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Adsorption Studies of Methylene Blue using Activated Carbon Derived from Sweet Detar Seed Shell

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ABSTRACT

Adsorption capacity of sweet detar seed shell activated carbon (SDAC) was evaluated using batch adsorption technique. The SDAC was characterized by pH at point of zero charge (pH_{PZC}), Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). In batch optimization studies, the maximum adsorption capacity obtained at the optimum levels of different parameters were; 9.78 mg/g at 60 minutes, 8.61 mg/g at 0.1g adsorbent dose, 97.61 mg/g at 75µm particle size, 500 mg/g at 247.45 mg/g initial dye concentration, 10.99 mg/g at pH12 and 9.85 mg/g at temperature of 303 K. The adsorption data were found to closely fit to Freundlich isotherm model. The adsorption mechanism was found to be best described by the pseudo-second order kinetic model. Thermodynamic investigations indicates that the adsorption was spontaneous, exothermic, and decreased in the system randomness at adsorbent – adsorbate interfaces due to the negative values of enthalpy change (ΔH = -75.72 kJ/mol), entropy change (ΔS = -0.22 kJ/K) and Gibbs free energy change of adsorption; ΔG = -8.58 kJ/mol, 7.47 kJ/mol, 6.36 kJ/mol, 5.25 kJ/mol and 4.15 kJ/mol at 303, 308, 313, 318 and 323 K respectively. Desorption studies for adsorbent regeneration revealed that hydrochloric acid offered the highest recovery and reusability test revealed the good adsorbent performance after five successive adsorption cycles. Therefore, this study confirmed that activated sweet detar seed shell adsorbent could be used as an alternative low cost adsorbent for the removal of toxic dyes such as methylene blue dye.

Keywords: Adsorption, Desorption, Kinetics, Methylene blue, Reusability, Thermodynamics

INTRODUCTION

The need to preserve a cleaner and safer environment for the survival of terrestrial and aquatic lives such as human beings is extremely important and is a field of increasing interest to the environmentalist. The environment is rendered unfavorable and posed healthy concern to population as a result of the pollution caused by several agents like dyes and heavy metals (Umoren *et al.*, 2013). Different dyestuffs are contained from the effluent discharged by many industries such as food, plastic, printing paper, leather and textile. Dye is a colored material either natural or synthetic containing at least one color bearing groups (chromophore) and color helpers (auxochrome), that transmit a color to them and are disgusting and undesirable in wastewater (Lin *et al.*, 2017).

Methylene blue is a cationic dye used by many above mentioned industries for a variety of purposes. It can cause burn to human eye and aquatic animals which may result persistent injury. Gastrointestinal tract irritation with nausea symptoms, diarrhea and vomiting can be caused by this dye. It can also result in skin irritation when in contact with it (Iqbal, 2016).Human health and ecological balance are adversely changed by the pollution effect of dyes as most of them are toxic, carcinogenic, mutagenic and non-biodegradable, though removal of dye from effluents in the environment is routinely needed (Ajay *et al.*, 2019).

Numerous techniques have been employed for the removal of dyes from wastewater; biological method requires long fermentation time while chemical approaches display the disadvantages of secondary pollution and the large amounts of sludge formation making the two techniques less effective for the treatment (Lu *et al.*, 2019). Therefore, adsorption as one of the physical method has been employed to remove several pollutants due its simplicity of design, easy to operate, more efficient and cost effective; hence, it's one of the preferable technique to purify the wastewater containing dyes (Rai 2020; Ayuba and Abdulmumini 2022).Several substances such as activated carbon, clays, agriculture waste, silica, polymers and industrial solid wastes have been used as adsorbents (Bai *et al.*, 2022).

Activated carbon is usually the preferred adsorbent for the removal of contaminant due to its high adsorption capacity (Enenebeaku *et al.*, 2016). However, commercially available activated carbon is too cost and has irreversible nature of adsorption (Klemes *et al.*, 2018). Special attention on the

preparation of activated carbons from various agricultural wastes has been given, due to the growing concern in the preparation of low cost activated carbons for application involving treatment of wastewater. Previous works have studied the production of activated carbon from several plants material and agricultural byproduct (Akbartabar *et al.*, 2017).

However, research interest into production of more economical, easily available and highly efficient adsorbents are still under development. As part of our contribution to the growing interest of using agricultural material as adsorbent in elimination of dye from wastewater, the present research aimed on the use of sweet detar seed shell as low cost adsorbent to eliminate MB from aqueous solution.

MATERIALS AND METHODS

Sample Collection and Adsorbent Preparation

The adsorbent sample was prepared according to the procedure reported by Ibrahim and Umar (2016); Moharm *et al.* (2022): Sweet detar seed shell samples were collected and washed thoroughly using tap-water to eliminate any dirty particles and air-dried for 72 hours. The sample was grounded to a granular mess size and impregnated with (30%) phosphoric acid solution for 24 hours and dried prior to carbonization. The carbonization was performed at 400^0C for 2 hours using furnace. The activated samples were then washed with distilled water to neutral solution, and then oven dried at 105^0C to constant weight. The sample was then sieved and stored in an air-tight container leveled SDAC (Getasew *et al.*, 2019).

