Research Article

Biosorption of Acid Dye in Single and Multidye Systems onto Sawdust of Locust Bean (*Parkia biglobosa*) Tree

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Properties of raw sawdust of *Parkia biglobosa*, as a biosorbent for the removal of Acid Blue 161 dye in single, binary, and ternary dye systems with Rhodamine B and Methylene Blue dyes in aqueous solution, were investigated. The sawdust was characterized using Scanning Electron Microscopy, Fourier Transform Infrared spectrophotometry, X-ray diffraction, and pH point of zero charge. Batch adsorption experiments were carried out to determine the equilibrium characteristics, thermodynamics, and kinetics of the sorption processes. The data obtained were subjected to various isotherm and kinetics equations. The results showed that the adsorption processes were described by different isotherm models depending on the composition of the system; they were all spontaneous (ΔG ranges from -0.72 to -5.36 kJ/mol) and endothermic (range of ΔH is 11.37 – 26.31 kJ/mol) and with increased randomness with ΔS values of 55.55 and 98.78 J·mol⁻¹/K for single and ternary systems, respectively. Pseudo-second-order kinetics model gave better fit for all the sorption systems studied irrespective of the differences in composition, with the initial and overall rate constants higher for the mixtures than for the single system (6.76 g·mg⁻¹·min⁻¹). The presence of Rhodamine B and Methylene Blue had a synergetic effect on the maximum monolayer capacity of the adsorbent for Acid Blue 161 dye.

1. Introduction

Many industries make use of dyes to colour their products in order to make them more attractive; and the unspent dyes are eventually discharged as coloured wastewater into the aquatic environment [1–3], which then impart colour to water bodies. An estimated fifteen percent of the dye produced globally is lost during the dyeing process and is released into textile effluents [4]. The discharge of highly coloured effluents into natural water bodies is aesthetically displeasing and reduces light penetration, thereby affecting biological processes in the aquatic environment [5]. Some dyes used in textile industries are toxic to aquatic organisms and can be resistant to natural biological degradation. Hence, the removal of synthetic organic dyestuff from effluents is of great importance to the environment [6]. Most of the dyes are stable against photodegradation, biodegradation, and oxidizing agents [7, 8].

Though many methods have been employed in the remediation of dye-containing wastewater, they are associated with different shortcomings [9–11] and adsorption has been reported by overwhelmingly numerous researchers, to be very effective, simple, and versatile [11–18]. Efforts are ongoing on the search for inexpensive materials to replace the efficient but uneconomical activated carbon which has gained wide acceptance as adsorbent in the treatment of wastewater. Serious attention has been drawn to investigating low-cost materials especially agricultural wastes, the disposal of which in many cases is a challenge in many communities. Several lignocellulosic waste materials such as sugarcane bagasse and peanut biomass have been investigated for their ability to remove dyes by adsorption from aqueous solutions [19–21].

However, wastewaters from textile and other related dye-using industries rarely contain only a single dye, but a mixture

of dyes. As stated by Olajire et al. [22], it is very important to note that the adsorptive characteristics of a dye may be influenced by the presence of other dye(s) in the system. Comparatively few studies have been reported on the removal of dyes in multicomponent and competitive environment [22–25].

Though many economic materials such as agricultural wastes have been investigated for their ability to remove different dyes in single systems, limited studies have been reported on the adsorption of dyes in multiadsorbate systems. It is therefore the aim of this study to investigate the biosorption of Acid Blue 161 in a competitive environment using the sawdust of locust bean tree (*Parkia biglobosa*). Though this agrowaste has been used for the adsorption of some heavy metals (copper, lead, and nickel) and a basic dye (Rhodamine B) in single, binary, and ternary systems [24, 26], its use for the removal of any acid dye and in a multidye medium has not been reported.

2. Materials and Methods

2.1. Preparation of Adsorbent. The sawdust of *Parkia biglobosa* used in this study was collected from a popular wood industry in Ogbomoso, Nigeria. It was washed several times with distilled water, drained, dried at 105°C for 15 hours, sieved, and then stored as *Parkia biglobosa* raw sawdust (RSD).

2.2. Characterization of Adsorbent. For the characterisation of RSD, its infrared spectra were recorded before and after the adsorption of dye with a Nicolet Avatar FTIR in the range of 4000 cm⁻¹ and 450 cm⁻¹. The surface morphology of the adsorbent was studied with the aid of a Hitachi 2300 scanning electron microscope. X-ray diffraction analysis was conducted to determine the X-ray diffraction patterns of the adsorbent using an X-ray diffractometer (by Philips Analytical) equipped with a monochromator and CuK radiation source (40 kV, 55 mA).

The pH point of zero charge (pH_{zpc}) of RSD was determined as reported in an earlier work by Nausheen et al. [21]. This was accomplished by adding 0.1 g of the adsorbent to a 200 mL solution of 0.1 M NaCl of predetermined initial pH (pH_i). The initial pH of NaCl solutions in different flasks to which the adsorbent was added was adjusted with 0.1 M NaOH or HCl. The flasks were covered and shaken for 24 hours after which the final pH (pH_f) was measured using a Jenway pH meter. A plot of change in pH (pH_i – pH_f) against initial pH gives pH_{zpc} where the plot crosses the horizontal axis [27].

2.3. Preparation of Adsorbate. The primary adsorbate in this study is an anionic dye, Acid Blue 161 (AB), by M & B Laboratory Chemicals. Working aqueous solutions of different concentrations of Acid Blue 161 dye were prepared from the stock solution of the dye (1000 mg/L) in the single dye system. In the binary system, either Rhodamine B (RB) dye or Methylene Blue (MB) dye was present in predetermined concentrations with the primary adsorbate, Acid Blue 161 dye. All three dyes were present as a mixture in the ternary system. Figure 1 gives the structure of the three dyes.

