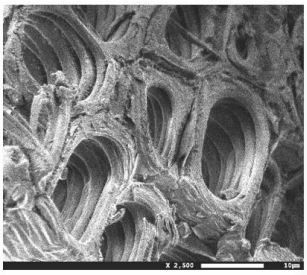
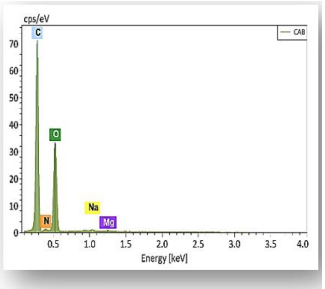
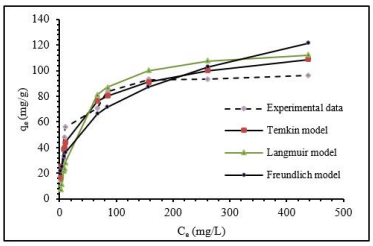
Graphical abstract



SEM image of NaOH-activated peanut shells



The spectrum EDS



The predicted curve fits for equilibrium isotherms of methylene blue adsorption

Abstract

The main purpose of this study is to evaluate the possibility of using a lignocellulosic residue, peanut shells after alkaline activation, as a low-cost adsorbent for the removal of methylene blue dye from aqueous solutions. Adsorption experiments were conducted by varying parameters such as the initial pH aqueous solution, contact time, temperature, and initial concentration of adsorbate. Results show that pH has no apparent effect on methylene blue adsorption; more than 95% of methylene blue was removed. The adsorption capacity of methylene blue was slightly improved when the particle size of the adsorbent and the temperature decreased. A temperature uptake from 298 K to 328 K induced a decrease in the percentage of methylene blue removal from 91.36% to 84.31%. The kinetic data obtained at different concentrations were analyzed using pseudo-first-order and pseudo-second-order kinetic models. Also, the modeling of isotherm was considered by applying Langmuir, Freundlich, and Temkin models. Kinetic and equilibrium data were best represented by pseudo-second-order and Langmuir models respectively according to determination coefficient R^2 and error function values. The ultimate adsorption capacity reached approximately 100 mg/g. Thermodynamics findings revealed that the adsorption proposed is exothermic and spontaneous process. These results show that peanut shells can be a potential adsorbent for organic dyes removal from aqueous solutions.

Keywords: Adsorption, methylene blue, peanut shells, activation, kinetic, isotherm.

1. Introduction

Nowadays, with rapid industrialization, considerable concerns derive from the discharge of high quantities of wastewater containing organic and mineral pollutants. Among these components, dyes are predominating (Boumediene *et al.* 2018). Dyes are widely used in many industries such as textile finishing, printing, paper production, photoelectrical industries, food technology, leather tanning, plastics, etc. (Patawat *et al.* 2020). Since then, it has been reported that more than a hundred thousand kinds of commercial organic pigments and dyes have been produced (Hassan *et al.* 2023). It is also known that all synthetic dyes are toxic and cause water coloring even at low concentrations. In addition, they are resistant to many chemicals, oxidizing agents, and heat due to their complex chemical structure and poor bio-degradability (Liu *et al.* 2018). Therefore, they are difficult to decolorize once released into an aquatic environment (Fayoud *et al.* 2015; Kutluay *et al.* 2020; Ifguis *et al.* 2022).

Methylene blue (MB) is one of the most common dyes found in the waters discharged by industrial activities. Studies proved that prolonged exposure to methylene blue dye can cause harmful effects on human health such as Jaundice, difficulties in breathing, increased heart rate, eye

burns, nausea, and vomiting, etc. (Kandisa *et al.* 2021; Ifguis *et al.* 2022).

For this, it is of great value to try to treat colored wastewater before their discharged into the environment. Hence, various techniques have been developed to remove dyes from wastewater. These include solvent extraction, biological treatment, chemical treatment, membrane filtration, oxidation, electrochemical degradation, and photocatalysis (Young-Hua *et al.* 2020; Patawat *et al.* 2020). From the earlier studies, the adsorption process was found as an effective treatment and efficient method to remove pollutants such as dyes and heavy metals from industrial waste water due to its low operating costs, simplicity of design, and ease of implementation (Kandisa *et al.* 2021; Young-Hua *et al.* 2020; Ifguis *et al.* 2022). Also, activated carbon is the most popular material used as adsorbent. It has been widely used for the removal of organic matter, because of its excellent properties including high surface area, large pore volume, and presence of functional groups (Bayter *et al.* 2018; Abas *et al.* 2019; Lafi *et al.* 2019). However, it's high manufacturing and regeneration cost has encouraged researchers to find and develop other low-cost and efficient materials to remove dyes from wastewater effluents before discharging them to the environment.

In this context, several researchers studied the possibility and the effectiveness of using low-cost agro wastes as alternate adsorbents for the removal of dyes from aqueous solutions including, peanut shells (Boumchita *et al.* 2017; Md.Tariqul *et al.* 2019; Wu *et al.* 2019; Mohd Azmier *et al.* 2021), sugar can (Peñafiel *et al.* 2021; Etin 2019; Wu *et al.* 2019), pistachio green hull (Sami *et al.* 2018; Haniyeh & Francesco, 2019), dates stones (Gherbia *et al.* 2019) and many others.

