Kinetic, Equilibrium and Application Studies for Removal of Methylene Blue from Aqueous Solution Using Sesbenia Dates Activated Carbon

Mohammed Saleh Bashanaini
College of Science, Hadhramout University

Gameel Ahmed Baghaffar
College of Science, Hadhramout University

Waheeb Abdellah Bin Frejan
College of Science, Hadhramout University

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Mohammed Saleh Bashanaini* **Gameel Ahmed Baghaffar***

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Abstract

In the present work, sesbenia dates as local agriculture waste, has been successfully used for the preparation activated carbon (AC) by sulphuric acid. This sulphuric acid based activated carbon (SD) and (MSACS) were used for the removal of one cationic dye viz., methylene blue (MB) from aqueous solutions. The structure and physical and chemical properties of (SD) and (MSACS) are investigated using (FTIR) and (SEM) analysis and pH surface and Boehm titration. The effect of the differential experimental parameters controlling the adsorption of dye onto (SD) and (MSACS), were thoroughly investigated, such as the effect of pH, initial dye concentration, contact time and adsorbent dosage in batch mode .Employment of equilibrium isotherm models for the description of adsorption capacities of (SD) and (MSACS) explores the good efficiency of Langmuir model for the best presentation of experimental data with maximum adsorption capacity of 38.02 mg/g (SD) and 277.77 mg/g (MSACS) for (MB) dye. The kinetic data were fitted to the pseudo-second-order kinetic model. Thermodynamic parameters were evaluated to predict the nature of adsorption. These results point out the exothermic and spontaneous nature of the sorption process. The results demonstrate that (SD) and (MSACS) are effective in the removal of MB dye from aqueous solutions and can be used as an alternative to the high-cost commercial adsorbents.

Keywords: sesbenia dates; Activated carbon; Methylene Blue; Adsorption.

Introduction:

As a result of rapid development of chemical and petrochemical industries, the surface and ground waters are polluted by various organic and inorganic chemicals such as phenolic compounds, dyes and heavy metals [41]. Dyes are colored organic compounds which can colorize other substances. These substances are usually present in the effluent water of many industries, such as textiles, leather, paper, printing, and cosmetics. The complex aromatic structures of dyes make them more stable and more difficult to be removed from the effluents discharged into water bodies. There are several methods to remove dyes such as physical and chemical processes to treat wastewaters including organic pollutant and dyes [48]. Dyes can be classified as cationic (basic dyes), anionic (direct, acid, and reactive dyes) or non-ionic (disperse dyes)] [2]. Due to Methylene blue (MB) as cationic dye and its known strong adsorption onto solids, MB often serves as a model compound for removing dyes and organic contaminants from aqueous solutions . Although not strongly poisonous, MB can have some harmful effects on human beings [39]. The dye can cause eye burns in humans and animals. It may stimulate the gastrointestinal tract and cause nausea, vomiting, and diarrhea if ingested. It may also cause dyspnea, tachycardia, cyanosis, methemoglobinemia and convulsions if inhaled [28]. Owing to these harmful effects on humans, it is necessary to remove MB from aqueous solution. The methods used to remove Methylene blue are adsorption, chemical precipitation, ionexchange, reverse osmosis, electrochemical reduction, electrodialysis, etc. Adsorption process is the most frequently applied method in industries. A lot of studies on this process have been carried out [35]. Adsorption process is strongly affected by the chemistry and surface morphology of the adsorbent. Therefore, new adsorbents, which are economical, easily available, having strong affinity and high loading capacity, have been required [41]. A number of adsorbents such as activated carbon [32], red mud [43], and rubber seed coat , etc. have been used for Methylene blue removal. Activated carbon is known to be a very efficient adsorbent because of its large surface area, highly developed porosity, changeable characteristics of surface chemistry, and the high degree of surface reactivity [36]. Activated carbon, as an adsorbent has been widely investigated for the adsorption of dyes, but its high cost limits its commercial application. In the last two decades, there has been growing interest in finding inexpensive and effective alternatives to carbon, such as jute sticks [4], A corn [14], Lantana camara [32], Cocoa shell [33], Aegle marmelos [47], Pea shells [12], sugarcane bagasse [45], Rice Husk [34], Waste Weed [37], Pistachio shell [2].

The objective of the present study is the preparation of Modified sesbenia dates activated carbon based sulphuric acid (MSACS). Sesbenia

dates are considered as waste matter in the environment and have low cost. Similar to other agro-residues, sesbenia dates chiefly consist of lignin, hemicellulose, and cellulose, such composition which makes sesbenia dates a good raw material for the output of new adsorbents for the processes of water treatment.

Experimental:
Chemicals and Materials:
Methylene Blue (MB), basic blue 9, C.I. 52015; chemical formula, $C_{16}H_{18}N_3ClS$, and molecular weight 319.85 g/mol, λ_{max}: 661 nm, (Figure(1)), were supplied by Merck. A 2000 mg/L stock solution of MB dye was prepared by dissolving the required amount of dye powder in distilled water. Calibration curves were constructed in the concentration ranges 1.0-10.0 mg/L and the concentrations of the investigated dyes were determined spectrophotomterically at $\lambda_{max}=661$ MB, respectively. The chemicals used in this research were $NaHCO_3$, $NaOH$, Na_2CO_3, HCl, H_2SO_4,
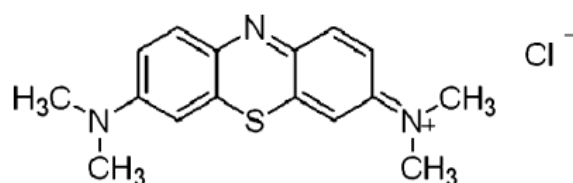
Figure 1: Molecular structure of Methylene Blue (MB)

Apparatus:
The laboratory measurements of pH were performed using OAKTON pH-meter 10N 700 (Singapore). The concentrations of MB dye was determined using UV-Vis spectrophotometer (Japan), Fourier Transform Infrared (FT-IR) spectra were characterized by JASCO 4600 FT/IR spectrometer (Japan),

Preparations of Adsorbents:
Sesbenia dates were collected from local markets, cleaned with tap water hardly and rinsed with distilled water for several times, then dried in at 373 K for 12 h. The modified sesbenia dates activated carbon based sulphuric acid (MSACS) was prepared by mixing 150 mL of 15 mol/L sulphuric acid with 30 g of sesbenia dates. The mixture was put in furnace whose temperature was kept about 423-430 K for 90 min with occasional stirring. After cooling, the resulting black residue was filtered using a Buchner funnel under vacuum. Activated carbon was washed for some time with distilled water until pH value became 5-6 and dried at 373 K.

