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Competitive Biosorptive Removal of a Basic Dye From Ternary Dye Mixture Using Sawdust

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Abstract

Adsorption equilibrium isotherm, kinetics and thermodynamics of the removal of Methylene blue dye by biosorption onto sawdust of *Parkia biglobosa* from aqueous solutions of binary and ternary dye mixtures was investigated. The sawdust was characterized and adsorption experiments were conducted in batch mode to determine the effects of adsorbent dose, initial concentration and pH of the dye solution, temperature and contact time, on the adsorption process. Experimental data obtained were subjected to various equilibrium isotherm and kinetics models, and the results validated using R^2 and χ^2 goodness-of-fit functions. The results showed the biosorption processes in single and binary systems fitted well to Freundlich isotherm while the ternary system followed Langmuir model. The processes were better described by pseudo-second order kinetics; they were all endothermic and increasingly thermodynamically spontaneous with rise in temperature as ΔG values are -9.33, -10.68, -11.17 and -11.87 kJ/mol at 303, 313, 323 and 333 K respectively.

***Keywords*:** Biosorption, *Parkia biglobosa*, dye mixture, Sawdust, Methylene blue, Adsorption, Kinetics, Isotherm, Thermodynamics.

INTRODUCTION

Treatment of textile effluents using various physical and chemical methods such as chemical oxidation, activated sludge, biodegradation, membrane separation electrochemical, chemical oxidation, reverse osmosis, aerobic and anaerobic microbial degradation, photodegradation and adsorption has been widely studied [1, 2, 3]. Adsorption method has been reported to be more efficient and versatile when compared with other physico-chemical wastewater treatment techniques [3, 4, 5, 6]. Activated carbon which is widely used as adsorbent for wastewater treatment is expensive and therefore uneconomical. In addition, the laboratory preparation of activated carbons have been accompanied by a number of disadvantages such as combustion at high temperatures, pore blocking, and hygroscopicity [7]. It is therefore imperative to search for cheaper and simpler substitutes.In this respect, different agricultural residues have been investigated for their potentials for biosorptive treatment of wastewater. However, most of the reported studies were on single adsorbate systems. Since wastewaters from textile industries and dye houses hardly contain only a single dye, and it has been reported that the adsorption of a dye can be affected by the presence of other dye(s) in the matrix [3, 8, 9, 10, 11], it is therefore important to always consider adsorption in a multiple component environment. Thus, this study aims at investigating a multi-adsorbate system by focusing on the adsorption of methylene blue in competitive aquatic medium using the sawdust of locust bean tree (*Parkia biglobosa*). However, the biosorption of rhodamine B and acid blue 161 dyes using this agrowaste has been investigated and reported by these authors [3, 11].

EXPERIMENTAL DETAILS

Preparation and characterization of adsorbent

The processes of preparing and characterizing this adsorbent have been described elsewhere as its adsorption of rhodamine B and acid blue 161 dyes has been reported by us [3, 11]. Sawdust of locust bean tree was collected, washed, oven-dried at 105 ^{o} C, ground, sieved and stored as SDP adsorbent, without any further chemical treatment. It was characterized using scanning electron microscope Fourier Transform Infrared Spectroscopy, X-ray diffraction and pH point of zero charge (pH_{zpc}).

Preparation of dye solution

The main adsorbate targeted in this research, methylene blue (MB); a basic dye was supplied by M & B Laboratory chemicals. It was present in aqueous solution in single and multi-component (together with rhodamine B and acid blue dyes) systems in different mass ratios. A stock solution (1000 mg/L) of each dye was prepared. Working solutions of the desired concentrations were further prepared from the stock solution by dilution. The structure of Methylene blue is shown in Figure 1.

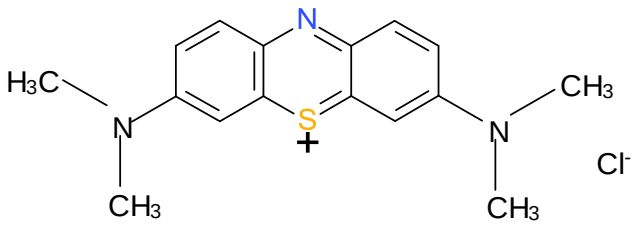


Figure 1. Chemical structure of Methylene blue.