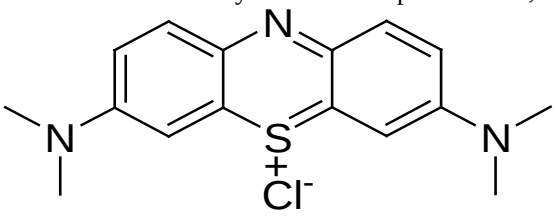
Point of Zero Charge Determination

The point of zero charged was determined by using salt addition method in which the pH of 0.1 M $NaNO_3$ was adjusted between 2 – 12 values using 0.1 M HCl and 0.1 M NaOH. 0.2 g of adsorbent was added to 40 ml of the adjusted solution. The initial pH values of each solution in each conical flask was denoted as pHi and shaken for 24hours. After settling the pH value of each solution was measured and denoted as pH_f. Change in pH (ΔpH) was plotted against the initial pH. The point at which the curve intersected with the pH line was pH_{pzc} of the adsorbent (Ayuba *et al.*, 2020).

Preparation of Stock Solution

The stock solution of methylene blue dye was prepared by dissolving 1.0 g of the dye in 1000 cm^3 distilled water to prepare 1g/L stock solution. This stock solution was used as adsorbate in batch adsorption experiments and other working solutions were prepared by serial dilutions.

The concentration of un-adsorbed (residual) methylene blue (MB) dye was measured at a wavelength (λmax = 664.20nm) using UV-visible spectrophotometer (Hitachi 2800 model). The structure of Methylene blue is represented as;



Adsorption Experiment

The procedure reported by Ibrahim *et al.* (2015) was adopted in batch adsorption experiment to study the effect of experimental parameters including (i) contact time (ii) particle size (iii) amount of adsorbent (iv) adsorbate concentration (v) pH (vii) temperature. This was carried out by shaking 100 ml conical flasks containing 0.1 g of adsorbent in 50 ml of adsorbate solution of desired concentration with adjusted pH on an orbital shaker machine using 200 rpm at constant temperature. The pH of the solution was adjusted using0.1 M of HCl and NaOH solutions. After adsorption period, the supernatant solution separated by filtration and the residual concentration of the dye solution was determined spectrophotometrically (using UV–Vis spectrophotometer) by absorbance monitoring at a wavelength corresponds to the dye maximum absorbance. Percentage of dye removal (% R) was calculated using equation 1.

$$R\ (\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad 1$$

Where C_0(mg/L) and C_e(mg/L) are dye concentration initially and at time t, respectively. Equilibrium adsorption capacity qe of the dye was be calculated by equation 2.

$$qe = \frac{(C_0 - C_e) \times v}{m} \qquad 2$$

Where Ce is the dye equilibrium concentration (mg/L)in solution; V is the volume (L) of the dye solution and m is the mass (g) of the adsorbent.

Regeneration and Reuse

Regeneration studies for the MB-loaded adsorbent was carried out in different desorbing agent; distilled water (H_2O), sodium chloride (NaCl), sodium hydroxide (NaOH) and hydrochloric acid (HCl). Distilled water was used to wash the spent adsorbent to eliminate any trace of unadsorbed dye and later allowed to dry. Spent adsorbent (0.1g) was added to a set of flasks containing 50ml of desorbing solution and agitated at 200 rpm for a period of 90 minutes. The best desorbing agent was selected for the effect of contact time and concentration (Shakoor and Nasar 2020). The reusability of the adsorbent was performed in a number of 5 cycles.

Desorption efficiency and desorption capacity were calculated using equations 3 and 4

$$\text{Desorption efficiency (\%)} = \frac{q_{de}}{q_{ad}} \times 100 \qquad 3$$

$$\text{Desorption capacity}(q_{des}) = \frac{C_{des} \cdot V_{des}}{m} \qquad 4$$

Where C_{des} is dye desorbed concentration (mg/dm^3), V_{des} is the volume of desorbing solution (dm^3), m is the mass of the pre-adsorbed adsorbent (g) and q_{ad} is the quantity adsorbed per unit mass of adsorbent (mg/g).

Fourier Transform Infrared Spectroscopy Analysis (FTIR)

FTIR analysis was performed to get the information about the functional groups of the adsorbent sample that might involve during the binding mechanism process. The analysis was conducted on both fresh and loaded adsorbent sample in the whole of the fundamental FTIR wave number range 4000 - 650 cm^{-1} using a spectral resolution of 8 cm^{-1} and a total number of 32 scans (Husaini *et al.*, 2020).