Adsorption Studies of Dye:
To perform batch adsorption experiments, 0.05 grams of (SD) or (MSACS) with 50 mL aqueous solution of dye, shak well in a temperature controlled water bath shaker using variable concentrations of dye between 4 and 70 mg/L of MB (SD) and between 50 and 500 mg/L of MB (MSACS), pHs (between 2-11 for MB), temperatures (between 25°C and 40 °C and 50 °C), doses of adsorbent (between 0.015 and 0.1 g) and ionic strength (between 0.005 and 0.2 mole/L) and shaking at a constant rate of 200 rpm. The concentrations of the non-adsorbed in the solution, was determined spectrophotometrically at 661 nm for MB, respectively. The capacity of adsorption of dye was removed by adsorbent (q), and the removal percentage (R %) of cationic dyes are determined by the following equations. (1) and (2):

$$q = \frac{V(C_o - C_e)}{m} \qquad (1)$$

$$R\% = \frac{C_i - C_e}{C_i} 100 \qquad (2)$$

Where q is the adsorption capacity of dye (mg/g), C_i and C_e are the initial and equilibrium state concentrations of dye (mg/L), respectively. The term m is the mass of the adsorbent used (g), and V is the solution volume of the dye (mL).

Results and Discussion:
Characterization of Adsorbents:
Scanning Electron Microscopy Analysis:
The surface morphology of sesbenia dates (SD) and the preparation of Modified sesbenia dates activated carbon based sulphuric acid (MSACS) were examined using scanning electron microscopy, the corresponding SEM micrographs being obtained using an accelerating voltage of 20 kv at (x2500,and x2500) magnification (Fig. 2,a&b). At such magnification, SEM micrographs clearly revealed that wide variety of pores are present in activated carbon along with fibrous structure. It is also found that there are holes and caves type openings on the surface of the adsorbent, which would have more surface area available for adsorption [42].
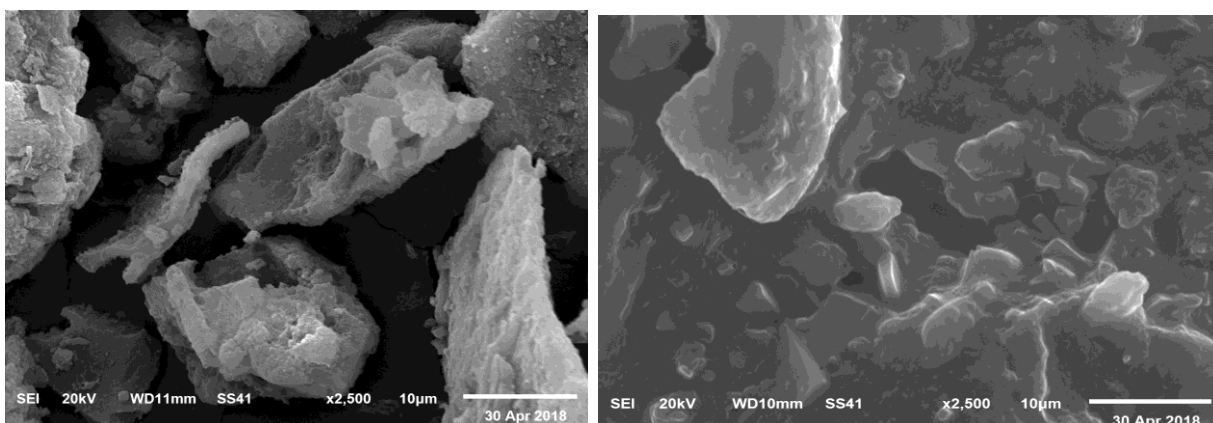
(a)   (b)

Figure2: SEM micrograph of onto (a) SD and onto (b) MSACS.

FTIR Analysis:
The FTIR spectra (Fig. 1) showing the OH groups were observed in the range of 2500–3700 cm^{-1} strong and broad band show the appearance of carboxylic group. The bands observed at about 2900 cm^{-1} could be assigned to the aliphatic C-H groups. The shoulder at the wave number of 1700 cm^{-1} could be due to the carbonyl stretch of carboxyl for SD and SD -MB. The band at1625 cm^{-1} represented the C=O stretching for MSACS before and after adsorption of MB. From the IR spectra, it was clear that AC possessed several surface functional groups.
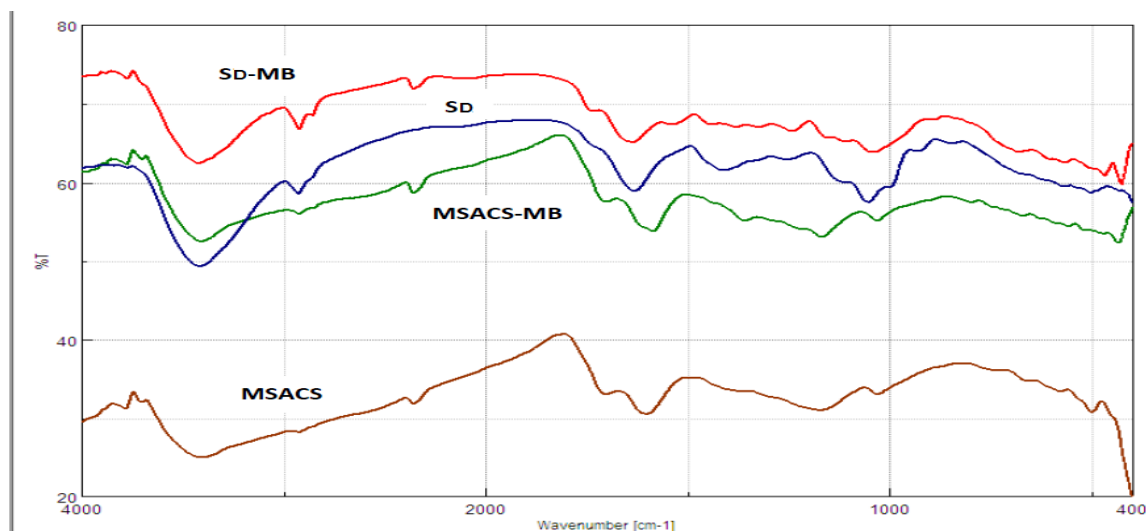