Adsorption studies

Adsorption experiments were conducted in batch mode to determine the effects of initial concentration of methylene blue and the other competing dyes (Acid blue 161 and Rhodamine B), dose of biosorbent, pH of the dye solutions, temperature and contact time. A 50 mL solution of different initial concentrations of the dye (or dye mixture) at different temperature and pH were applied onto different SDP doses in glass bottles which were agitated for predetermined contact times in a horizontal mechanical shaker, SM 101 by Surgifriend medicals [3, 11].

The amount of dye removed was determined thus:

$$q = \frac{(C_o - C)V}{m}$$

Where q is the amount of dye adsorbed (mg/gb); C_o and C (mg/l) are the initial and concentrations of dye respectively. V is the volume of the solution (l) and m is the mass of SDP (g).

RESULTS AND DISCUSSION

Characterization of SDP

The textural structure of the surface of SDP as recorded with scanning electron microscope is given in Figure 2. The image shows clearly the rough texture and porous nature of the surface of the adsorbent. Irregularity of the surface of an adsorbent generally signifies a high surface area which enhances adsorption [3, 8, 12].

Before the adsorption process, the FTIR spectrum of SDP (Figure 3a) consists of some absorption peaks that reveal the complexity of the substance. The presence of COOH, C = O, and C =C functional groups (as signified by the bands at3417 cm^{-1} representing bonded – OH in the oxygen containing functional groups, C-H (2885 cm^{-1}), aromatic C = C (1647 cm^{-1}), and carbonyl (1734 cm^{-1}) vibrations,) on the sawdust is an indication of potential adsorption sites [11, 13]. Comparing the FTIR spectra of SDP before and after the adsorption of dye, show that there are some changes in the position or occurrences of some diagnostic bands (Figure 3). A new band at 3726 cm^{-1}which can be assigned to O-H stretching vibration, appeared after the adsorption process(Figure 3b). A shift in the position of -OH band at 3417 cm^{-1} (before adsorption) to 3421 cm-1 (after adsorption) was also observed. Similarly, C≡C band shifted from 2065 cm^{-1} to 2077 cm^{-1}. The shift in adsorption bands may be an evidence that confirms the adsorption of methylene blue onto the surface of SDP.

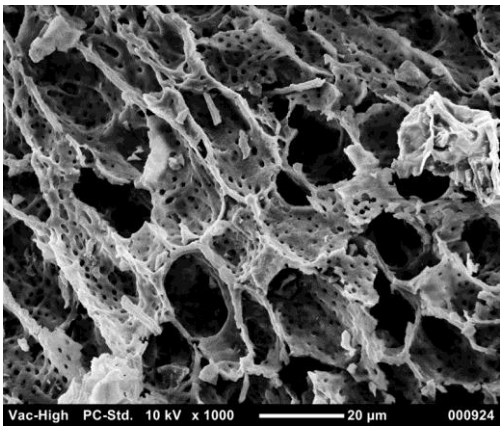
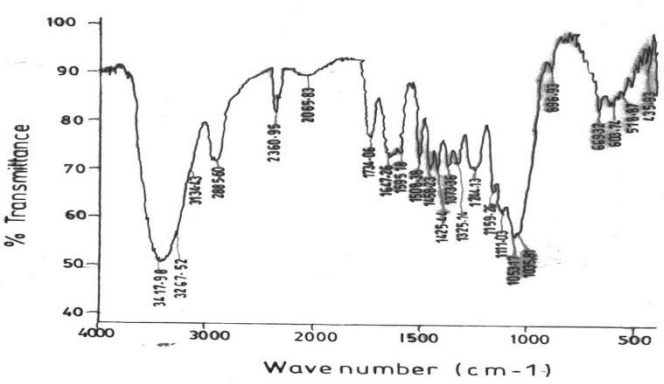
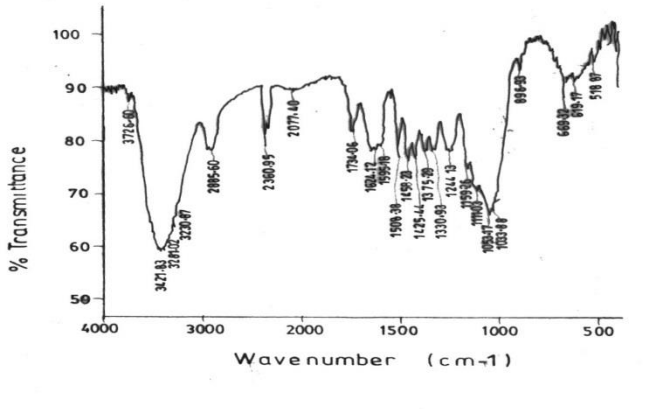