Scanning Electron Microscopy (SEM)

Scanning electron microscope examined the adsorbent samples before and after the adsorption process to analyze their surface and morphological structure. Analysis was performed using proxy Scanning Electron Microscope (Phenom World Eindhoven). The sample was placed on the sample holder using adhesive tape which was then inserted inside the machine. SEM image was taken at an accelerating voltage of 15.00 kV at 1000 magnifications (Husaini and Ibrahim 2019).

RESULTS AND DISCUSSION

Characterization of Adsorbents

FT-IR Analysis

The FTIR spectra of SDAC before and after adsorption (SDAC-MB) presented in Fig. 1, displayed minor significant changes in the observed adsorption band. The assigned functional groups to the absorption bands in the spectra are presented in Table 1. The shift in band obtained after the adsorption implies the involvement of these groups in the adsorption process and small changes could be attribute to electrostatic and weak interactions between the adsorbent functional groups and adsorbate (Asbollah *et al.*, 2021).

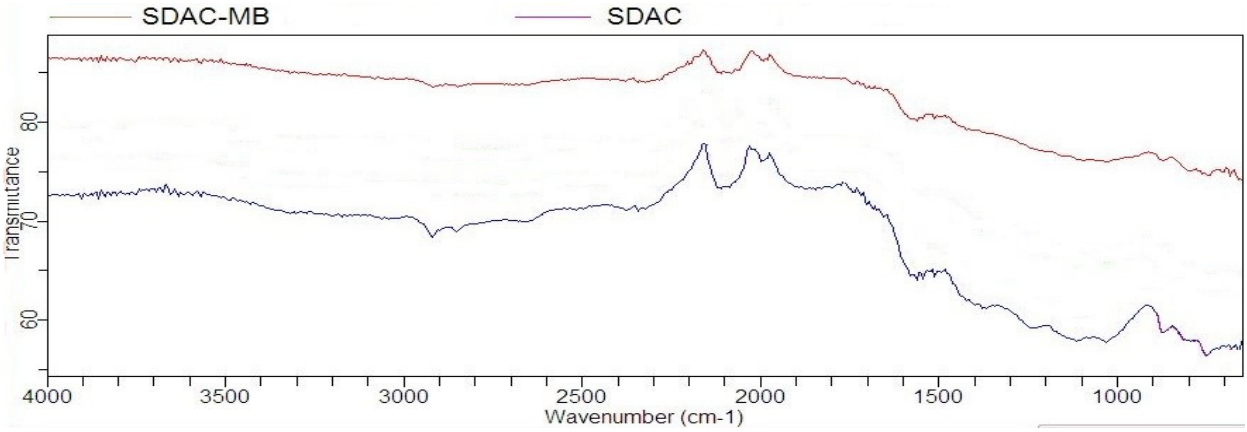


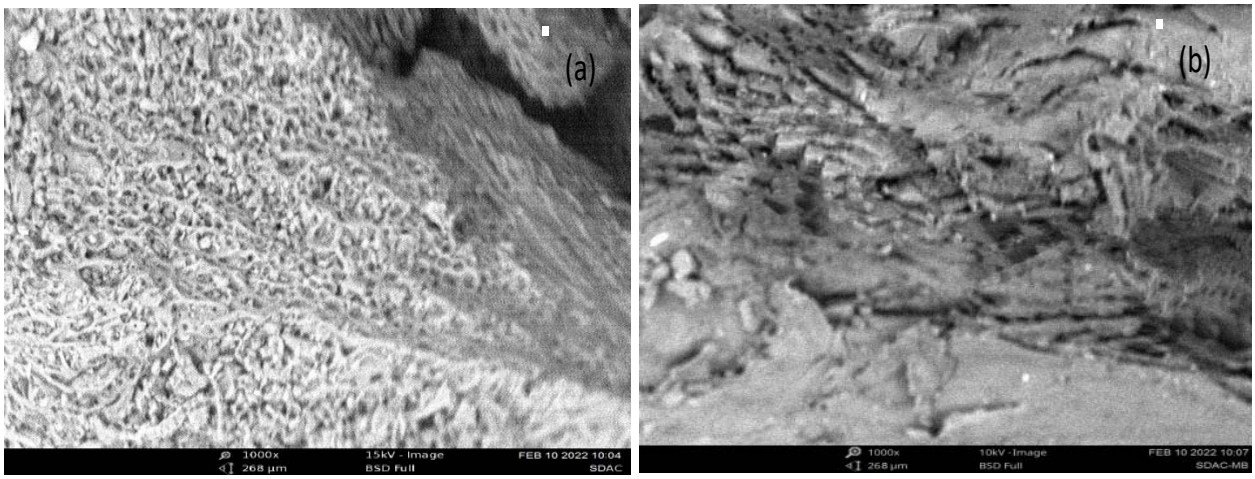
Fig. 1: FTIR Spectra of SDAC and SDAC-MB