Figure 3: FTIR spectra SD, SD-MB, MSACS and MSACS-MB

Characterization of Adsorbent:
Some chemical and physical characteristics of sesbenia dates are presented in Table 1 [9]. The study of the presence of acidic or basic functional groups on the adsorbents is very important, this groups effect to the surface charge of the adsorbate and adsorption solution. According to Boehm's method [3], a 0.075 gm of dried adsorbent was placed in four Erlenmeyer flasks added to each 25 mL of following 0.05 N aqueous solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid. The samples were shaking for 72 h at 25 ^{0}C. The equilibrated solutions were filtered to remove adsorbent particles; 5 ml were taken off and then titrated with 0.05 HCl or NaOH. The pH of the point of zero charge (pH$_{PZC}$) and pH Surface were calculated for each adsorbents,

The results of Behom titration and pH determination presents in table(1), the amounts of acidic and basic total surface groups, expressed in meq/g, MSACS prepared with H_2SO_4 present a higher number of acidic functions than SD adsorbent. The Ash content, crucibles were heated in 0.30 g of samples in crucibles at 600^oC using electrical furnace for 6

h, then cooled in a desiccator and weighed. The oven dried samples from the previous section were placed in the crucible content and were allowed to cool in a desiccator and then weighed to obtain the weight of the ash. The ash content was expressed as a percentage of the oven dry weight. [38].

Table 1: Chemical and physical Parameter of SD and MSACS adsorbent

parameter Adsorbent	Acidic groups(meq)				Basic Group (eq/g)	Surfaces PH	Point of zero charge	Moisture%	Ash Content%
	carboxylic	Laconic	Phenolic	Total					
SD	1.9	6.9	8.78	17.58	5.68	7.38	6.84	57.233	2.767
MSACS	3.3	24.6	15.21	43.11	4.98	4.23	3.79	46.967	5.267

The Effect of pH on the Dye Adsorption:
The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity [5]. The effect of solution pH (2 - 9) on the equilibrium uptake capacity of MB dye was studied at room temperature and initial dye concentration of 20 mg/L and 150 mg/L onto SD and MSACS, respectively. The dye uptake was found to

increase with an increase in pH (**Figure 4**). At lower pH, the surface charge may be positive, thus making (H^+) ions compete effectively with cationic dyes causing a decrease in the amount of dye adsorbed [19]. And at higher pH, the surface of SALC may be negatively charged which enhances the positively charged on MB dye through electrostatic force attraction [9].
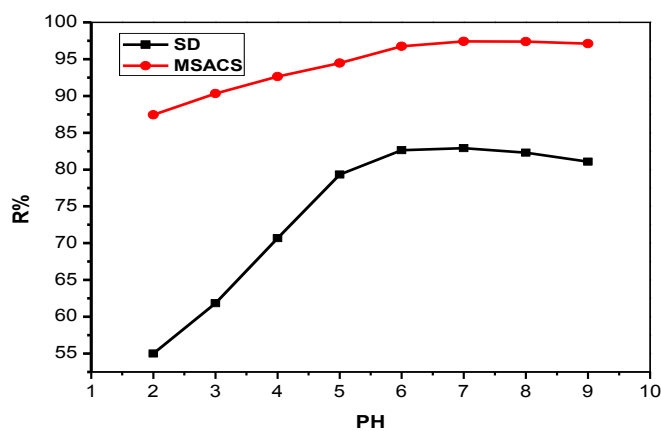

Figure 4: Effect of pH on removal% MB by
(Conditions: Ci (SD) = 20 mg/L; Ci (MSACS) = 150 mg/L

The Effect the Initial Concentration of Dyes:
Generally, the removal of dye was dependent on the initial concentration of the MB dye [9 , 8]. The initial concentration effect was studied by varying the initial concentrations of the MB dye solution for adsorption by SD and MSACS to a range of 2 - 70 mg/L and 5 – 450 mg/L [40]. The sharp increase in the adsorption capacity in the early phase can be attributed to the great driving force of the concentration gradient at the solid-