Figure 2. Scanning electron microscope image of SDP (X 1000 magnification)



(a)



(b)

Figure 3. FTIR spectra of SDP before and after the adsorption of methylene blue

The point of zero charge pH, $pH_{zpc,}$of the adsorbent was determined to be 7.83 (Fig. 4). The surface charge of the adsorbent depends on this value based on the pH of the adsorbate solution. This in turn influences the adsorption of the adsorbate species depending on the charge they carry [14].

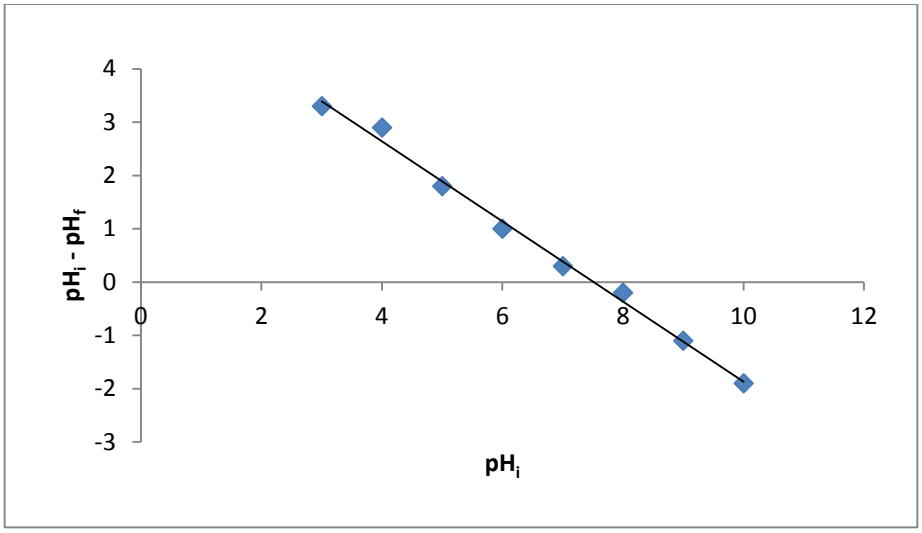


Figure 4. pH Point of zero charge (pH_{ZPC}) of SDP

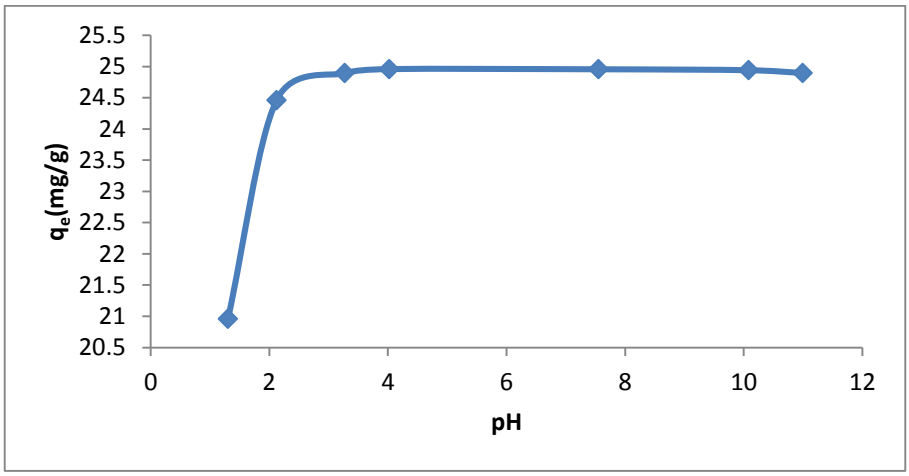


Figure 5. Influence of pH on adsorption of methylene blue on SDP

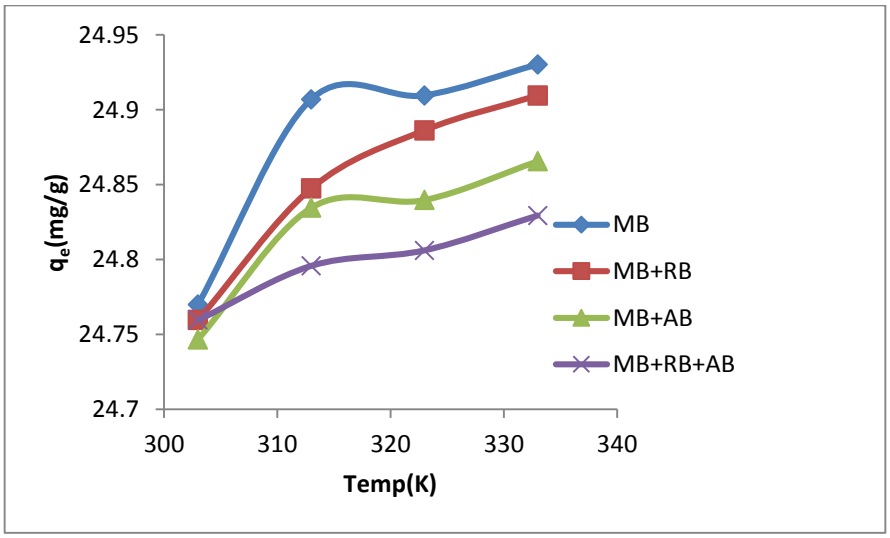


Figure 6. Influence of temperature on adsorption of methylene blue on PSD

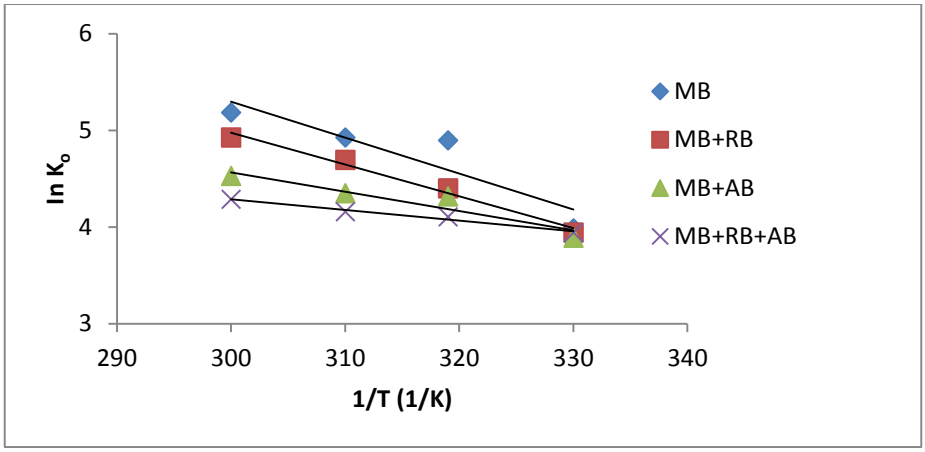


Figure 7. A plot of In Ko against 1/T for the adsorption of methylene blue in single, binary and ternary mixture on PSD

Batch adsorption experiments

Effects of pH on the adsorption of Methylene blue

During adsorption in aqueous environment, the influence of pH of the solution cannot be over-emphasized as the speciation of the adsorbate, and its level of ionization greatly depends on it [3]. In this study, the adsorption capacity, q_e (mg/g) of SDP for methylene blue increased with increasing pH from pH 1.3, reaching a maximum at pH 4.02 and then remained constant as shown in Figure 5. The low adsorption of MB at low pH is probably due to the presence of excess H^+ ions competing with the cationic dye. Adsorption reached a maximum at pH 4.02 which is lower than the pH_{ZPC} due to the presence of OH^- from the ionization of water which would have given the adsorbent surface a negative charge for MB to be adsorbed. At increased pH, electrostatic forces of attraction between the cationic dye and the adsorbent surface set in at high pH as the surface of the SDP particles gets negatively charged, which enhances attraction of the positively charged dye species. Similar reports were given by Hameed *et al.*, (2008) [15] and Mohamad *et al.*, (2011) [6].