Table 1: Functional group observed before and after adsorption of MB onto SDAC

Functional group	Vibration Frequency (cm^{-1})	Observed Frequency (cm^{-1})	
		Before Adsorption	After Adsorption
O-H stretching vibration in alcohol	3700-3584	3651	3633
C-H stretching vibration in alkane	3000-2840	2910	2851
C ≡ C stretching vibration in alkyne	2260-2100	2248	2260
C ≡ C stretching vibration in alkyne	2260-2190	2117	2199
C = O stretching of carboxylic acid	1720-1706	1704	1794
C = O stretching of ketone	1685-1666	1685	1680
N-O stretching of nitro groups	1550-1500	1550	1547
C-O stretching of alcoholic groups	1124-1087	1110	-
C-H bending of 1,3-disubstituted	880±20	873	863
C-H bending of monosubstituted	750±20	747	750

SEM Analysis

The scanned micrograph obtained from SEM analysis before adsorption presented in Fig. 2a, displayed an irregular, crack, rough surface, cavities and pores. While after the adsorption (Fig. 2b) the crack broadened and the pores are smothered with deposition of adsorbed MB molecules.



Figures 2: SEM Micrograph (a) SDAC before the adsorption (b) SDAC-MB after the adsorption

pH at Point of Zero Charge (pH_{pzc})

The point of zero charge is an isoelectric kinetic property of materials termed as isoelectric point, its defined as the point at which the net charge surface of biosorbent functional groups equalize to zero under certain condition of pressure and temperature. This does not indicate that the surface has no charge at pH_{pzc}, but rather amount of positive and negative charge are equal (Chham *et al.*, 2018). In surface characterization pH_{pzc} plays an important role, as it ascertain how easily potential harmful ions can be adsorbed by the adsorbent. According to the literature pH > pH_{pzc} make the surface of the adsorbent negative allowing the adsorption of cations more favorable. Contrary, the adsorbent carries a net positive charge at pH < pH_{pzc} values, capable of repelling cations (Shoukat *et al.*, 2017). pH_{pzc} value obtained for SDAC is 6.9 as presented in Fig. 3, the pH value above this make the surface of the adsorbent negative and that favors the cationic dye adsorption such as MB due to the increased electrostatic force of attraction.

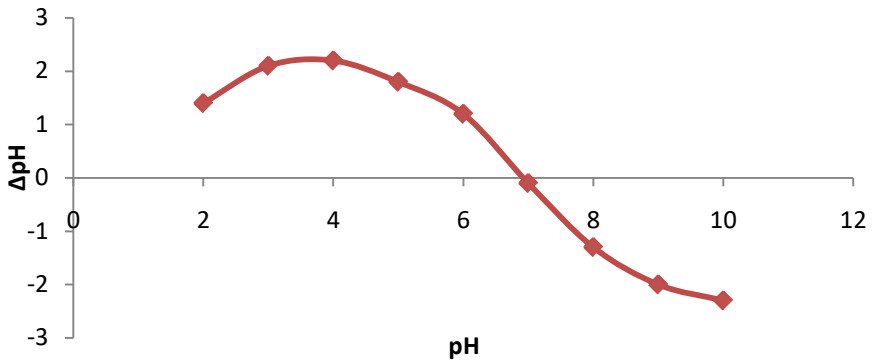


Fig. 3: pH at Point of Zero Charge of SDAC

Optimisation of Experimental Parameters

Effect of contact time

Contact time is an important parameter that affects all transfer process including adsorption phenomena. The impact of agitation time on the amount of MB adsorbed per unit mass of SDAC adsorbent is displayed in Fig. 4 indicating the efficacy of adsorptions from aqueous solutions (wastewater). Increases in contact time (5- 60 minute) increases the adsorption capacity of adsorbent and the process attained the equilibrium time at 60 minute. However, extending the time above 60 minute might lead to desorption (decrease in the sorption capacity) due to inaccessibility of available active site of adsorption. At the first stage the initial adsorption was rapid and later proceeded at a slower rate until equilibrium is reached. With increase in contact time the diffusion rate of adsorbent molecules becomes higher from bulk liquid to the liquid - adsorbent interphase due to decreased in thickness of the interphase layer and enhanced turbulence. Similar finding was reported by Ibrahim and Umar (2016) on the study of adsorption thermodynamics of some basic dyes uptake from aqueous solution using *albizia lebbeck* shells.