In this paper, efforts have been made to investigate the feasibility of using NaOH-activated peanut shells as an economical and available adsorbent for the removal of methylene blue, a basic dye, which was found to be the most commonly usedin the textile industry (Kandisa *et al.* 2021).

First, preliminary characterization of NaOH-activated peanut shells was carried out and followed by an adsorption study for the removal of methylene blue dye from an aqueous solution. The effects of parameters such as initial pH value, contact time, particle size, initial methylene blue concentration, and temperature on adsorption have been investigated. Equilibrium and kinetic models were applied to fit experimental data. The non-linear regression root mean square error (RMSE) and the chi-squared test (χ^2) were examined to select the most adequate kinetic and isotherm models. Adsorption thermodynamic parameters were also determined.

2. Materials and methods

2.1. Instruments and reagents

All the chemicals used in this study are of analytical reagent grade (Merck, Germany). The pH of a solution is adjusted by the addition of NaOH (0.1M) and HCl (0.1M). Methylene blue concentration is analyzed by UV-visible Spectrophotometer (Prim Secoman) at a wavelength of 664 nm. The pH is measured by a standard pH-meter Hanna instruments pH 21.

2.2. Preparation and activation of adsorbent

In this study, peanut shells were used as adsorbent to remove methylene blue dye from aqueous solutions. They were washed several times with distilled water to eliminate impurities and dried in an oven at 70°C. The dried peanut shells were grounded through a 250 µm sieve, and immersed in a solution of NaOH (0.1M) for 24 hours at 25°C, with the impregnation ratio of adsorbent: activating agent of 0.5:1 by weight. After filtration, the solid residue was thoroughly washed with distilled water until the pH of the filtrate reached the value of 6.5 ± 0.5. The obtained solid was dried in an oven at 70°C for 48 hours.

2.3. Characterization of adsorbent

First, the basic characteristics of the activated peanut shells are determined. The moisture content of the adsorbent was obtained by the gravimetric method. The pH in the water (2%) was determined after 24 hours of contact. The pH of the point zero charge (pH_{pzc}) which is defined as the pH value at which the net surface charge of adsorbent is equal to zero, was determined by the equilibrium technique (Cerovic *et al.* 2007)

Second, the surface morphology and elemental composition of the activated peanut shells powder were obtained using scanning electron microscopy coupled by energy dispersive X-ray spectroscopy SEM-EDS Bruker apparatus.

2.4. Adsorption experiments

Methylene Blue (MB) stock solution (1000 mg/L) was first prepared by dissolving the accurate weight of MB in distilled water and then diluted to obtain the desired concentrations.

Batch adsorption tests were carried out to study the effect of initial pH solution, contact time, particle size of adsorbent, initial adsorbate concentration, and temperature on the adsorption efficiency of methylene blue onto NaOH-activated peanut shells.

The effects of both the initial pH solution and particle size of the NaOH-activated peanut shells were studied by shaking a series of Erlenmeyer flasks containing each one 100 mL of methylene blue solution with a concentration of 30 mg/L and 0.1g of adsorbent at a temperature of 24 ± 2°C during 24 hours. The pH was adjusted between 2 and 10 using a solution of either NaOH or HCl (0.1 mol/L), and the selected particle sizes are below 250, 315- 400, 400-500, and above 500 µm, respectively. The amount of adsorbed dye per g of NaOH-activated peanut shells q_e (mg/g) and removal percentage (R %) at equilibrium were evaluated using the equations (1) and (2) respectively:

$$q_e = V(C_0 - C_e)/m \quad (1)$$

$$R(\%) = (C_0 - C_e)100/C_0 \quad (2)$$

Where, C_0 (mg/L) and C_e (mg/L) are the initial and the equilibrium concentrations of methylene blue, V (L) is the

volume of aqueous solution and m (g) is the amount of adsorbent.

The kinetic adsorption samples were prepared by adding 0.1 g of NaOH-activated peanut shells into 100 mL of methylene blue solution (at initial pH) with initial methylene blue concentration of 30, 60 and 100 mg/L. Batch process was carried out at 24 ± 2°C (ambient temperature laboratory). The samples were put in the shaking batch (300 rpm) during different time intervals. After each adsorption experiment, the samples were centrifuged and analyzed by spectrophotometer UV/visible. The methylene blue adsorption capacity q_t (mg/g) at time t (minutes) was calculated by equation (3):

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (3)$$

Where, C_t (mg/L) is the concentration of methylene blue in aqueous solution at time t (minutes).

The effect of temperature on the adsorption of MB was carried out in a thermostatic bath, by adding 0.1g of adsorbent to 100 mL of methylene blue solution (30 mg/L) at initial pH. The experiment was conducted at different temperatures (25, 35, 45 and 55°C). The solutions were shaken at 300 rpm during the equilibrium contact time obtained from the kinetic study.