liquid interface causing an increase of the amount of MB dye adsorbed on the adsorbent [23]. When the initial concentration of MB dye increases from 2 - 70 mg/L into SD and 5 – 450 mg/L into MSACS at 25°C, the amount of dye adsorbed at equilibrium (q_e), increases from 1.79 to 38.79 mg/g into SD and from 4.80 to 272.80 mg/g into MSACS, for MB, respectively (Figs. (5- a; b)) [1].
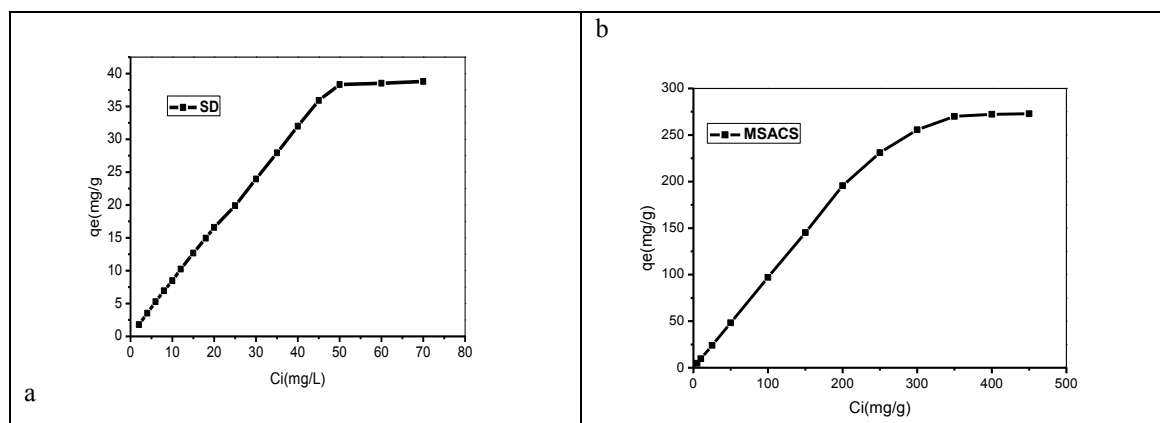
Figure 5: Effect of initial concentration of MB on the adsorption capacity
of (a) SD, and (b) MSACS adsorbent.

The Effect of Adsorbent Dose:
Figure 6 presents the equilibrium adsorption of MB against SD and MSACS by agitating in the range of (0.015 - 0.1g), The adsorption of dye varied with varying adsorbent mass and it increased with the increase in adsorbent dose [27]. Increasing the dose of adsorbent would provide more functional sites on the adsorbent capable of binding more dye molecules and thus increasing the removal %. The removal % of MB dye adsorbed increased from 82.88% to 90.50% into SD and 59.85% to 99.42% into MSACS as the adsorbent dose increased from 0.015 to 0.1 g, respectively [2].
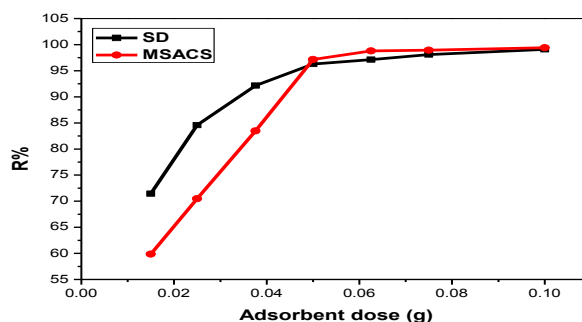
Figure 6: Effect of adsorbent dosage of SD and MSACS on MB removal%

The Effect of Interferents:
The interference of some foreign cations such as Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{3+}, and $Ba^+(I)$ as well as anions (Cl^-, acetate and oxalate) on the process of MB dye adsorption from aqueous solutions was studied and estimated by SD and MSACS. The estimation of the possible interference of foreign ions was performed on the basis of 10 mg/L of dye versus other interfering species. The results presented in Table 2, show that the presence of anions and cations do not affect the adsorption percentage of MB dye on the SD and MSACS adsorbent, especially Ca^{2+}, Mg^{2+}, Na^+, K^+, Ba^{2+}, Fe^{3+}, at the concentration of 200 mg/L.

Table 2: Effect of interferents on the removal % of MB (10ppm) on SD and MSACS.

Foreign Ion	MB removal%	
	SD	MSACS
Acetate	99.99%	99.9%
Oxalate	99.77%	99.8%
NO_3^-	99.98%	99.9%
Cl^-	99.46%	99.6%
Na^+	99.81%	99.7%
K^+	98.97%	99.2%
Ca^{2+}	97.42%	99.3%
Ba^{2+}	96.56%	99.5%
Fe^{3+}	94.45%	97.6%
Mg^{2+}	95.31%	98.9%

The Effect of Contact Time:
The effect of contact time is studied by batch adsorption processes. Figure 7, shows that the adsorption capacity of MB dye increased with time and reached equilibrium at 240 minutes and 300 minutes on SD and MSACS for MB dye, respectively. It is obviously that the adsorption of MB depends on the concentration of the dye. Similar results in MB removal have been reported in Refs [2].
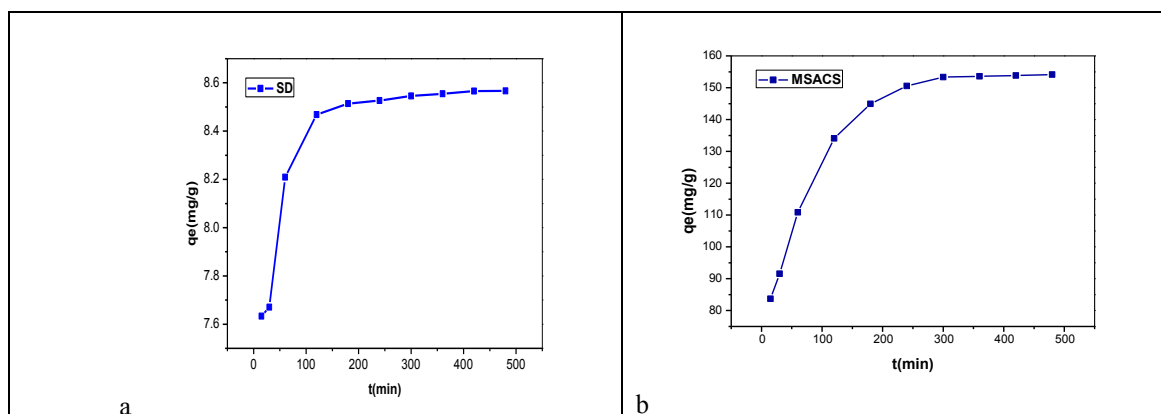

Figure 7: effect of contact time for adsorption of MB onto (a) SD and (b) MSACS

Adsorption kinetics:
The aim of this part is to investigate the mechanism of adsorption of MB by the pseudo-first-order, pseudo-second-order and the intraparticle and Boyd diffusion models [44].
Pseudo-first-order kinetics model
The pseudo-first-order or Lagergren equation represents by equation [16]. is shown in Eq. (3):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (3)$$