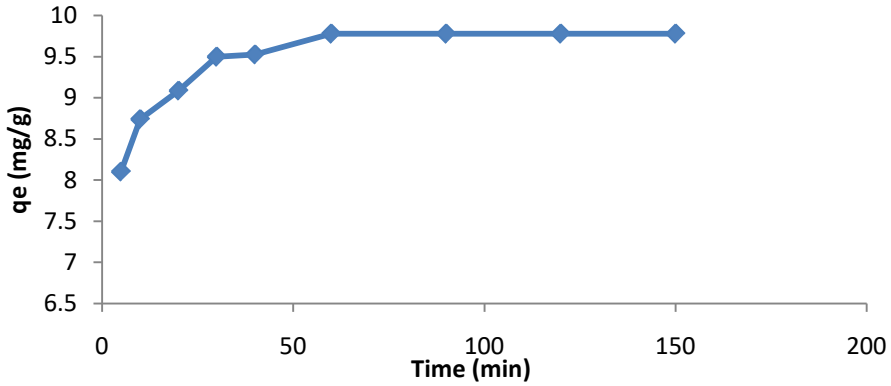


Fig. 4: Variation of q_e with Agitation Time

Effect of Adsorbent Dosage

Adsorbent dosage is an important parameter that stimulate the adsorption process as it determine the amount of dye adsorbed per unit mass of the adsorbent at different operating conditions. Effect of SDAC dose on the removal MB dye was investigated and displayed in Fig. 5, which shows the decreased adsorption capacity with increase in adsorbent dosage from 100-600 mg. The decrease in adsorption capacity with increasing adsorbent dose might be due to partial attribution to the saturation of the adsorption sites. Similar work was reported for adsorption of methylene blue and malachite green in aqueous solution using jack fruit leaf ash as low cost adsorbent (Banerjee *et al.*, 2017).

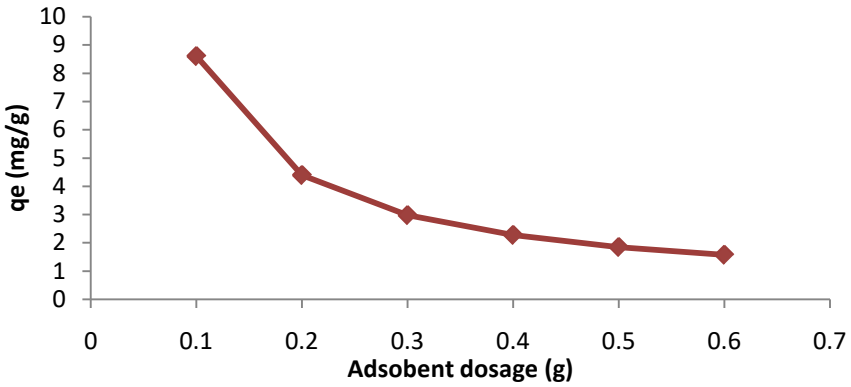


Fig. 5: Variation of q_e with Adsorbent Dosage

Effect of Initial Concentration

Initial concentration of adsorbate molecules strongly influences the adsorption of dyes by the adsorbent molecules. In the aqueous-solid interphases mass-transfer resistance of dye molecules disturbs from the main driving force of the initial concentration (Thitame and Shukla 2016). Fig. 6 displayed the effect of initial MB concentration on the adsorption capacity of SDAC increases with increase in initial concentration (20 – 500mg/L) of the dye. For a less solution (20mg/L), the amount of dye adsorbed per unit mass was just 9.8 mg/g which increased to 247.5 mg/g in higher concentrated solution. This openly shows that the adsorption process was highly initial concentration dependent.

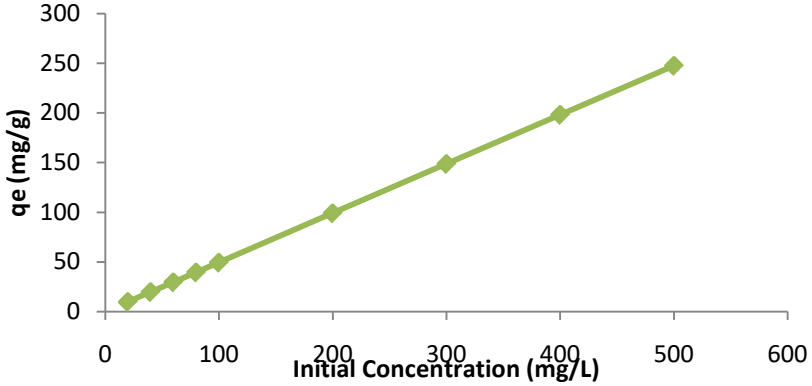


Fig. 6: Variation of q_e with Initial Concentration

Effect of Particle Size

Adsorption of dye molecule is highly influence by higher surface area therefore decrease in adsorbent particle size increases the surface area which leads to increase in dye adsorption. The adsorption capacity of SDAC decreases from 9.76 to 5.13 mg/g with increase in particle size from 75 to 900 µm as shown in Fig. 7. This could be ascribe that larger particle sizes broaden diffusion path and reduce the surface area that shorten the capability of dye the dye to penetrate the whole internal cavity structure of the adsorbent while the smaller particle size lowered diffusion path and increment the surface area that make it possible for the dye molecule to infiltrate all the internal cavity structures of the adsorbents (Ibrahim *et al.*, 2015).

