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Chemisorptive removal of a synthetic dye from single and binary basic dye systems using sawdust of locust bean tree: Isotherm, kinetics, error function and thermodynamics

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Abstract
Adsorptive properties of sawdust of locust bean tree, an agrowaste toward the removal of methylene blue from single and binary dye systems in aqueous solution is investigated so as to determine the effects of the composition of the solution on adsorption process. The sawdust was characterized using Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) spectrophotometry, X-Ray diffraction and pH point of zero charge. Batch adsorption experiments were carried out to investigate the effects of adsorbent dose, solution pH, contact time, initial dye concentration and temperature on the dye adsorption. The equilibrium data obtained were subjected to Langmuir, Freudlich, Temkin and Harkin- Jura isotherm equations. The data on kinetics were tested with pseudo-first order, pseudo-second order and Weber-Morris equations, while the thermodynamics of the sorption processes were also studied. The adsorption isotherm in all the dye systems follow Freundlich model. The adsorption process in single and binary dye systems is well described by both pseudo first order and pseudo second order kinetics. All the adsorption processes were spontaneous, endothermic and with increased randomness (+ve ΔS).

Keywords: adsorption, methylene blue, binary dye system, error functions

Introduction
Most water pollutants contain dyes and other organic compounds and are from textile and other chemical industries **(**Saeedeh and Mohammad, 2013) [18]. The carcinogenic and mutagenic nature of dyes makes it of utmost importance that wastewater containing dyes be treated (Banat *et al*., 1996) [2]. Though, many physical and chemical treatments methods are available for dye removal from wastewater, the efficiency and simplicity of adsorption made it the most favoured (Batzias and Sidiras, 2007) [3].

Methodology
Preparation and Characterization of Adsorbent
The method of Giwa *et al*., 2016 was used to prepare and characterize the adsorbent used in this research. The sawdust was washed several times with distilled water, dried at 105 ^{o}C, sieved with 60-80 µm mesh and stored as the adsorbent, RSD. The adsorbent was characterized using the Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and pH point of zero charge (pH_{zpc}).

Preparation of adsorbate
The adsorbate consist of Methylene blue in a single dye system and as a component of binary mixtures with Malachite green, Crystal violet and Rhodamine B respectively. Analytical grade of the dyes were obtained and used without any further purification. A 500 mg/L stock solution of each of the dyes was prepared Experimental solutions of binary dye mixture of desired concentrations were prepared by mixing appropriate volumes of the stock solutions and accurately diluting it with distilled water.

Mixed Dye Batch Adsorption
Experiments to determine the adsorption capacities of RSD were all carried out in batch mode at different experimental conditions. The effect of pH on the adsorption was defined by manipulating the initial pH in the range 2-10. The pH was adjusted using a 0.1M HCl solution and NaOH (0.1M) solution. Effects of other parameters such as RSD dose (0.1 g -1g), temperature (30-60 ^{o}C), contact time (5-180 min), and initial dye concentration (10 mg/L-100 mg/L) were also investigated. The batch solutions were placed in a mechanical shaker at 150 rpm, where it was constantly being agitated for approximately 3 hours. The solution was then filtered and the absorbance of the filtrate taken. The amount of dye adsorbed was calculated using the following equations:

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

$$q = \frac{(C_o - C)V}{W} \quad (2)$$

Where % R is the percentage of dye removed; C_o and C (mg/L) are the initial and final concentrations of the dye respectively; and q is the amount of dye adsorbed per unit mass of adsorbent (mg/g).

Error Functions

The usual way to validate the kinetics is to consider the goodness-of-fit using the linear regression coefficients, R^2. However, for comparing the goodness of fit of different kinetics, using only the linear regression method may not be appropriate. This is because the deduction may be affected by an occurrence of the inherent bias resulting from linearization. Therefore, in this study in addition to the linear regression analysis, the experimental data were tested with a non-linear error function: the sum-of-square error (SSE), to determine the best fitting kinetics (Giwa *et al*., 2015b) [9]. The error function is given by:

$$SSE = \sqrt{\frac{\sum (q_{e,\exp} - q_{e,calc})^2}{N}} \quad (10)$$

Where $q_{e,\exp.}$ is the experimentally determined sorption capacity; $q_{e,calc.}$ is the theoretical sorption capacity obtained from the model, and *N* is the number of data points.

The lower the values of SSE and the higher the value of R^2, the better is the goodness-of-fit and therefore the applicability of the given model.