Effects of SDP dose on Methylene blue adsorption

The specific uptake of methylene blue,q_e, (i.e adsorption of methylene blue per unit mass of adsorbent) decreased with increasing dose of SDP for all the adsorbate- adsorbent systems i.e single, binary and ternary systems.. As adsorbent dose was increased from 0.1 to 0.6 g, q_e decreased: from 24.95 to 4.15 mg/g in the single adsorbate system, 24.92 to 4.15 mg/g in the binary system (comprising of Methylene blue and R hodamine B), 24.79 to 4.13 mg/g in the second binary system (comprising of Methylene blue and Acid blue 161) and 24.53 to 4.09 mg/g in the ternary dye system. These observations may be due to the fact that at low doses of SDP, the active sites on its surface were effectively utilized. But, as the adsorbent dose increased, a significant amount of the available active sites on the adsorbent overlapped which resulted in the reduction of specific uptake [16].

Effects of initial concentrations of Methylene blue on its adsorption

To study the effects of the initial concentration of methylene blue on its biosorption by SDP, six different dye mixture compositions were used:

(i) Methylene blue single system

(ii) Binary system; comprising of different concentrations of Methylene blue together with 10 mg/L of Acid blue ($MB+AB_1$;);

(iii) Binary system; comprising of different concentrations of Methylene blue together with 20 mg/L of acid blue ($MB+AB_2$);

(iv) Binary system; comprising of different concentrations of Methylene blue together with 10 mg/L rhodamine B ($MB+RB_1$)

(v) Binary system; comprising of different concentrations of Methylene blue together with 20 mg/L Rhodamine B ($MB+RB_2$)

(vi) Ternary system, comprising of a mixture of methylene blue and 20 mg/L each of acid blue 161 and Rhodamine B (MB+RB+AB).

The specific uptake of methylene blue by SDP increased with increasing initial concentration of methylene blue for all the systems investigated. As the initial concentration of MB increased from 10-100 mg/L, q_e increased from 4.97 to 49.79 mg/g in the MB single dye system; from 4.96 to 49.75 mg/g in the MB binary system of $MB+RB_1$; from 4.92 to 49.63 mg/g in the MB binary system $MB+RB_2$, from 4.79 to 48.80 mg/g in the MB binary system of $MB+AB_1$; from 4.84 to 46.46 mg/g in the MB binary system $MB+AB_2$; from 4.71 to 49.81 mg/g in the ternary dye system. The increase in the dye specific uptake with increasing initial dye concentration in all the systems may be as a result of the availability of low number of dye molecules at low concentrations. At higher concentrations however, the number of dye molecules available is high enough to overcome the resistance to mass

transfer. Similar

observation was made by [3, 8, 11, 17].

Adsorption kinetics

The adsorption of methylene blue onto SDP in single, binary and ternary dye systems increased with increasing contact time, and reached an optimum value at 150 minutes when equilibrium was attained. The adsorption was very rapid at the initial stage; it decreased gradually with time and became constant at equilibrium. As agitation time increases, the surface of the adsorbent has longer contact with the dye thereby increasingly allowing more dye molecules to interact with the adsorbent. At equilibrium however, the surface of the adsorbent has been saturated leaving no more active site to be occupied hence, the adsorption capacity, q_e becomes constant. Similar trend has been reported [11, 18, 19].

The study of adsorption dynamics describes the solute uptake rate which controls the residence time of adsorbate uptake at the solid-solution interface. In this work, the pseudo-first order and pseudo-second order kinetics equation were employed for modeling. The linear forms of the models are given as:

Pseudo-first-order equation: $\ln (q_e - q_t) = \ln (q_e) - K_1 t$ (3)

Pseudo-second-order equation: $\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$ (4)

Where q_t is the adsorption capacity at time t (mgg^{-1}), k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}), k_2 ($gmg^{-1}min^{-1}$) is the pseudo-second order overall rate constant and h (which is equal to $k_2 q_e^2$) is the pseudo-second order initial rate constant of adsorption.

The kinetics constants and other parameters calculated from the models are given in Table 1. The high linear regression coefficient, R^2, values and the closeness of the equilibrium adsorption capacity, $q_{e,calc}$ calculated for Pseudo-second order kinetics model to the experimentally obtained, $q_{e,exp}$, show that the biosorption of methylene blue in single, binary and ternary dye systems by the sawdust of *Parkia biglobosa*, is better described by this model. This, therefore, suggests that the biosorption process involved chemisorption.