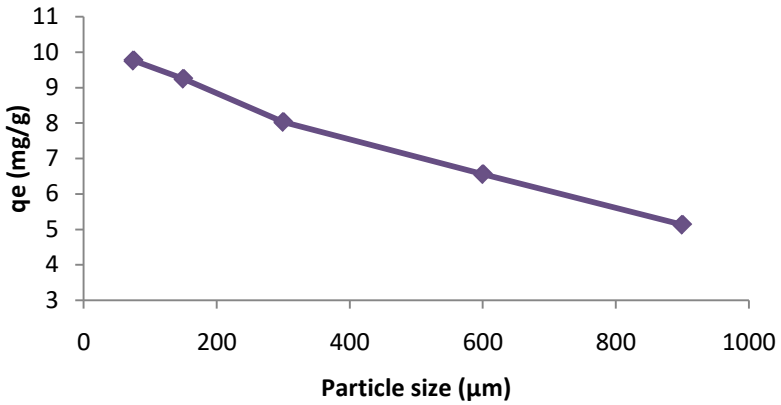


Fig. 7: Variation of q_e with Particle Size

Effect of pH

The amount of dye adsorbed per unit mass of the adsorbent was found to have a profound effect on initial pH. Variation for the amount of MB adsorbed by SDAC versus pH is presented in Fig. 8. The pH of the solution was varied from 2 – 12 using NaOH and HCl for the adjustment. At low pH value there is high H^+ concentration and the adsorption capacity increases from 8.0 mg/g at pH 2 to 9.99mg/g at pH 12. This could be due to the negative charge of the adsorbent surface according pH_{pzc} value (6.9) which makes the adsorption of MB favorable at pH above pH_{pzc} value. surface properties of the adsorbent and degree of ionization of dye molecules varies due to the variation of pH values from acidic to alkaline medium affecting the rate of dye adsorption (Haghdoost and Aghaie 2015).

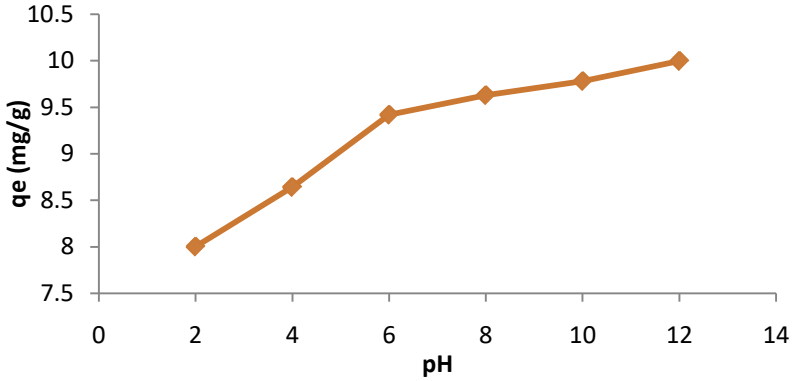


Fig. 8: Variation of q_e with pH

Effect of Temperature

Variation of temperature effect with adsorption capacity on the adsorption of MB is presented in Fig. 9. There is decrease in adsorption capacity with increase in temperature supporting exothermic process. The decrease in the adsorption capacity of SDAC with increasing temperature is ascribed to desorption of physisorbed MB molecules as a result of increased solubility in liquid-phase. The physisorbed molecules are distant from the surface and require lower energy for desorption. Increase in temperature lead to the escaping tendency of pollutant species that result to decrease in adsorption capacity. This suggests that the adsorption of MB onto SDAC is controlled by physical process, because for in chemical adsorption, adsorption capacity increases with increase in temperature due to the increase in kinetic energy of the adsorbate molecules which enhance their mobility inside the adsorbent pores (Husaini *et al.*, 2019).

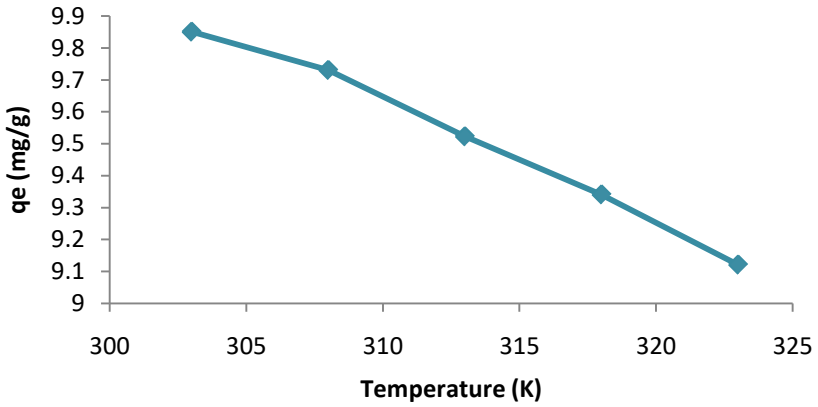


Fig. 9: Variation of q_e with Temperature

Adsorption Isotherms

The adsorption isotherm models are significant tools which provide insights into the process of adsorption and derive important parameters describing the mechanism of adsorption. Langmuir, Temkin, Freundlich and Dubinin – Radushkevich are usually the most used isotherms to describe the nature of adsorption. After MB adsorption onto SDAC the derived adsorption data was fitted into these models to propose the best fit adsorption process. The adsorption parameters were computed and presented in Table 2.The correlation coefficient (R^2) parameter was used to determine the isotherm that best fit to the experimental data. The values of R^2obtained from this research were correspondingly found to be higher in Freundlich isotherm than the values in other tested isotherm. Base on this Freundlich isotherm is therefore the model that best fitted to the experimental data. Similar result was reported by Usman *et al.* (2022).