Adsorption Thermodynamics

The adsorption characteristics of a material can be expressed in terms of thermodynamic parameters such as free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) change of adsorption which can be evaluated from temperature parameters using Van't Hoff equation and is given as

$$\Delta G = -RTInK_0 \quad (11)$$

Where

$$K_0 = \frac{q_e}{C_e} \quad (12)$$

Also,

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

Therefore,

$$\Delta H - T\Delta S = -RTInK_0 \quad (14)$$

Linear form

$$InK_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (15)$$

Where K_0 is the coefficient of adsorption distribution, ΔG ($KJmol^{-1}$) is the free energy of adsorption, T (Kelvin) is the absolute temperature, R is the universal gas constant, ΔH ($KJmol^{-1}$) is the heat of adsorption, ΔS ($KJmol^{-1}K^{-1}$) is entropy change.

Results and Discussion

Characterization of RSD

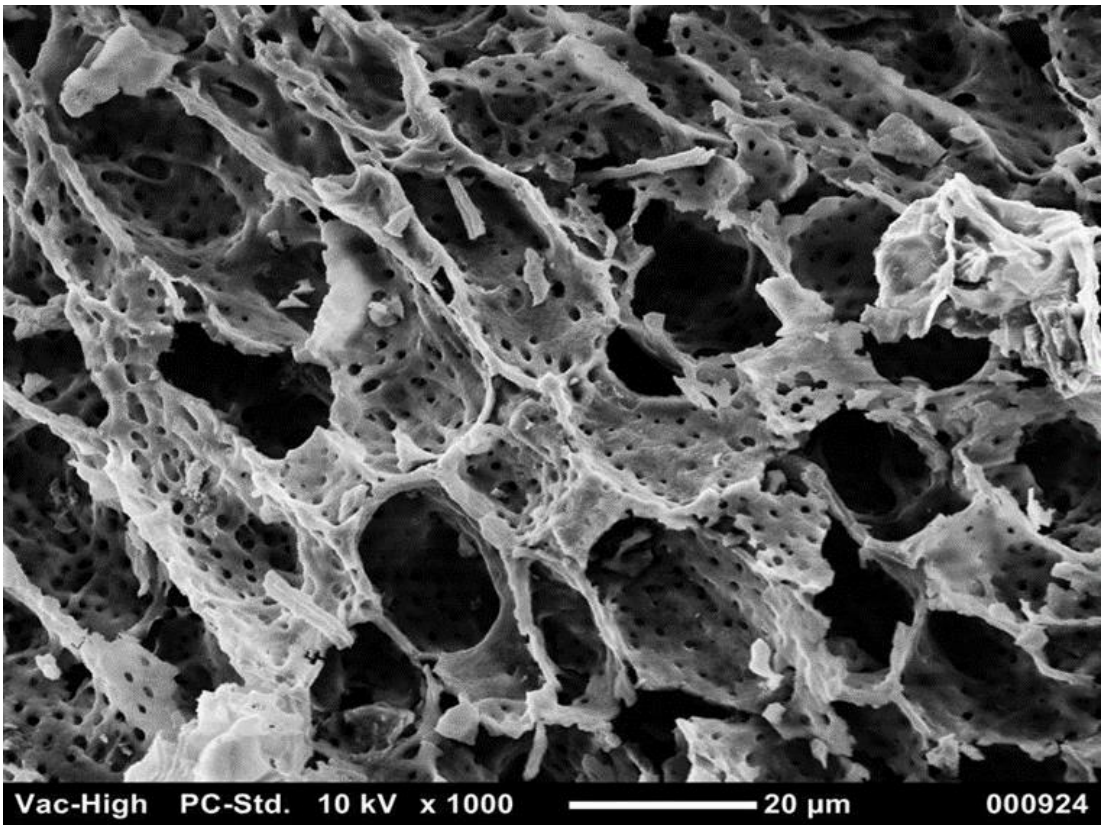

Fig 1: Scanning electron microscope image (X 1000) of RSD

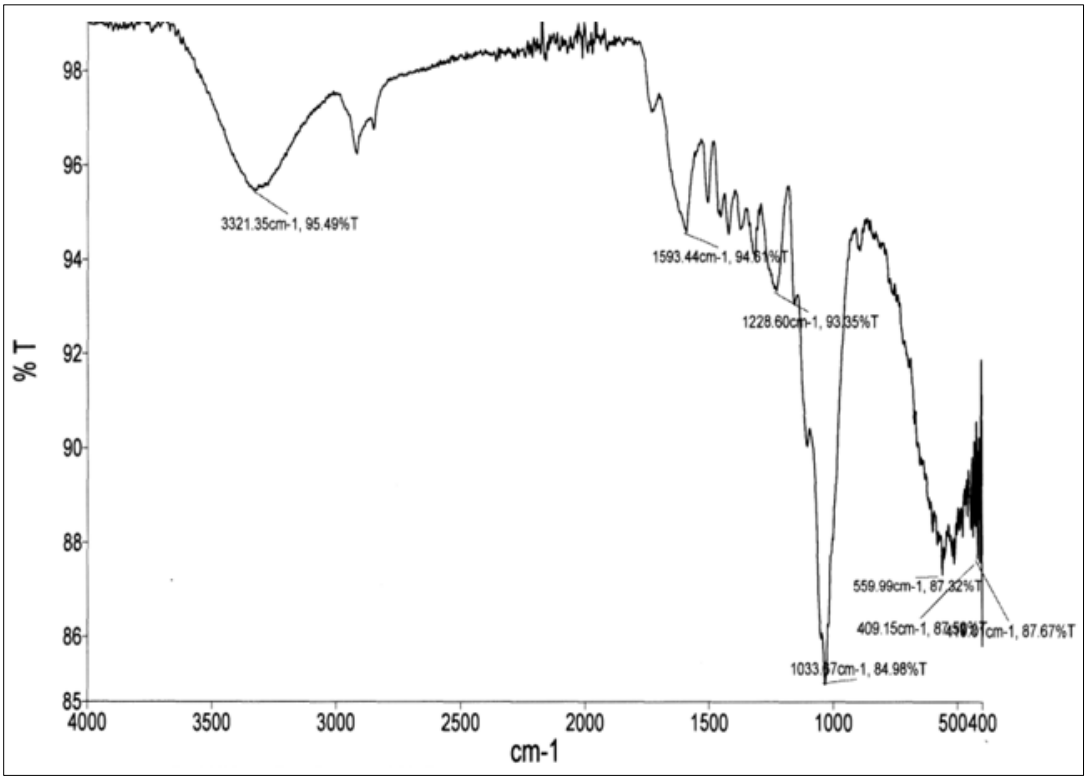

Fig 2: FTIR spectra of raw sawdust

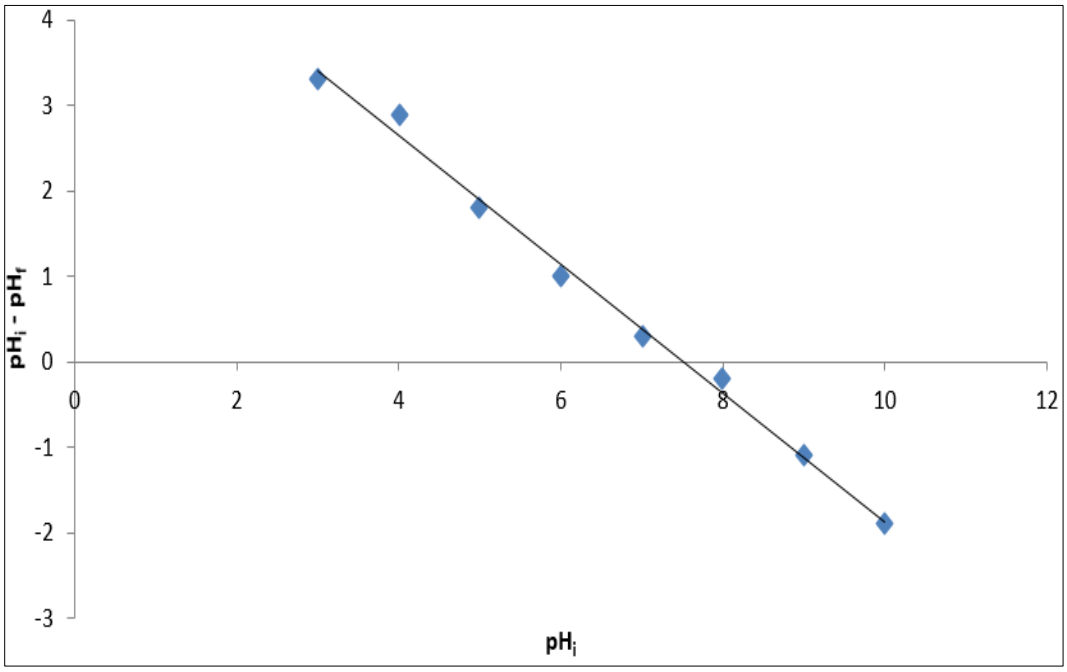

Fig 3: pH Point of zero charge (pH_{ZPC})

The surface morphology of RSD is presented as scanning electron micrograph observed at × 1000 magnification (Fig. 1). From the SEM image of RSD, it shows that the surface of the adsorbent is porous. Its rough surface is an indication of having sites for bonding with dye molecules which enhances adsorption (Demirbas *et al.*, 2004; Giwa *et al.*, 2013) [7, 10].