Pseudo-first-order and pseudo-second-order models are considered and fitted with the experimental data. The linear forms of these models are expressed as follows:

Pseudo-first order model:

$$Ln(q_e - q_t) = Ln\, q_e - k_1 t \quad (4)$$

Pseudo-second order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where, k_1 (min^{-1}) and k_2 (mg/g.min) are the rate constant pseudo-first order and pseudo-second order, respectively.

The adsorption isotherm experiments are carried out in 250 mL Erlenmeyer flasks, by adding 0.1 g of NaOH-activated peanut shells to 100 ml of methylene blue solution with different initial concentrations (10-1000 mg/L). The solutions were shaken (300 rpm) during equilibrium contact time obtained from kinetic study. This study was performed at initial pH of solutions and 24 ± 2°C.

The Langmuir [Eq. (6)], Freundlich [Eq. (7)] and Temkin [Eq. (8)] isotherm models were used to fit the equilibrium adsorption data of methylene blue. The linear form of these equations can be written as follows:

Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{(q_m K_L)} + \frac{C_e}{q_m} \quad (6)$$

Where, q_m (mg/g) is the maximum adsorption capacity determined by the Langmuir model, K_L (L/mg) is the Langmuir constant related to the rate of adsorption.

The Langmuir parameters can also be used to provide affinity between methylene blue and NaOH-activated peanut shells using the dimensionless separation factor R_L, which is defined by the equation (7):

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

Where, C_0 is the initial concentration of methylene blue dye solution (mg/L). The values of R_L indicate the type of isotherm as follows:

- R_L = 0 Irreversible
- R_L = 1 Linear
- 0 < R_L < 1 Favorable
- R_L > 1 Unfavorable

Freundlich isotherm:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (8)$$

Where, K_F ((mg/g) (L/mg) $^{1/n}$) and n are Freundlich constants that characterize the adsorption capacity and the adsorption intensity of the NaOH-activated peanut shells for methylene blue retention.

Temkin isotherm

$$q_e = B \ln K_T + B \ln C_e \quad (9)$$

K_T is the Temkin isotherm equilibrium binding constant (L/mg), corresponding to the maximum binding energy, and B is the Temkin isotherm constant related to adsorption heat (J/mol). T is the absolute temperature (K) and R the universal gas constant (8.314 J/mol.K).

2.5. Error analysis

Due to the inherent error that results from the linearization of kinetic and isotherm models, two different error functions were used as criteria for the quality of fitting, the non-linear regression root mean square error (RMSE) and the chi-squared test (χ^2). These error functions allow selecting of the most adequate kinetic and isotherm models. The best-fit model is the one for which the error function is the lowest and the coefficient of determination (R^2) is close to unity (Jasper *et al.* 2020)

The previous error functions are given by the following equations:

$$RMSE = \sqrt{\frac{\sum_1^n (q_i - q_{ie})^2}{n-2}} \quad (10)$$

$$\chi 2 = \sum_{i=1}^{n} \frac{(q_i - q_{ie})^2}{q_{ie}} \quad (11)$$

Where, q_i (mg/g) is the experimental adsorption capacity, q_{ie} (mg/g) is the adsorption capacity estimated by the model, and n is the number of observations in the experiment.

The thermodynamic study of methylene blue adsorption by NaOH-activated peanut shells was realized at 25, 35, 45 and 55°C, respectively. The thermodynamic parameters for the adsorption process, such as, the change in standard enthalpy (ΔH°), standard entropy (ΔS°) and standard free-energy (ΔG°) were evaluated by using the following equations:

$$\mathrm{Ln}K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (12)$$

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

Where, K_d is the thermodynamic equilibrium constant. It is calculated by the equation (14):

$$K_d = \frac{q_e}{C_e} \quad (14)$$

T is the absolute temperature (K) and R is the universal gas constant (8,314 J/mol.K).

The values of standard change in enthalpy (ΔH°) and entropy (ΔS°) were obtained respectively, from slope and intercept of Ln K_d versus 1/T plots. The change in standard Free Gibbs energy (ΔG°) was calculated by the equation (13).

3. Results and discussions

3.1. Characterization of peanut shells

The Scanning electron microscopy (SEM) image (Figure 1) shows the presence of considerable numbers of various-sized cavities; however, there is a great possibility for methylene blue adsorption.