Where q_t (mg/g) is the amount of adsorbed dye at time t, q_e (mg/g) is the amount of MB adsorbed at equilibrium, and k_1 (1/min) is the rate constants of the pseudo-first-order equations of the adsorption. The constants of pseudo-first-order kinetic can be defined by plotting $\log(q_e-q_t)$ versus t. (Figure 8a).
Pseudo-second-order kinetic model
The pseudo-second-order or Ho and Mckay equation [17]. is shown in Eq. (4):

$$\frac{t}{q_t} = \frac{1}{k_2 q_2} + \frac{1}{q_e} t \qquad (4)$$

Where, q_t and q_e (mg/g) are the amounts of adsorbed dye at time t, and at equilibrium, respectively, k_2 (g/mg·min) is the rate constant of pseudo-second-order equation. The constants of pseudo-second-order kinetic can be defined by plotting t/q_t versus t. (Figure 8b)
Intra-particle diffusion model
The rate of the adsorption process is believed to be controlled by four steps. These steps include: (a) molecular diffusion from the bulk solution to

a film layer surrounding the adsorbent particle; (b) diffusion from the film to particle surface or "film diffusion"; (c) migration inside the adsorbent particle by "surface diffusion" or diffusion within liquid filled pores, "pore diffusion"; (d) and adsorption uptake, which includes several ways of interaction such as chemisorption, physisorption, ion exchange or complexation. The slowest step affects the rate of the adsorption process and hence it is essential to predict the rate-limiting step [18].

Intra-particle diffusion shown below in Eq. (5):

$$q_t = K_{int} t^{0.5} + C \qquad (5)$$

Where qt (mg/g) is the amount of MB adsorbed at time t, ki (mg/g min$^{0.5}$) is the initial rate of intra-particular diffusion, and y is the intercept. The values of ki and y were obtained from the slopes (k_i) and intercepts (y) of the plots of q_t versus $t_{1/2}$, (Figure 8c) respectively. The constants obtained from the model kinetic equations (the pseudo-first-order, pseudo-second-order and the Intra-particle diffusion) are shown in Table 4.

The kinetic data were further investigated using the Boyd [2].Equation kinetic expressed by equation (6)

$$F(t) = 1 - \frac{6}{\pi^2} \sum_{1-n}^{\infty} \frac{1}{n^2} \exp^{-n^2 Bt} \qquad (6)$$

Where F(t) is the equilibrium fractional at different times t, and B(t) is mathematical function of F, n is an integer that defines the infinite series solution and F(t) is the fractional achievement of equilibrium at time (t) which is determined by the following equation:

$$F = \frac{q(t)}{q(e)} \qquad (7)$$

Where q(e) and q(t) are the adsorbent capacity of dye adsorbed at equilibrium and the time t, respectively. Reichenberg [7]. succeeded to obtain the following approximations:

For F values>0.85;

B (t)=-0.4977-ln (1-F) $\qquad (8)$

And for F values<0.85

$$B(t) = \{\sqrt{\pi} - \sqrt{\pi - (\frac{n^2 F(t)}{3})}\}^2 \qquad (9)$$

The plots of Boyd's equation (Figure 8d) did not go through the origin denoting that film diffusion is the rate-limiting process of sorption for the sorption of dyes into SD and MSACS.

Table 3: Kinetic parameters for the adsorption of MB onto SD and MSACS

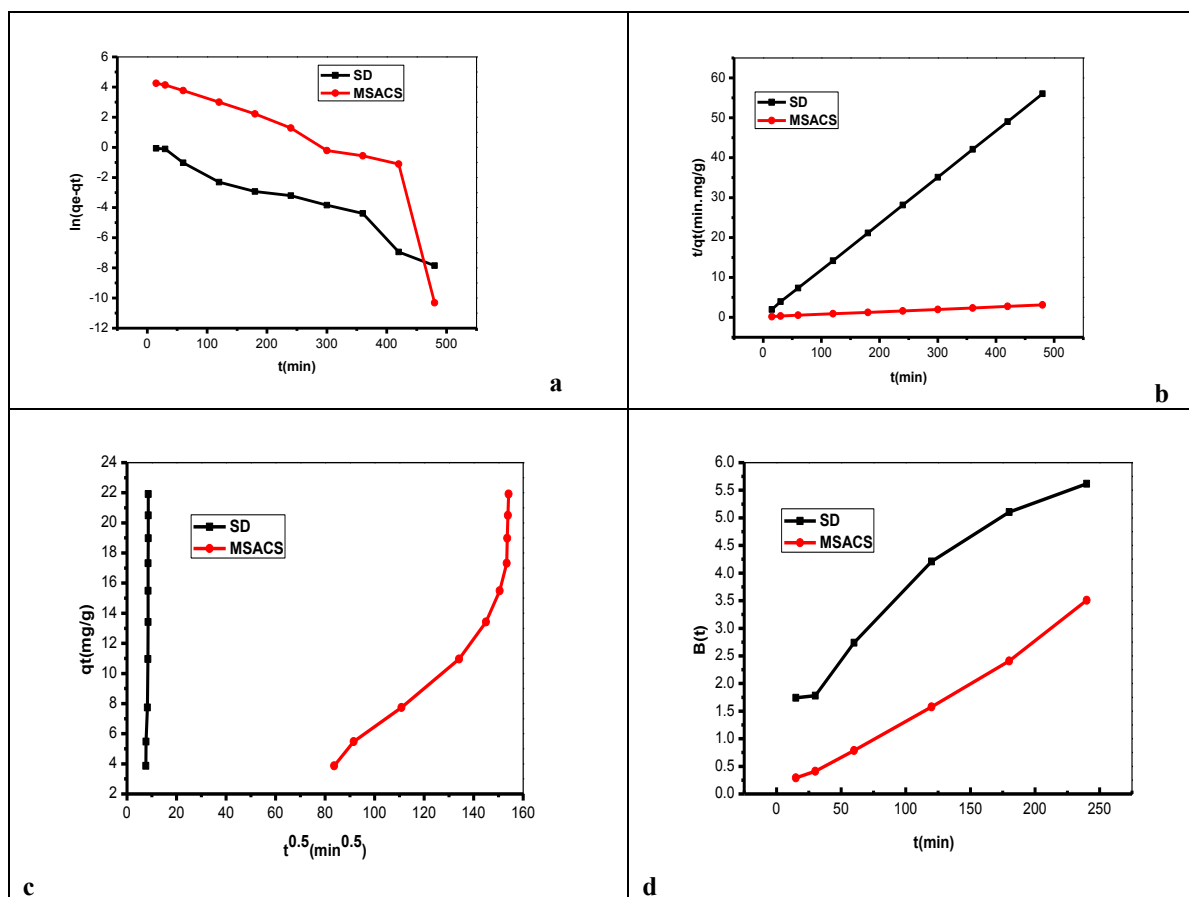| Kinetic studies doodles	parameter	MB	
		SD	MSACS
Pseudo- first order	qe_1	0.1382	5.6221
	K_1	0.0155	0.0226
	R^2_1	0.9539	0.7523
Pseudo- second order	(at C_0) qe_2	8.662(10)	188.4(200)
	qe_2	8.62	188.7
	K_2	0.044	2.73×10^5
	R^2_2	1	0.999
Intrapartical	K_{int}	-110.6	-15.347
	C	14.914	0.2173
	R^2	0.7528	0.8813
Boyd	intercept	3.584	1.2983
	R^2	0.2495	0.0612