The FTIR spectrum of RSD before adsorption (Fig. 2) displays a number of absorption peaks, indicating the complex nature of the material. The spectrum indicates that the adsorbent has potential adsorption sites as represented by functional groups COOH, C = O, and C =C.

The point of zero charge pH of RSD is 7.83 as depicted in Figure 3. At a pH below pH_{zpc} of the adsorbent, the surface of the adsorbent is positively charged and attracts anions. At pH above pH_{zpc} of the adsorbent, the surface of the adsorbent is negatively charged and attracts cations (Wang *et al.*, 2006) [23].

Effects of Adsorbent Dosage

When the adsorbent dose was increased, the percentage of methylene blue dye removed consequently increased for all the adsorption systems. The single system has the highest percentage removal and the least removal is observed in methylene blue - malachite green binary system (as shown in figure 4). This may have resulted from the quick adsorption of malachite green (equilibrium time of 3 hrs) which makes the two dyes to compete for sorption sites.

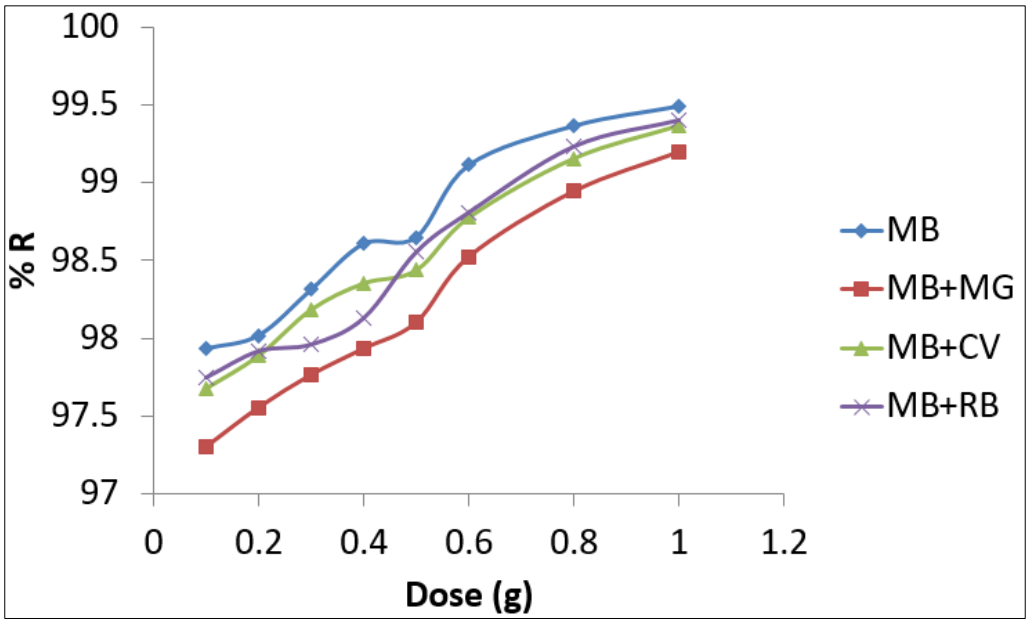

Fig 4: Effects of adsorbent dose on adsorption of methylene blue

Influence of Solution pH

Solution pH is a measure of acidity (pH<7) or basicity (pH>7) of the solution. Percentage removal of MB is low at acidic pH and increased with increase in pH, then reached an optimum at pH of 6. This is because at high solution pH, the positive charge at the solution interface decreases and the adsorbent surface appears negatively charged (Ozcan *et al*., 2007). As a result, the adsorption of cationic dye adsorption increases (Salleh *et al*., 2011) [19] till the adsorbent became saturated at pH 6.