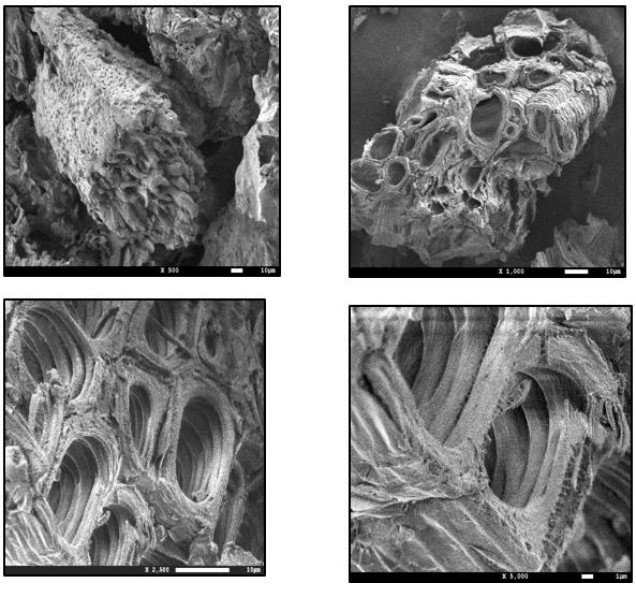


Figure 1: SEM image of NaOH-activated peanut shells

The elemental composition of the material is illustrated by the spectrum EDS of Figure 2 and Table 1. The main elements are carbon (54.32%) and oxygen (43.51%). This analysis reveals the organic nature of the adsorbent. Whereas, other elements, azote, sodium, and magnesium are present in small percentages.

Table 1: Chemical composition of NaOH-activated peanut shells.

Element	Mass %	Atom %
Carbon	54.31	61.31
Oxygen	43.51	36.87
Azote	1.43	1.38
Sodium	0.4	0.24
Magnesium	0.36	0.20

NaOH-activated peanut shells have a moisture content of 10.65%. The pH in water is 6.58. The determination of pH_{pzc} is important because it allows deducing the charge of the adsorbent which plays an important role in the adsorption process. The value of pH_{pzc} was found to be around 5.70; indicating that the surface of NaOH-activated peanut shells acquired a negative charge at pH greater than 5.70. While at pH below 5.70, the surface acquired a positive charge, promoting cationic and anionic dye adsorption, respectively.

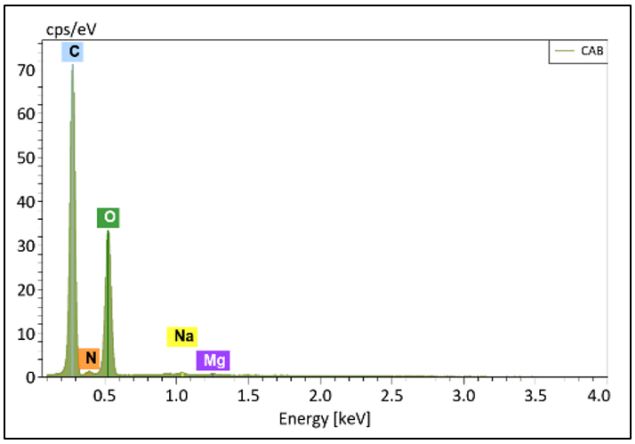


Figure 2: EDS analysis of NaOH-activated peanut shells.

3.2. Effect of various parameters on methylene blue removal

3.2.1. Effect of pH

Figure 3 shows the effect of the initial pH value of the solution on the uptake of methylene blue by NaOH-activated peanut shells.

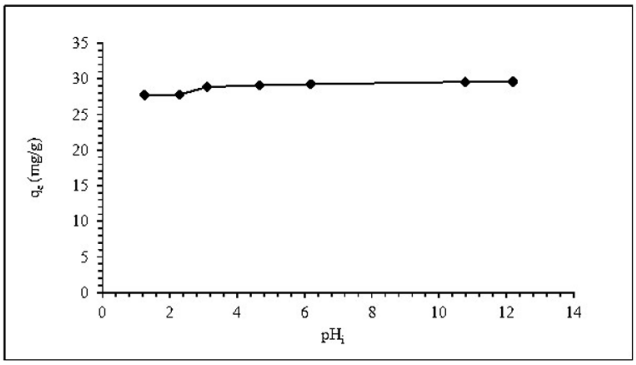


Figure 3: Effect of initial pH on methylene blue adsorption onto activated peanut shells. C_0=30mg/L, dose of adsorbent=1g/L, contact time= 24 h, T=25°C.

As seen in Figure 3, a slight increase in the adsorption capacity of methylene blue was observed when the pH solution increased. Indeed, the adsorption capacity passes from 27.72 to 28.85 mg/g when the pH of the solution increases from 1.25 to 3.1; corresponding to an increase of the removal percentage from 91.24 to 95.52 %. For pH values ranging from 3.1 to 12.2, there is no variation in adsorption capacity and removal percentage of methylene blue. This showed that NaOH-activated peanut shells could remove MB at any pH. Hence, all experiments were performed at the initial pH of methylene blue solution (6.5-6.8) without any adjustment.

3.2.2. Effect of particle size

The effect of particle size on the adsorption capacity of methylene blue was considered. The selected particle sizes of NaOH-activated peanut shells were: below 250, 315-

400, 400-500, and above 500 µm. As shown in Figure 4, the adsorption capacity was slightly improved when the particle size decreased. This is mainly due to the increase in the external surface area of NaOH-activated peanut shell particles. As a result, more active sites become available for methylene blue retention. The maximum adsorption of methylene blue was obtained for particle sizes below 250 µm which showed the highest removal percentage and sorption capacity, reaching 90% and 29 mg/g, respectively. Hence, all experiments were performed with particles having a diameter size below 250 nm.