Table 2: Adsorption Isotherm Parameters

Isotherm Model	Parameters	Values
Langmuir	q_m (mg/g)	105.26
	K_L (dm^3 mg/g)	0.23
	R_L	0.18
	R^2	0.9812
Freundlich	K_F (dm^3/mg)	34.94
	n	1.32
	1/n	0.76
	R^2	0.9918
Temkin	K_T (dm^3 mg/g)	1.77
	b (kJ/mol)	97.18
	R^2	0.8985
D-R	q_m (mg/g)	147.43
	β (mol^2/J^2	3×10^{-7}
	E (kJ/mol)	1.29
	R^2	0.8497

Thermodynamic Studies

The thermodynamic parameters of adsorption such as changes in entropy (ΔS), enthalpy (ΔH), and Gibb's free energy (ΔG) parameters were evaluated by equation 5 and 6.

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

$$lnK_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

The ΔG values were obtained using equation 5, while ΔH and ΔS, presented in Table 3, were obtained from the slope and the intercept of lnKc versus the 1/T- plot, T is the absolute temperature and R is gas constant (8.314 J/mol K).

Table 3: Thermodynamic Parameters

Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/K)
303	-8.58		
308	-7.47		
313	-6.36	-75.72	-0.221
318	-5.25		
323	-4.15		

From the values of thermodynamic parameters given in Table 3 it can be seen that ΔG values are all negative which indicate the spontaneous adsorption of MB onto SDAC and suitability of the process increase with decreasing temperature, therefore the reaction is more favorable at low temperature. The negative value of ΔH demonstrates the MB adsorption onto SDAC is exothermic process (i.e heat evolved from the reaction vessel). The negative value of ΔS corresponds to a decrease in degree of freedom of the adsorbed species. Similar trend was reported by Muhammad and Ibrahim (2018).

Kinetic Studies

Study of adsorption kinetics is important as it provide information about adsorption mechanism. The experimental data was analyzed by using two kinetic models whose linear forms are given in equations 7 and 8.

Pseudo-first order: $\ln (q_e - q_t) = \ln q_e - k_1 t$ 7

Pseudo-second order: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ 8

Where q_e and q_t are the quantity (mg/g) of dye adsorbed at equilibrium and at time t (min) and k_1 and k_2 are the rates of adsorption constant for pseudo – first and second order. The values of the various parameters in the two models are presented in Table 4.

Table 4: Kinetic Parameters

Kinetic Model	Parameters	Values
Pseudo-first order	$k_1(min^{-1})$	0.06
	$q_{e\ exp}$ (mg/g)	9.78
	$q_{e\ cal}$ (mg/g)	1.98
	R^2	0.9521
Pseudo-second order	K_2 (g/ mg min)	0.08
	$q_{e\ exp}$ (mg/g)	9.78
	$q_{e\ cal}$ (mg/g)	9.87
	R^2	1.00

The R^2 value of pseudo-second order was close to unity and q_{cal} values was also in good agreement with q_{exp} value obtained from the experimental data indicating the applicability of pseudo-second order kinetic models for the MB adsorption onto SDAC. Therefore, pseudo-second order model fits to describe the kinetic data of the process.

Desorption and Reusability Studies

The result obtained from the desorption using four different regenerates are presented in Fig. 10. Hydrochloric acid offered better desorption with 85.31% desorption efficiency while distilled water offered the least with 13.01 % desorption efficiency. In acidic medium, the availability of H^+ make the desorption of MB more favorable therefore it was chosen to be the best desorbing medium.

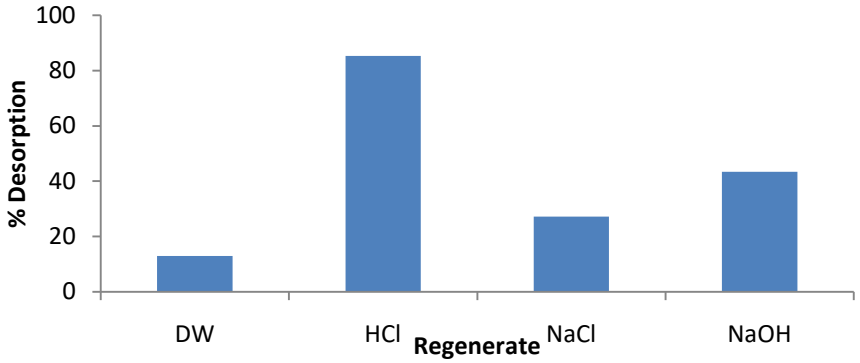


Fig. 10: Effect of Regenerating Agents on the Desorption Efficiency

The effect of contact time on the best desorbing medium is presented in Fig. 11 where the desorption efficiency was observed to increase from 69.99 % until it reached highest the value of 85.13 % after 30 minutes. The effect for the initial concentration of the desorbing medium was also presented in Fig. 12. It was observed that desorption of MB increased with the increase in concentration of hydrochloric acid.