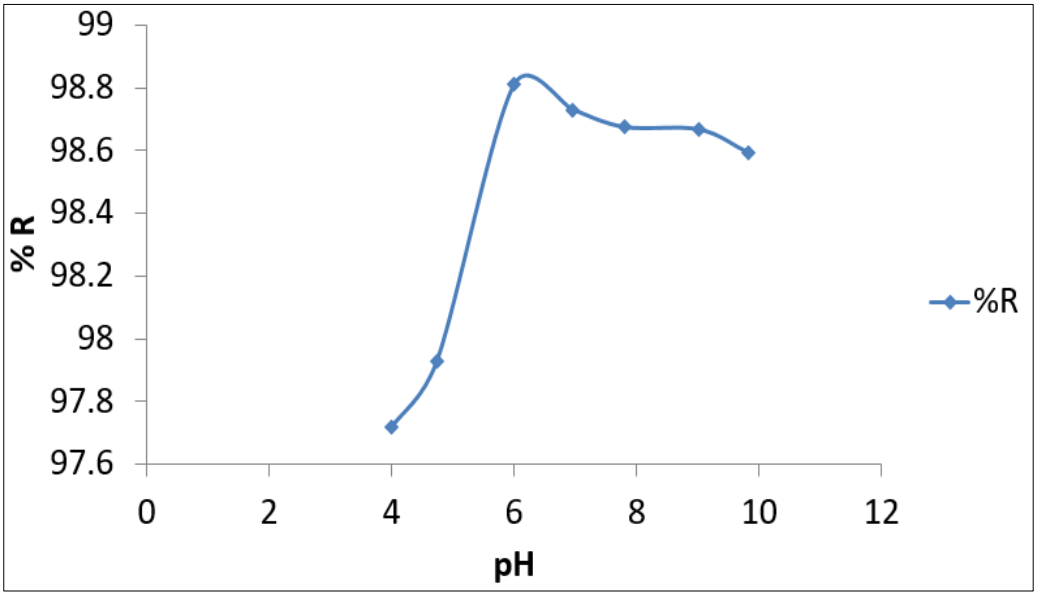

Fig 5: Effects of solution pH on adsorption of methylene blue

Influence of Initial Dye Concentration

As the initial dye concentration is increased, the specific uptake capacity of sawdust for the adsorption of methylene blue in single and binary systems (q_e) increased consequently.This influence may have resulted because there is a high driving force for mass transfer at a high initial dye concentration (Bulut and Aydin, 2006).