The initial rate constant, h, is higher for the biosorption in the ternary mixture of dyes than for the single and binary systems (Table 1). The results show that the presence of Acid blue dyes may have little or no effect on the initial and even the overall rate of methylene blue uptake by the adsorbent. This suggests that there was no competition between the two dye species. In contrast, the presence of Rhodamine B in both the binary and ternary dye mixtures had significant effect on the Pseudo-second order rate constants, both the initial and overall (Table 1). The guest-guest interaction between methylene blue and Rhodamine B may be repulsive, which may have affected the guest-host relationship between methylene blue and the surface of SDP.

Adsorption equilibrium studies

Many theories have been developed to explain the interaction between adsorbate and adsorbent in adsorption at a given temperature. The distribution of adsorbate particles between the solid and liquid phases at equilibrium and constant temperature is considered as isotherm. There are many isotherm models but four are considered in this study: Langmuir, Freundlich,Temkin and Harkin-Jura isotherms. The equilibrium adsorption data obtained were fitted to te linear forms of these isotherm models. They are:

Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{Qob} + \left(\frac{1}{Qo}\right) C_e \quad (5)$$

Freundlich equation

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

Temkin equation

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (7)$$

Harkin-Jura equation

$$\frac{1}{q_e^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) \log C_e \quad \ldots\ldots\ldots\ldots\ldots (8)$$

Where C_e is the equilibrium concentration of adsorbate (mg/l); q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mgg^{-1}); q_o is Langmuir constants related to monolayer adsorption capacity and b is a constant indicating the affinity of an adsorbent towards an adsorbate,. K_f is a rough indicator of the adsorption capacity related to the bond energy; $\frac{1}{n}$ is the adsorption intensity of adsorbate onto the adsorbent or surface heterogeneity; A_T and b_T are Temkin constants; R is the universal gas constant ($8.314 Jmol^{-1}K^{-1}$)

T is the temperature in Kelvin; A and B are Harkin-Jura constants

As was also observed and reported by Giwa *et al*. (2016) for the biosorption of Acid blue 161 from single, binary and ternary systems, the coefficient of correlation, R^2, values for in the present study are high (> 0.9) for the Langmuir, Freundlich and Temkin isotherms. These and other isotherm parameters obtained from the plots of equations (5) – (8) above are given in Table 2. Since correlation coefficients, R^2, is used to assess the conformity of the experimental data with the isotherm equations, and the closer the R^2 value to 1, the better the applicability of the isotherm, the high values may be a pointer to a complex mechanism of the biosorption. The final overall mechanism might have been influenced by different characteristics that might have been exhibited at different stages of the biosorption.

The R^2 for the adsorption of methylene blue in single and binary systems for Freundlich isotherm are high (>0.99), an

indication of a possible heterogeneous surface of SDP, and that the biosorption of the dye onto the adsorbent was in layers. Conformity of the biosorption mechanism with Freundlich model also is suggestive of heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [20]. The values of the Freundlich constant, $1/n$, which is a measure of adsorption intensity,for all the adsorption systems are less than unity, indicating favourable biosorption processes [21].

The value of b, a Langmuir constant, which describes the affinity of an adsorbent towards an adsorbate, is higher in the adsorption in single adsorbate system than for the mixtures (Table 2). This indicates a weaker guest-host (adsorbate – adsorbent) interaction in the binary and ternary systems. The antagonistic effect was more pronounced with Rhodamine B (b= 0.33L/g), being a basic dye, than with Acid blue (b = 0.67 L/g). The maximum monolayer coapacity, q_0, another Langmuir constant, for the adsorption of methylene blue in single system was 40mg/g. This is compared with the reported monolayer capacities of some other agricultural waste-based adsorbents for the adsorption of methylene blue in single dye systems (Table 3). However, the maximum monolayer adsorption value for the mixture systems are lower. This suggests that the overall effect of the presence of Rhodamine B and/or Acid blue on the adsorption of methylene blue by SDP was generally antagonistic. This is similar to what has been reported for the adsorption of Rhodamine B but contrary to that reported for Acid blue 161by the same adsorbent, in the same matrix and under the same set of conditions [3, 11].