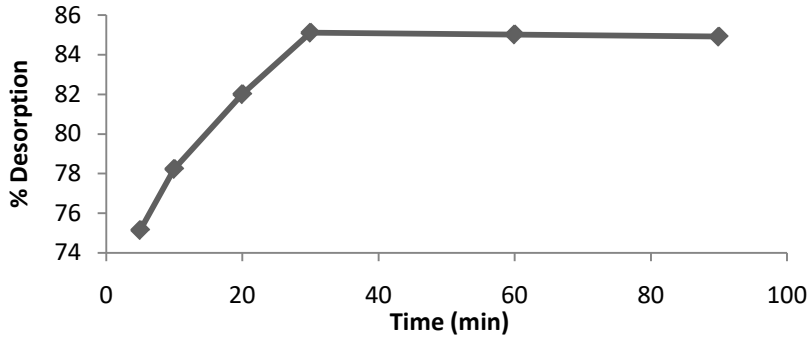


Fig. 11: Effect of Contact Time on Desorption Efficiency

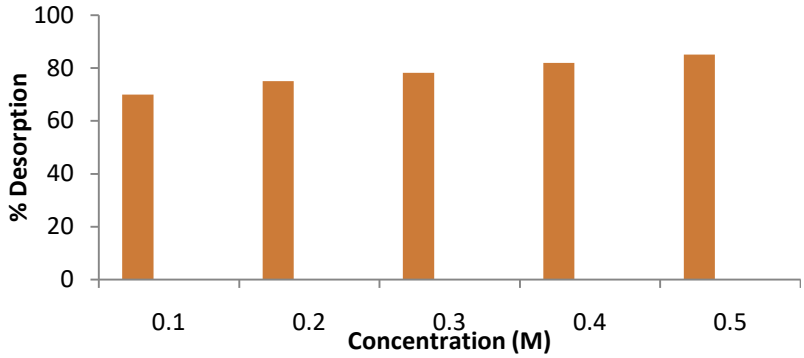


Fig. 12: Effect of HCl Concentration on Desorption Efficiency

Fig. 13 presents the efficiency of the reused adsorbent after five different adsorption cycles. It can be seen that there is decrease in adsorption efficiency in the first cycle from 97.01 % to 71.34 % in the fifth cycle. This confirmed that SDAC can be successively used for the removal of MB from wastewater. The reason for the decrease in efficiency of adsorption is because the active sites become fewer after every cycle of adsorption.

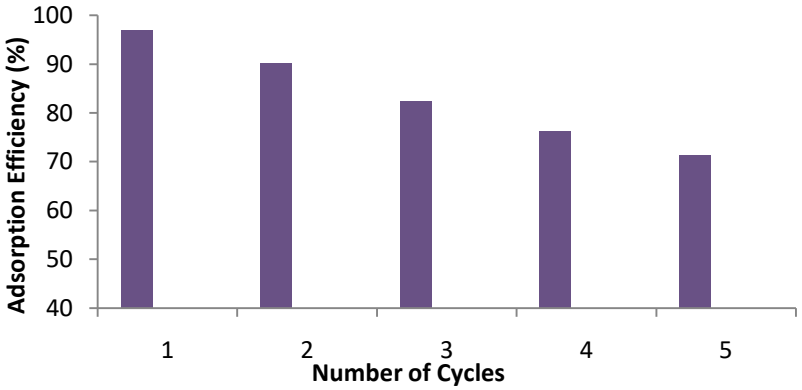


Fig. 13: Efficiency of regenerated adsorbent after five cycles

CONCLUSION

The present research shows that activated carbon of sweet detar seed shell derived adsorbent served as an effective adsorbent for the removal of methylene blue from aqueous solution. Surface adsorbent characterization before and after adsorption using scanning electron microscopy and Fourier transform infrared spectroscopy, as well as determination of pH at point of zero charge confirmed the success of adsorption process. Basic experimental parameters such as agitation time, adsorbent dosage, particle size, initial dye concentration, pH and temperature were found to affect the entire adsorption process. Methylene blue adsorption onto SDAC was kinetically followed pseudo-second order kinetic model and obeyed Freundlich adsorption isotherm. However, the thermodynamic investigation confirmed the process to be spontaneous, exothermic, and decreased in randomness of the system on the adsorbent-adsorbate surface. SDAC could finally be recovered by hydrochloric acid and reused after five successive adsorption cycles.

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