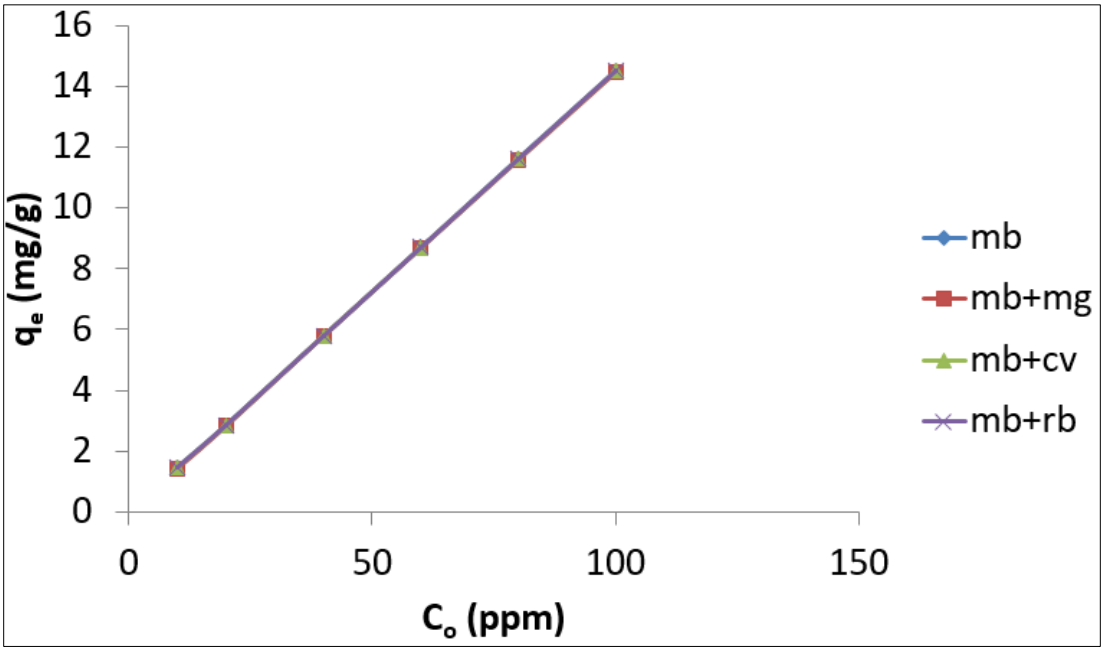

Fig 6: Effects of adsorbate concentration on adsorption of methylene blue

Influence of Contact Time

Increase in contact time consequently increased the percentage dye removal for all the systems The influence of increase in time was rapid in the first 60 minutes after which the increase was minute and the systems reached equilibrium at 160 min. This point is the state of dynamic equilibrium where the amount of the dye desorbing from the adsorbent is same as the amount of the dye being adsorbed onto the adsorbent (Bharathi and Ramesh, 2013) [5].

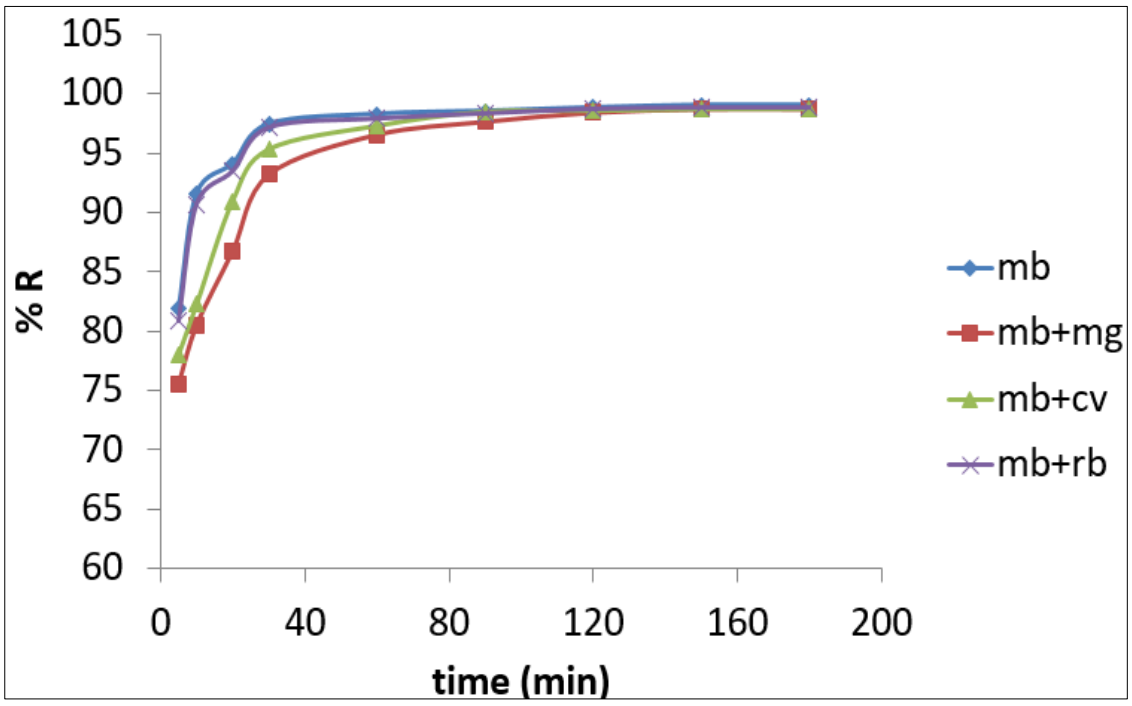

Fig 7: Effects of agitation time on adsorption of methylene blue

Influence of Temperature

The adsorption capacity increases with increasing temperature indicating that the adsorption process is endothermic. This may be because an increas in temperature will increase the energy of the system and hence the mobility of the dye molecules (Senthilkumaar *et al*., 2006) [20].