Figure 8: Kinetic models for adsorption of MB (a) Pseudo-first order (b) Pseudo-second order, (c) Intraparticle diffusion and (d) Boyd model.

Effect of Solution Thermodynamic Studies:
The thermodynamic parameters such as free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) give a description of adsorption behavior related to temperature. Parameters can be calculated from [10].

$$\Delta G^0 = -R\,T\,Ln\,K_d \qquad (10)$$

$$LnK_d = \frac{\Delta S^O}{R} - \frac{\Delta H^O}{RT} \qquad (11)$$

Where K_L (L/mol) is from Langmuir equation, R is the gas constant (8.314 J/(mol.K)), and T (K) is the temperature in Kelvin, $Lnk_d\{\,Ln(q_e/C_e)\}$ at different temperatures were treated according to Van't Hoff equation. Plotting $Ln(q_e/C_e)$ against 1/T gives a straight line with slope and intercept equal to ($-H/R$) and S/R, respectively (Figure 9). The negative value of ΔH (Table 4) shows exothermic nature of adsorption process. Gibbs free energy of adsorption ΔG is calculated from the following relation

$$\Delta G = \Delta H - T\,\Delta S \qquad (12)$$

The negative value of ΔG (Table 4) indicated that the adsorption reaction was spontaneous. The observed decrease in negative values of ΔG with increasing temperature implied that the adsorption became less favorable at higher temperatures [11].

Table 4: Parameters of thermodynamics for the adsorption of MB on SD and MSACS

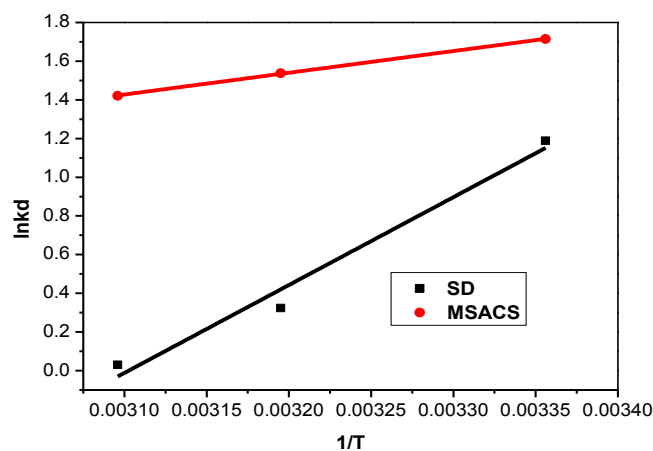| Dye	Adsorbent	ΔH Kj/mol)(	ΔS (Kj/mol)	ΔG (Kj/mol)		
				298 K	313 K	323 K
MB	SD	-37.9	-0.11	-2.953	-0.845	-0.080
	MSACS	-9.37	-0.0172	-1.339	-1.407	-1.449

Figure 9: Van't Hoff isotherm for adsorption of MB onto SD and MSACS

Effect of Solution Temperature Studies:
The temperature is one of the most important factors to determine the process of adsorption. The effect of temperature on adsorption of MB onto sesbenia dates was investigated at (298, 313 and 323 K), and the results were presented in Table (5) and Figure (10a), (10b) show that the capacity of adsorption of SD and MSACS

decrease from 38.02 mg/g to 30.58 mg/g and 277.78 mg/g to 222.22 mg/g as the temperature increases from 25 to 50 °C, it can be seen that the increasing temperature of the adsorption process translated to a decrease in adsorption capacity. The experimental results demonstrate that the process of adsorption of MB into sesbenia dates is exothermic.