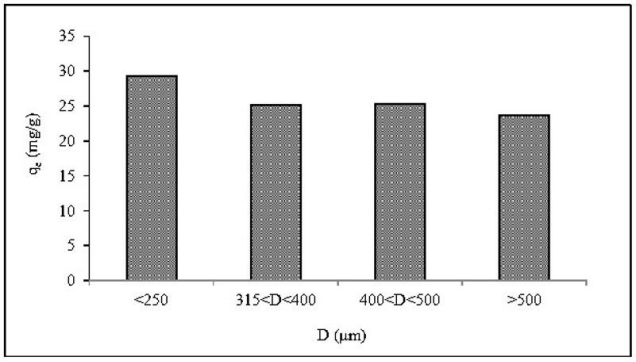


Figure 4: Effect of particle size on methylene blue adsorption onto NaOH-activated peanut shells. C_0=30 mg/L, dose of adsorbent=1g/L, pH=6.5, contact time= 24 h, T=25 ± 2°C.

3.2.3. Effect of initial dye concentration and contact time

The influence of contact time on methylene blue adsorption is a very important step, as it determines the time required to reach equilibrium. The effect of this important parameter was studied for three initial concentrations of MB (30, 60, and 100 mg/L).

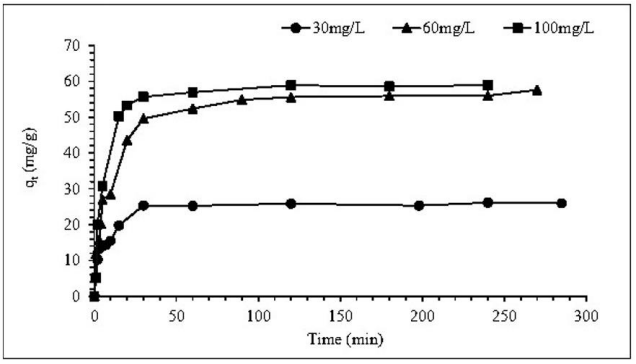


Figure 5: Effect of contact time and MB concentration on adsorption capacity onto NaOH-activated peanut shells. pH= 6 6, dose of adsorbent=1g/L, T=24± 2°C.

The effect of dye concentration and contact time on the removal of methylene blue, are shown in Figure 5. It is observed that the adsorbed amount of dye increases with contact time. We note that the removal of methylene blue was rapid in the first 30 min. The equilibrium was reached around 30 or even 60 minutes for all studied concentrations indicating the saturation of the adsorbent.

This trend was observed for each kinetic curve. Indeed, we distinguish two kinetic steps: the first one is characterized by a high adsorption rate. This is probably due to the abundant availability of active sites on the external surface of NaOH-activated peanut shells at the beginning of the adsorption process. According to (Wan *et al.* 2020), the rapid MB removal by NaOH-activated peanut shells indicates a strong interaction between MB and active sites of adsorbent. Subsequently, the rate of adsorption decreased gradually until the equilibrium because of the decrease of free sites number on the surface of the adsorbent (Md. Tamez *et al.* 2022).

It is also shown in Figure 5 that the adsorbed amount of methylene blue increased with an increase in the initial methylene blue concentration ~~of~~. This result means that the adsorption of methylene blue depends on time and MB concentration. The equilibrium capacity was found to increase from 25.33 mg/g to 58.92 mg/g with the increase in initial concentration dye from 30 mg/L to 100 mg/L. The increase in initial concentration also enhanced the interaction between adsorbent and dye (Md. Tamez *et al.* 2022) According to (Kandisa *et al.* 2021, (Ibrahim A. *et al.* 2022, adsorption is influenced by initial dye concentration as the available sites of adsorbent become few at higher concentrations. Similar behavior was reported by several authors in the literature (Kifuani *et al.* 2018; Huifang *et al.* 2019; Kutluay *et al.* 2020; Sifoun *et al.* 2020).

3.2.4. Effect of temperature

Another important parameter that affected the adsorption phenomenon is temperature. It has a significant influence on the rate of adsorption process.

Figure 6 presents the plot of methylene blue adsorption percentage as a function of temperature. This figure revealed that there was a decrease in the percentage of methylene blue uptake from 91.36% to 84.31% with an increase in the solution temperature from 25 to 55°C; the maximum removal percentage was achieved at 25°C. This decrease in the percentage removal implies that the process is exothermic and that increasing temperature has a negative effect on the adsorption process (Ifguis *et al.* 2023)

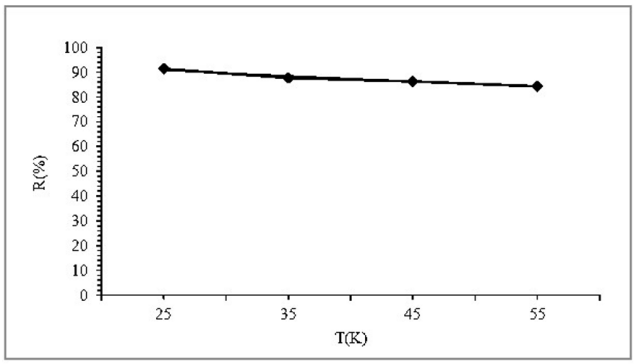


Figure 6: Effect of temperature on adsorption capacity of MB onto activated peanut shells. pHi = 6.6, $C_{0,\,BM}$=30 mg/L, dose of adsorbent=1g/L, contact time = 3 h

3.2.5. Kinetic adsorption studies

The experimental kinetics data of methylene blue adsorption on NaOH-activated peanut shells were fitted with pseudo-first order and pseudo-second order models (Eqn. (4-5)).