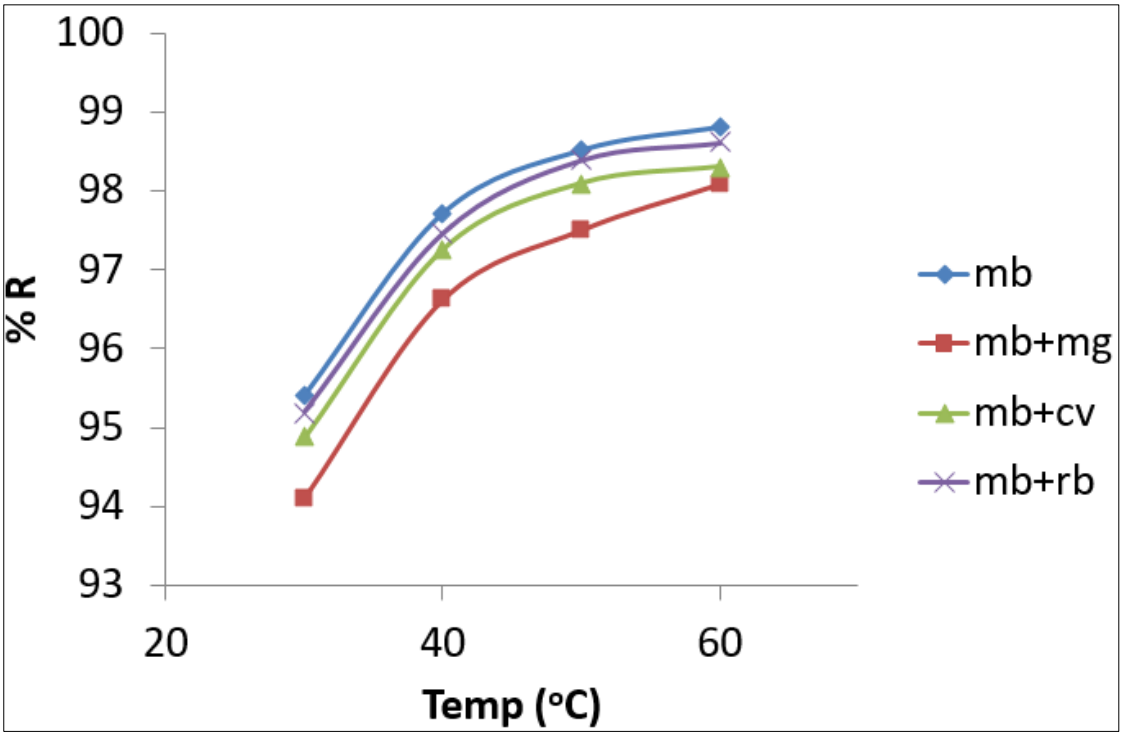

Fig 8: Effects of temperature on the adsorption of methylene blue

Adsorption Isotherm

Isothermal parameters were calculated from the plots of Langmuir, Freundlich, Temkin and Harkin- Jura isotherm equations for adsorption of methylene blue in single and binary dye systems and presented in Table 1. The Co-efficient of correlation (R^2) for the adsorption of methylene blue (MB) in all the dye systems considered have values highest for Freundlich isotherm model. Therefore they all follow Freundlich isotherm model. This suggests that locust bean tree sawdust is heterogeneous.

The maximum monolayer adsorption capacity (q_o) is maximum in binary system MB+MG with a value of 125.00 mg/g followed by binary system MB+RB, then by binary system MB+CV and least in the single system with a value of 24.39 mg/g. Affinity oflocust bean tree sawdust for adsorption of methylene blue (b) ismaximum in binary system MB+RB followed bythe single system, then by binary system MB+CV and least in binary system MB+MG. The adsorption is favourable for all dye systems as they all have their $\frac{1}{n}$ values less than 1.

Table 1

Isotherm Models	**Adsorbate Systems**			
LANGMUIR	MB	MB+MG	MB+CV	MB+RB
R^2	0.593	0.319	0.453	0.485
q_o(mg/g)	24.39	125.00	30.30	40.00
B	0.130	0.030	0.104	0.159
R	0.134	0.397	0.162	0.112
FREUNDLICH				
R^2	0.986	0.997	0.992	0.988
$\frac{1}{n}$	0.813	0.965	0.849	0.806
k_f	5.358	3.936	5.129	5.260
TEMKIN				
R^2	0.985	0.930	0.850	0.750
A_r	1.411	2.707	5.552	5.307
b_r	263.67	442.73	606.15	705.25
HARKIN-JURA				
R^2	0.962	0.858	0.959	0.962
A	2.53	1.92	2.56	2.54
B	0.38	0.41	0.42	0.40

Adsorption Kinetics

Kinetics parameters calculated from pseudo-1st order, pseudo-2nd order and Weber- Morris equations are presented in table 2.