Table 5: Effect of temperature on maximum adsorption capacities of MB into SD and MSACS

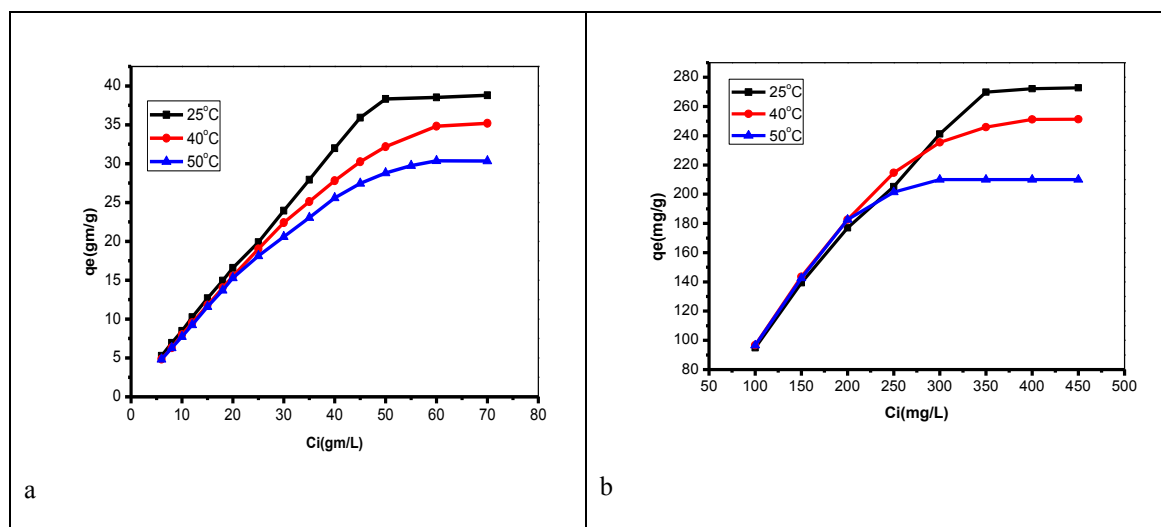| Adsorbent	MB		
	q_{max}(mg/g)		
	$25C^0$	$40C^0$	$50C^0$
SD	38.02	35.34	30.58
MSACS	277.78	250	222.22

Figure 10: Effect of temperature on maximum capacities of MB into (a) SD and (b) MSACS

Adsorption Isotherms:

The adsorption isotherm indicates how the adsorption molecules are distributed between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [6]. An adsorption isotherm study was carried out on two well-known isotherms (Langmuir and Freundlich) at different temperatures. The Langmuir model assumes that the adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes [13].

The Freundlich model endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energy levels of adsorption [26]. The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2.

The linear form of Langmuir isotherm equation is given as

$$\frac{1}{q_e} = \frac{1}{K_L q_m} \cdot \frac{1}{C_e} + \frac{1}{q_m} \qquad (13)$$

Where, q_e the amount was adsorbed at equilibrium (mg/g), q_m is the theoretical maximum adsorption capacity (mg/g), C_e is the equilibrium concentration of dye (mg/L) and k_L is Langmuir adsorption constant (L/mg) related to the energy of adsorption. A plot of $1/q_e$ against $1/C_e$ (Figure 11a) gave a straight line graph with a slope $1/k_L.q_m$ and intercept of $1/q_m$. Values of q_m and k_L are calculated from the graph and

reported in Table 6. The fundamental characteristics of the Langmuir isotherm can be expressed by a dimensionless separation factor, R_L, defined by:

$$R_L = \frac{1}{1 + K_L C_O} \qquad (14)$$

Where K_L is Langmuir constant and C_0 is the highest initial dye concentration (mg/L). The R_L parameter indicates the type of the isotherm as follows: $(R_L > 1)$, unfavourable; $(R_L = 1)$, linear; $(0 < R_L < 1)$, favourable; $(R_L = 0)$, irreversible. The R_L value was found to be $(0 < R_L < 1)$ in the present study which indicated that SD and MSACS adsorbent exhibit favourable adsorption for both MB dye (Table 6).

Isotherm model of Freundlich is expressed as equation [10].

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (15)$$

Where k_F and n are Freundlich constants, the characteristic of the system, k_F and n are the indicators of adsorption capacity and adsorption intensity, respectively (Figure 11b).

The parameters of Langmuir and of Freundlich isotherm models are given in Table 6. The examination of Table 4 reveals that the values of R^2 acquired from Langmuir model are closer to the unit than that of the model of Freundlich. This finding denotes that the isotherm of Langmuir fits better with the adsorption of both MB dye into SD and MSACS.

Table 6: Langmuir and Freundlich isotherm Parameter removal of Methylene blue.

Adsorbent	Langmuir				Freundlich		
	qmax	Kl	Rl	R^2	n	Kf	R^2
SD	38.022	0.232	0.079	0.996	1.509	6.593	0.957
MSACS	277.78	0.089	0.032	0.999	1.730	25.57	0.884
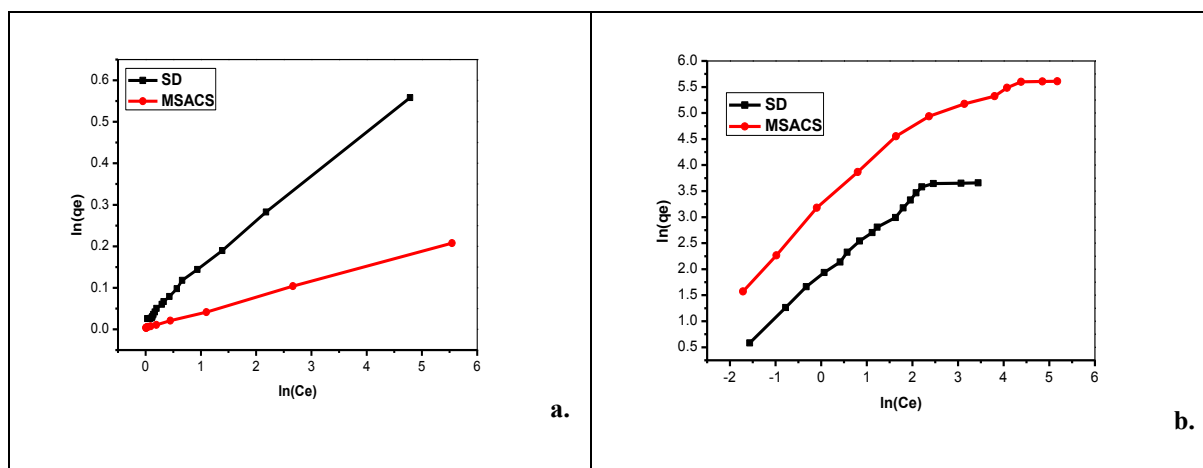
**Figure 11: Adsorption isotherm model for MB dye into SD and
MSACS (a) Langmuir and (b) Freundlich Isotherms**

Analytical Applications:

By spiking known concentrations of MB dye, the ability of application of the SD and MSACS for uptake of the MB dye from different samples of water was investigated. Table 7 shows that the recovery percentage (R %) is more than 99.18% with less than 1% of relative standard deviation (RSD%).