The high R^2 values for Temkin isotherm is a pointer to the likelihood of interaction between the particles of the adsorbate in the solution during the course of the biosorption. It also suggests that the heat of biosorption , especially in the single and binary systems, decreases linearly, rather than logarithmic as implied in the Freundlich equation, with the coverage of the adsorbent as a result of the adsorbate-adsorbate interaction. This is an essential assumption of the Temkin model [22, 23]. This implies that the process of biosorption was by chemisorption, and the more energetic sites on SDP were occupied first [24]. by methylene blue molecules. The value of Temkin constant b_T, for the biosorption processes ranges from 0.06 to 0.35 kJ/mol (Table 2). This constant is related to the heat of adsorption. If the magnitude is between 8 and 16 kJ/mol, then the sorption process involves ion exchange [25]. The energy associated with the adsorption of methylene blue from the single system is higher than for the binary and ternary systems. However, these energies are very low and therefore the adsorption in all the systems seems not have involved ion–exchange mechanism. Another Temkin parameter, AT, which is the equilibrium binding constant and a measure of adsorption potential, has highest value for the single system (67.58 l/mg), and the least for the ternary system (1.17 l/mg) (Table 2). This somehow confirms the deduction that has been stated above (from Langmuir constant, b) on the higher affinity of SDP for the biosorption in the single system than in the multi-dye systems.

Effect of Temperature and adsorption thermodynamics

The adsorption capacity of *Parkia biglobosa* for Methylene blue (MB) in single, binary and ternary dye systems increased marginally with increase in temperature (Fig. 6), which may be an indication endothermic adsorption processes. The effect is relatively more pronounced in the single system than in the binary and ternary mixtures. This may not be unconnected with the competition among the various dye species present in the multi-component systems. Lowest increase in adsorption capacity was recorded for the ternary system (Figure 6) The increase in the adsorption capacity, q_e with increasing temperature may be due to an increase in the number of molecules that become more mobile and acquire sufficient energy to undergo an interaction with active sites at the surface [3]. In addition, an increase in temperature may produce a swelling effect in the internal structure of the adsorbent thereby enabling more dye particles to penetrate further [26].

Figure 7 gives the plots of ln K_0 versus 1/T from which the thermodynamic parameters [free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes] of the adsorption processes were evaluated from the temperature parameters using Van't Hoff equation and is given as

$$\Delta G = -RTInK_0 \quad (9)$$

Where

$$K_0 = \frac{q_e}{C_e} \quad (10)$$

Also,

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

Therefore,

$$\Delta H - T\Delta S = -RTInK_0 \quad (12)$$

Linear form

$$InK_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (13)$$

Where K_0 is the sorption distribution coefficient, 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 ($Jmol^{-1}K^{-1}$) is the change in entropy associated with the adsorption. Values for ΔH and ΔS calculated from the slope and intercept of the plots (Fig. 7), and ΔG obtained from equation (11) above for the adsorption of methylene blue from the various adsorbate systems are presented as Table 4.

It can be seen from the negative values of the Gibb's free energy given in Table 4, that the adsorption of Methylene blue in all the systems (single, binary and ternary) being studied in this work are spontaneous and thermodynamically feasible as they were accompanied with reduced energy of the systems. The spontaneity of the process increased with increasing temperature in the single adsorbate system and the various mixtures.This is a pointer to an endothermic change. However, at the same temperature, the adsorption of the dye was generally more feasible in the single system than for the mixtures as it has more negative ΔG. The adsorption in the ternary mixture is generally less spontaneous than in the binary mixtures (Table 4). These observations indicate that the feasibility and spontaneity of the biosorption decreases with

the level of complexity and competitiveness of the system.

The enthalpy change, ΔH, has positive values for all the systems investigated. This further confirms that the process is endothermic. As for change in entropy, ΔS; it is positive for all the processes studied. The value, however, decreases with increasing complexity of the composition of the systems. That is, ΔS is of the trend Single system > Binary systems > Ternary system. This suggests that, though the adsorption process in all the adsorbate systems is feasible, the degree of disorderliness at the solution-adsorent interphase decreases with the total number of all the dye molecules in the systems.. Similar reports were given by lnbaraj and Sulochana (2006) [27]; Ahamad *et al.,* (2011) [28] and Giwa *et al*., 2015a [3].