From the table, R^2 values for Pseudo second order kinetics > pseudo – 1st-order kinetics. The adsorption capacity calculated, $q_{e(calc)}$, for pseudo second order kinetics (7.462 - 7.519) is closer

to q_e experimented (7.402 - 7.427) than q_e calculated for pseudo – first order kinetics (0.731 - 1.772) for the adsorption of methylene blue in all the dye systems in consideration. Also, the SSE values for pseudo-second order kinetics (0.016 - 0.039) is very small compared to the values for pseudo- second order kinetics (2.13 -2 53). Hence, these adsorption processes follow pseudo-2nd – order kinetic model which suggest a chemisorption process. Similar observations were reported by Inbaraj and Sulochana (2006) [13]; Hammed *et al.*, (2009); and Jabli *et al.*, (2011) [14].

For all the dye systems investigated, the plot of sorption capacity at a given time, q_t, versus √t for Weber-Morris model gave straight lines which, however, they do not pass through the origin. This suggests that the adsorption mechanism in addition to boundary layer resistance, involves intraparticle diffusion.

Table 2: Kinetics Parameters for Adsorption of Methylene Blue on locust bean tree sawdust

Kinetic models		Pseudo-first order				Pseudo-second order				Weber- Morris			
Adsorbate	$q_{e(exp)}$	R^2	k_1	$q_{e(calc)}$	SSE	R^2	k_2	H	$q_{e(calc)}$	R^2	SSE	K_d	C
MB	7.427	0.901	0.034	0.731	2.53	1.000	0.142	8.00	7.519	0.697	0.031	0.126	6.336
MB+MG	7.405	0.984	0.036	1.772	2.13	1.000	0.058	3.29	7.519	0.872	0.038	0.218	5.474
MB+CV	7.402	0.969	0.045	1.507	2.23	1.000	0.082	4.61	7.519	0.811	0.039	0.187	5.772
MB+RB	7.413	0.940	0.039	0.891	2.46	1.000	0.133	7.41	7.462	0.709	0.016	0.134	6.256

Adsorption Thermodynamics

Values for ΔH and ΔS were calculated from the slope and intercept of plot InK_0 versus1/T, ΔG was calculated using Van't Hoff equation for the adsorption of MB and shown in table 3.

ΔG has negative values for all the dye systems (-31.48 to -42.44KJmol^{-1}) at the investigated temperature values. These negative values of ΔG show that the adsorption process is feasible. ΔH has positive values (3.226 to 3.903KJmol^{-1}). These positive values of ΔH confirm that the reaction is endothermic (Hengpeng and Zhijuan,2010; Giwa *et al*., 2015a). Moreso, ΔS has positive values (114.57 to 139.18Jmol^{-1}K^{-1}). These positive values of ΔS increased with temperature indicating the increased random movement of dye molecules with increase in temperatures. Similar reports were given by lnbaraj and Sulochana (2006) [13]; Ahamad *et al.*, (2011) [1] and Giwa *et al*., 2015a [9].

Table 3: Thermodynamic Parameters for Adsorption of Methylene Blue onto Sawdust

Temp	Single system			Binary system(MB+MG)			Binary system(MB+CV)			Binary system(MB+RB)		
	ΔG(KJmol^1)	ΔH (KJmol^1)	ΔS (Jmol^{-1}K^1)	ΔG(KJmol^1)	ΔH (KJmol^1)	ΔS (Jmol^{-1}K^1)	ΔG(KJmol^1)	ΔH (KJmol^1)	ΔS (Jmol^{-1}K^1)	ΔG(KJmol^1)	ΔH (KJmol^1)	ΔS (Jmol^{-1}K^1)
303	-38.27			-31.48			-31.89			-35.76		
313	-39.66	3.903	139.18	-32.63	3.233	114.57	-33.05	3.226	115.90	-37.06	3.640	130.03
323	-41.05			-33.77			-34.21			-38.36		
333	-42.44			-34.92			-35.37			-39.66		

Conclusion

It was established from the spectrum and characterization that the adsorbent has potential porous adsorption sites as well as functional groups: COOH, C = O, and C =C. The point of zero charge pH of RSD is 7.83. With increase in adsorbent dose, pH, contact time, initial dye concentration and temperature; the adsorption of methylene blue in all dye systems studied was increasing. The adsorption isotherms in all the dye systems have best fits for the Freundlich model with kinetics following pseudo-second-order model. The maximum monolayer adsorption capacity (q_o) is maximum in binary system comprising of methylene blue and malachite green with a value of 125.00 mg/g. The adsorption processes are thermodynamically feasible, and endothermic. RSD adsorbent, therefore, is efficient for the treatment of wastewaters containing dye mixtures.

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