Table 7: Recovery (R %) of Methylene Blue from different samples of water

Sample Location	Adsorbate	MB added(C_i) (mg/L)	MB Concentration(C_e) equanimity (mg/L)	R%	RSD%
drinking water (Naga'a)	SD	2	0.082	95.91	0.639
		4	0.208	94.80	0.453
		8	0.431	94.61	0.726
	MSACS	5	0.052	98.97	0.388
		10	0.125	98.75	0.585
		15	0.222	98.52	0.806
See water (Sheher area)	SD	2	0.078	96.10	0.565
		4	0.176	95.60	0.579
		8	0.416	94.80	1.273
	MSACS	5	0.012	99.77	0.137
		10	0.075	99.25	0.423
		15	0.122	99.19	0.416

Khoor Almukla water)(	SD	2	0.064	96.80	0.421
		4	0.148	96.30	0.412
		8	0.360	95.50	0.323
	MSACS	5	0.019	99.62	0.246
		10	0.060	99.40	0.316
		15	0.242	98.39	3.135

R, %=Removal % of methylene blue;
RSD, %=Relative standard deviation

The removal of MB dye by the proposed MSACS activated carbons is in a good comparison with the results of the previous reported studies (Table 8). The prepared low cost material such as sesbenia dates activated carbon MSACS is beneficial to the one high-cost commercial activated carbon [2].

Table 8: Adsorption capacities of different adsorbents previously reported for the removal of MB compared with SD and MSACS

Adsorbent	Adsorption capacity (mg/g)	Reference
Modified Sesbenia dates Activated carbon (H_2SO_4) (MSACS)	277.78	Present study
Sesbenia dates (SD)	38.022	Present study
Pistachio shell Activated carbon (H2SO4) (ACS	205.42	)Akl et al. ,2016(
Wood waste activated carbon	4.937	(Ghaedi and Kokhdan. 2015)
Activated carbon prepared from coconut coirpith	93.40	(Kadirvelu et al. ,2003)
Activated carbon prepared from apricot Stone	33.57	(Kobya et al. ,2005)
Carbon aerogel	400.80	(Meena et al. ,2005)
Activated carbon prepared from olive stone by $ZnCl_2$ activation	1.56–1.85	(Kula et al. ,2005)
Activated carbon derived from bagasse	49.07	(Mohan et al. ,2002)
Activated carbon (Filtrasorb 400)	307.50	(Kapoor et al. ,1999)
Lime-preconditioned phosphogypsum	131.58	(Dermibas et al. ,2008)
Jute fiber-based activated carbon	225.64	(Joseph et al. ,2012)

Conclusions:

Sesbenia dates (SD) like other agricultural waste can be used in the treatment process of dyes in water samples. The adsorption capacity is dependent on pH solution, adsorbate concentration, adsorbent dosage, contact time and ionic strength. The kinetic studies indicated that follows pseudo-second-order and equilibrium in the adsorption of MB onto SD and MSACS were attained within 240 and 300 min, respectively. The equilibrium data were studied by Langmuir and Freundlich models, the adsorption equilibrium can be best represented by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 38.022 and 277.78 mg/g for MB onto the SD and MSACS, respectively. The results of thermodynamic indicated that the (AG°) as expected for a process is spontaneously under the optimum conditions. The prepared MSACS was successfully applied for the removal of the MB dye from samples of natural water.

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دراسة حركية ، اتزان و التطبيق على إزالة صبغة المثيلين الازرق من المحلول المائي باستخدام الكربون المنشط لثمار السيسبان

محمد صالح باشنيني   جميل أحمد باغفار

وهيب عبدالله بن فرجان

الملخص

في هذا العمل تمور السيسبان نفاية زراعية محلية استخدمت بنجاح لتحضير الكربون المنشط باستخدام حمض الكبريتيك المركز، المادة الطبيعية (SD) والكربون المنشط المحور (MSACS) لتمور السيسبان المعالجة بحمض الكبريتيك استخدمت لإزالة الصبغات الكاتيونية مثل أزرق الميثيلين (MB) من المحاليل المائية. خضعت إلى الخواص الفيزيائية والكيميائية والتركيب ل (SD) و(MSACS) للتحليل باستخدام MES ,FTIR والرقم الهيدروجيني pH بالنسبة للسطح ومعايره بوهم . وأيضا تأثير البارامترات التجريبية المختلفة لامتزاز الصبغات في (SD) و(MSACS) وخضعت للتجريب مثل تأثير PH والتركيز الابتدائي للصبغة ، زمن التلامس ، جرعة المادة المازة للنموذج المعد للعمل وفقا لنماذج أيسوثرمات الاتزان لوصف سعات الامتزاز (SD) و(MSACS) وأظهر كفاية جيدة حسب نموذج لانجمير حيث تم الحصول على نتائج تجريبية أفضل بسعة امتزاز عظمى (SD) أعطى قيمة mg/g 38.02 و (MSACS) أعطى قيمة mg/g277.77 أما البيانات الحركية فأظهرت التفاعل من الرتبة الثانية الكاذبة كما تم تقدير البيانات الثرموديناميكية للتنبؤ بطبيعة الامتزاز وأظهرت النتائج الطبيعية التلقائية الطاردة لعمليات الامتزاز بسبب أن ΔH قيمة سالبة ، كما أظهرت النتائج بأن (SD) و(MSACS) فعالة لإزالة (MB) من المحاليل المائية. وكذا يمكن أن تستخدم عوضا عن المواد المازة غالية الثمن.

كلمات مفتاحية : تمور السيسبان ، كربون منشط ، أزرق الميثيلين ، امتزاز .