CONCLUSIONS

The sawdust of *Parkia biglobosa*, SDP,used as biosorbent in this study was able to remove methylene blue dye from a single system comprising of the dye alone in aqueous solution, and from multi-dye systems (both binary and ternary) which included Rhodamine B or Acid blue 161 dyes or the two of them together. All the adsorption processes were feasible (negative Gibb's free energy), endothermic and with increased entropy. Their kinetics was of the Pseudo-second order with the equilibrium attained in 150 minutes. The biosorption process displayed a complex mechanism as the linear correlation coefficients for three equilibrium isotherms equations were all high. The presence of Acid blue 161 and Rhodamine B dyes had antagonistic effect on the rmaximum monolayer capacity of the adsorbent for removing Methylene blue dye.

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Table 1. Kinetic Parameters for Adsorption of Methylene Blue onto PSD

Kinetic model			First-order kinetics			Second-order Kinetics				
Dye System	qe(exp)	R2	qe(calc)	K_1	$\chi 2$	R^2	qe(calc)	K2	h	$\chi 2$
MB	24.90	0.951	0.863	0.025	0.93	1.00	25.00	0.10	62.50	$1.6x10^{-5}$
MB+RB	24.92	0.845	0.758	0.029	0.94	1.00	25.00	0.12	76.92	$1.0x10^{-7}$
MB+AB	25.00	0.067	0.372	0.003	0.97	1.00	25.00	0.10	62.50	$3.2x10^{-5}$
MB+RB+AB	24.86	0.914	0.567	0.027	0.96	1.00	25.00	0.16	100.00	$3.2x10^{-5}$

Table 2. Isotherm Model Parameters for Adsorption of Methylene Blue onto Raw sawdust

Isotherm model			Langmuir		Freundlich		Temkin			Harkin-Jura		
Dye system	R^2	q_o	b	R^2	K_f	1/n	R^2	A_T	b_T	R^2	A	B
MB	0.968	40.00	12.50	0.997	27.67	0.352	0.994	67.58	0.35	0.615	$1.0x10^3$	9
MB+RB	0.959	33.33	0.33	0.999	86.90	0.932	0.988	16.88	0.13	0.951	$1.8x10^2$	0.25
MB+AB	0.962	25.00	0.67	0.999	18.41	0.060	0.988	2.55	0.10	0.645	$6.2x10^2$	0.69
MB+RB+AB	0.982	5.38	3.26	0.738	4.55	0.658	0.541	1.17	0.06	0.619	$4.3x10^2$	0.48

Table 3. Comparison of Adsorption Capacities of Some Adsorbents for MB Removal

ADSORBENT	q_o (mg/g)	REFRENCE
P. biglobosa sawdust	40.00	This work
Langsat peel	45.45	Mohd Salleh *et al.,* (2012)
Wheat shells	16.56	Bulnut and Aydin (2006)
Neem leaf powder	19.61	Bhattacharrya and Sharma(2005)
Brazil nut shells	7.81	De Oliveria *et al.,* (2010)
Miswaks leaves	200	Elmorsi (2011)
Agrowaste mixture	93.46	Salleh *et al.,* (2011)

Table 4. Thermodynamic Parameters for Adsorption of Methylene Blue onto PSD

	Single system			Binary system (MB+RB)			Binary system (MB+AB)			Ternary system (MB+AB+RB)		
Temp	ΔG(kJ/mol)	ΔH (kJ/mol)	ΔS (J/Kmol)	ΔG	ΔH (KJ)	ΔS (J/Kmol)	ΔG	ΔH (KJ)	ΔS (J/Kmol)	ΔG	ΔH (KJ)	ΔS (J/Kmol)
303	-10.04			-9.93			-9.80			-9.928		
313	-12.74	30.75	136.2665	-11.45	27.32	123.30	-11.25	16.46	87.297	-10.68	9.15	63.10326
323	-13.22			-12.61			-11.68			-11.17		
333	-14.36			-13.63			-12.53			-11.87		

MB- Methylene blue; RB- Rhodamine B; AB- Acid blue 161

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