The calculated kinetic constants of the pseudo-first order and pseudo-second order were determined through the linearized form and their values along with the respective determination coefficients and error analysis, are listed in Table 2.

As reported in Table 2, experimental results follow a pseudo-second-order model. This is supported by the high values of the determination coefficients ranging from 94 to 99 % and the low values of RMSE and χ^2 obtained for all investigated methylene blue concentrations compared to those obtained with pseudo first order model. According to (Wang, Li, Wang, Zhaoo. and Jiang, 2012), the best correlation of experimental adsorption data with the pseudo-second-order model, indicates that the adsorption mechanism is highly dependent on both adsorbate /adsorbent material properties.

As seen from the table 2, the rate constant, k_2, values decreased from 6.10^{-3} to 2.10^{-3} g/mg.min with increasing initial concentration of methylene blue from 30 to 100 mg/L

A comparison between the calculated and the measured values fitted by non-linear pseudo-first-order and pseudo-second-order model equations is illustrated in Figures 7, 8, and 9.

Table 2: Parameters and error analysis data for kinetics adsorption of MB onto NaOH-activated peanut shells

Model	Kinetic parameters	C_0=30 mg/L	C_0=60 mg/L	C_0=100mg/L
Pseudo-first order	$q_{e\,cal}$ (mg/g)	16.37	40.358	50.345
	K_1 (min^{-1})	0.046	0.038	0.103
	R^2	0.981	0.940	0.962
	RMSE	5.593	17.083	8.989
	χ^2	45.466	328.247	28.468
	$q_{e,exp}$ (mg/g)	25.840	56.000	59.000
Pseudo-second order	$q_{e\,cal}$ (mg/g)	28.090	58.139	74.074
	K_2 (g.mg.min^{-1})	0.006	0.003	0.002
	R^2	0.985	0.992	0.941
	RMSE	2.728	2.316	8.211
	χ^2	2.680	4.202	11.722
	$q_{e,exp}$ (mg/g)	25.840	56.000	59.000

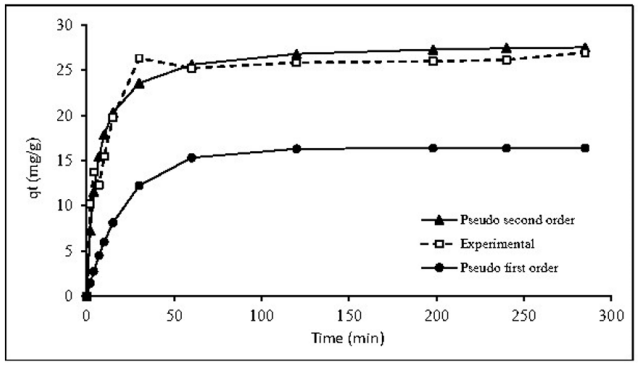


Figure 7: Predicted curve fits for the kinetics of methylene blue adsorption $C_{0,\,BM}$= 30 mg/L.

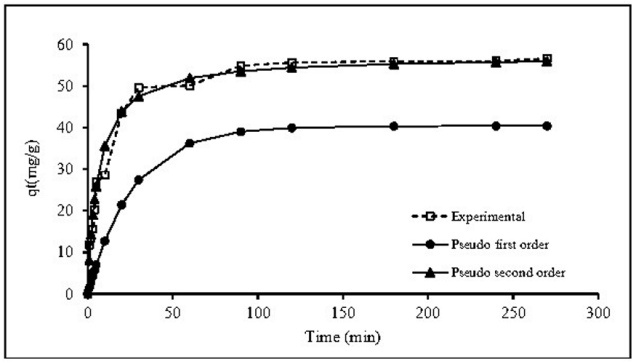


Figure 8: Predicted curve fits for the kinetics of methylene blue adsorption $C_{0,\,BM}$= 60 mg/L.

It is clear from non-linear form representations (Figures 7, 8, and 9) that the pseudo-second-order model is more appropriate than pseudo-first order, to describe the adsorption of methylene blue onto activated peanut shells for all studied concentrations.

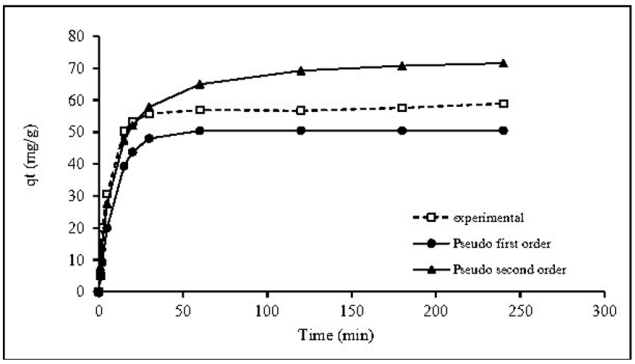


Figure 9: Predicted curve fits for the kinetics of methylene blue adsorption, $C_{0,\,BM}$=100 mg/L

3.2.6. Adsorption isotherm study

Adsorption isotherms or equilibrium data is used to describe how molecules or ions of adsorbate interact with the adsorbent surface sites (Patawat *et al.* 2020) The Isotherm of methylene blue Adsorption by NaOH-activated peanut shells is displayed in Figure 10. A high retention capacity of methylene blue was obtained for low dye equilibrium concentrations (10 – 20 mg/L). This result could mean that the adsorbent has a strong affinity for methylene blue dye.

The experimental data were studied by applying the most commonly used equilibrium models namely: Langmuir, Freundlich, and Temkin. The calculated isotherm parameters of the models were determined through the linearized form and their values, along with the respective

determination coefficients and error analysis, are listed in Table 3.

The validity of the models was determined by calculating the non-linear regression RMSE and χ^2. The low values of error functions reflect the best performance of the model for fitting with experimental data.

Table 3: Parameters and error function data for isotherm adsorption of MB onto activated peanut shells.

Model	Parameters	
Langmuir	q_e (mg/g)	100
	K_L(L/g)	0.031
	R_L	0.038-0.698
	R^2	0.998
	RMSE	7.760
	χ^2	8.060
Freundlich	K_f (mg/g)	16.945
	n	3.125
	R^2	0.846
	RMSE	13.920
	χ^2	30.662
Temkin	K_T(L/mg)	1.350
	B_T	16.970
	R^2	0.950
	RMSE	7.990
	χ^2	9.554

Table 4: Comparison of methylene blue adsorption capacity with various adsorbents in literature.

Adsorbent	**q_{max} (mg/g)**	**references**
Magnetic peanut husk	32.50	(Aryee *et al.* 2020)
Saw palmetto spent	90.90	(Papegowda & Syed, 2017)
Cactus	263.15	(Ifguis *et al.* 2023)
Activated carbon from *Dipterocarpus alatus* fruit	269.3	(Patawat *et al.* 2020)
Activated carbon prepared from dates stones	163.60	(Gherbia *et al.* 2019)
Activated carbon prepared from peanut shells	93,78	(Djedouni *et al.* 2013)
Sulfonated peanut shells	1250	(Md.Tariqul *et al.* 2019)
Peanut shells without treatment	46.80	(Lazarova *et al* , 2023)
Modified peanut shells	43.84	(Kutluay *et al.* 2020)
Activated carbon prepared from peanut shell	1,388	(Md. Tamez *et al.* 2022)
Biochar from peanut shells	16.21	(Dou & Jian, 2019)
NaOH-Activated peanut shells	100.00	Present work

Table 5: Thermodynamic parameters of methylene blue adsorption onto NaOH-activated peanut shells.

ΔH° (Kj.mol^{-1})	**ΔS° (J.mol^{-1}K^{-1})**	**ΔG° (Kj.mol^{-1})**			
-17.21	-38.768	T= 298K	T=308K	T=318K	T= 328K
		-28.762	-29.150	-29.538	-29.925

From Table 3, it can be observed that the best determination coefficients were in decreasing order: Langmuir (99.8%), Temkin (95%), and Freundlich (85%). The two first models (Langmuir and Temkin) respond well. However, the Langmuir model is more appropriate to describe equilibrium data with a high determination coefficient and lower error function values compared to other models.

This model assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. The Langmuir separation factor (R_L) and the Freundlich parameter (1/n) have both values in the range of 0 to 1, indicating that the adsorption of methylene blue onto activated peanut shells would be favorable and easily performed (Papegowda & Syed, 2017). The maximum monolayer adsorption capacity is estimated at 100 mg/g. Furthermore, these results are in line with those of previous studies (Boumchita *et al.* 2017; Kutluay *et al.* 2020; Md. Tamez *et al.* 2022).

A comparison between the calculated and the measured values of q_e fitted by non-linear Langmuir, Freundlich, and Temkin equations of methylene blue adsorption onto activated peanut shells is presented in Figure 11.

As can be seen from Figure 11, Langmuir, Freundlich, and Temkin equations provide a good correlation for the sorption process at low MB equilibrium concentrations until a value of approximately 40 mg/L. beyond this value, the isotherms begin to deviate slightly from the experimental curve, particularly for the Freundlich model, confirming the good fit of the Langmuir model and at a lesser degree of the Temkin model for the adsorption process.

The ability of activated peanut shells to adsorb methylene blue dye can be evaluated by comparison with other low cost adsorbents prepared from agricultural or plant waste and reported in the literature in terms of adsorptive

capacity as shown in Table 4. The difference in adsorption capacities of the listed adsorbents can be attributed to the adsorbent properities or experimental parameters adsorption. As reported in this table, the adsorption capacity of the activated peanut shells elaborated in this study shows an appreciable efficiency compared to some natural materials adsorbents and then can be effectively used for the removal of methylene blue dye from aqueous solutions.

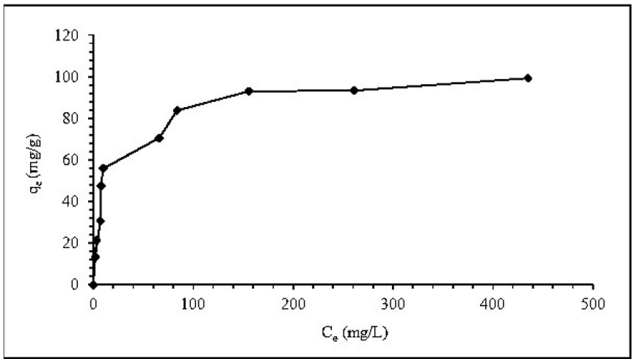


Figure 10: Isotherm of methylene blue adsorption. Dose of adsorbent=1g/L, pH_i= 6.7, contact time= 3 h, T=25±2°C.

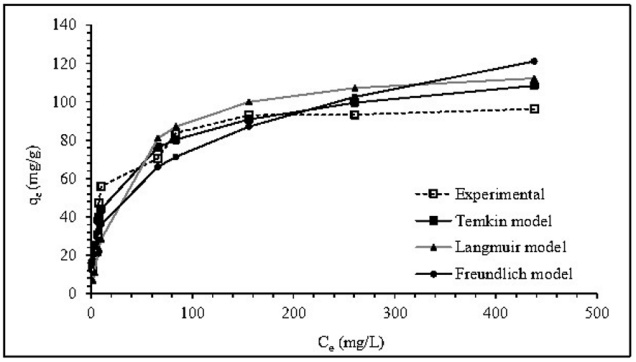


Figure 11: Predicted curve fits for equilibrium isotherms of methylene blue adsorption.

3.2.7. Adsorption thermodynamic study

A linear plot of $\ln k_d$ versus 1/T for the adsorption of methylene blue on activated peanut shells is presented in Figure 12. Values of thermodynamic parameters like standard enthalpy, entropy, and free energy changes are shown in Table 5.

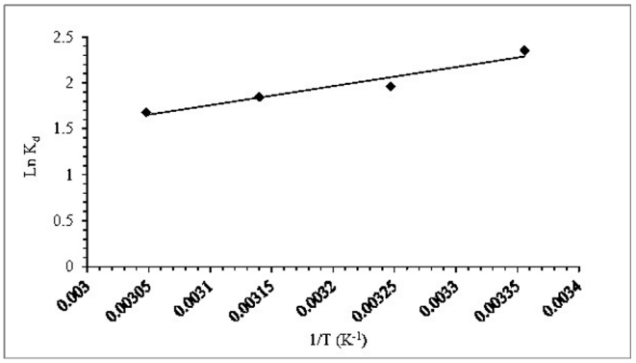


Figure 12: Plot of Ln K_d versus 1/T for estimation of thermodynamic parameters.

It can be stated that methylene blue adsorption by activated peanut shells is an exothermic process from the calculated ΔH° value of -17.21 $kj.mol^{-1}$, which is in the range of 5- 40 $Kj.mol^{-1}$, indicating that physisorption is the dominating mechanism (Crini & Badot, 2008). The negative value of free energy (ΔG°) for all studied temperatures confirms the feasibility and spontaneity of the adsorption process of methylene blue onto the prepared solid adsorbent. The negative value of the standard entropy ΔS°, suggests that the methylene blue molecules are more ordered on the substrate than in solution during the adsorption process.

4. CONCLUSION

In the present study, methylene blue was removed from an aqueous solution by adsorption on a low-cost material obtained from the valorization of a lignocellulosic by-product, namely peanut shells. The obtained results showed that activated peanut shells, present appreciable adsorption performances for methylene blue. It was found that the pH of the solution has no remarkable effect on the adsorption capacity of methylene blue and increasing temperature has a negative effect on the adsorption process. The adsorption kinetic was rapid and the equilibrium was totally reached in 30 or even 60 min. The kinetic process can be well described by a pseudo-second-order model for all studied methylene blue concentrations, whereas the equilibrium adsorption data are best fitted by the Langmuir model, indicating that methylene blue was adsorbed in a monolayer over homogeneous adsorbent surface. The maximum amount of methylene blue adsorbed onto NaOH-activated peanut shells surface was approximately 100 mg/g.

According to the thermodynamic parameters (ΔG°, ΔH°, ΔS°) the methylene blue adsorption onto NaOH-activated peanut shells is a spontaneous exothermic process, and methylene blue molecules are more ordered on the adsorbent solid than in solution.

According to the findings, NaOH- activated peanut shells can be effectively used as a potential, low cost and eco-friendly adsorbent material for removing of organic dyes pollutants from aqueous solutions. This study can also contribut to reduce agricultural solide wastes.

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