2.4. Batch Adsorption Experiments. A series of 50 cm³ solutions of different concentrations of Acid Blue 161 dye were added to a fixed mass of RSD in clearly labelled glass bottles with lids and were agitated in a Uniscope thermostated horizontal mechanical shaker (SM 101 by Surgifriend Medicals) at a constant speed, temperature, and pH, until equilibrium was attained. Additional series of batch experiments were performed to study the effects of RSD dose, contact time, and temperature using different masses of RSD, predetermined contact times, and temperature, respectively. The dye-RSD mixtures in the various flasks were filtered and the absorbance of the filtrate was measured with a GENESYS 10 UV-Visible Scanning Spectrophotometer at the predetermined absorption wavelength, λ_{max}, of Acid Blue 161 dye (610 nm).

The amount of dye adsorbed per unit mass of RSD (i.e., adsorption capacities of RSD), q (mg/g), was evaluated using the following equations:

$$q_e = \frac{(C_o - C_e)V}{m},$$

$$q_t = \frac{(C_o - C_t)V}{m},$$
(1)

where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at time t , respectively; C_o , C_e , and C_t (mg/L) are the initial concentration of dye (at $t = 0$), concentration of dye at equilibrium, and its concentration at time $t = t$, respectively; V is the volume of the solution (L); and m is the mass of RSD (g).

3. Results and Discussion

3.1. Characterization of RSD. FTIR spectra of RSD before and after adsorption of dyes are shown in Figure 2. *Parkia biglobosa* sawdust is a complex natural material as its FTIR spectrum presents several absorption peaks even before the adsorption of any dye (Figure 2(a)). As expected of a cellulosic, hemicellulosic, or lignin material, the spectrum displays diagnostic bands at 3417 cm⁻¹, 1647 cm⁻¹, and 1734 cm⁻¹ which can be assigned to bonded –OH, aromatic C=C, and carbonyl (C=O) functional groups, respectively. These are likely adsorption sites for the chemisorption of an adsorbate [4, 20].

After adsorption of Acid Blue 161, the FTIR spectrum of the adsorbent showed that there are shifts in the position of some bands to higher frequencies (Figure 2(b)). These include the shift in the band assigned to –OH from 3417 cm⁻¹ to 3421 cm⁻¹ and C=O band from 1647 cm⁻¹ to 1653 cm⁻¹. A new band was noticed at 3726 cm⁻¹ after the adsorption of the dye. This can be assigned to the O–H stretching vibration, possibly from water molecules of the dye solution. These shifts in adsorption bands suggest some kind of chemical interaction between the surface of RSD and the dye molecules.

Other results of characterization are presented in Figure 3. The scanning electron micrograph of RSD recorded at ×1000 magnification is depicted in Figure 3(a). The image reveals an irregular and porous surface topography of the adsorbent. This may be a pointer to a high surface area of

FIGURE 1: Structures of (a) Acid Blue 161, (b) Methylene Blue, and (c) Rhodamine B.

FIGURE 2: FTIR spectra of RSD (a) before and (b) after adsorption of Acid Blue 161.

the material, a quality of a good adsorbent [26, 28]. The pH at the point of zero charge, pH_{zpc} , is 7.83 as shown in Figure 3(b). At any pH below this value, the surface of the adsorbent should be positively charged and will attract negatively charged species in the solution. At pH above pH_{zpc} of the adsorbent, the surface of the adsorbent is negatively charged and attracts cations [29]. The X-ray diffraction patterns of RSD adsorbent are presented in Figure 3(c). The patterns were obtained by continuous scanning type from 5.04 to 60° . Raw results obtained were recorded using the PC-APD software. One sharp peak was recorded at 2θ value of 23.6 with the highest intensity, while two broad peaks were observed around 34.7 and 46.62 (Figure 3(c)).

3.2. Effects of Adsorbent Dose on Acid Dye Adsorption. Specific uptake of Acid Blue 161, q_e (i.e., adsorption of Acid Blue 161 per unit mass of adsorbent), decreased with increasing dose of RSD for all the adsorbate systems (single, binary, and ternary systems) studied as shown in Figure 4. As the dose of RSD increased from 0.1 to 0.6 g, the adsorption capacity, q_e ,

decreased steadily from 10.32 to 1.841 mg/g in single dye system containing Acid Blue 161 only; from 7.55 to 2.12 mg/g in the binary system comprising Acid Blue 161 and Rhodamine B (AB + MB); and from 10.36 to 1.79 mg/g in the binary system consisting of Acid Blue 161 and Methylene Blue (AB + RB). A decrease in the uptake density (7.59 to 1.69 mg/g) was also observed in the ternary system where all the three dyes were present. These observations may be due to the effective utilization of active sites on the surface of RSD at low doses. But a sizeable portion of the available active sites on the adsorbent may have overlapped as adsorbent dose increased, resulting in reduced specific uptake recorded. Similar observations have been reported elsewhere for the adsorption of Rhodamine B in single, binary, and ternary systems by Giwa et al. [24] and other sorption processes [29–31].

3.3. Effects of Solution pH on Acid Dye Adsorption. The pH of an aqueous system controls the speciation and degree of ionization of the adsorbate in an adsorption process. It is therefore a very important factor in adsorptive remediation

FIGURE 3: (a) SEM image (magnification: $\times 1000$), (b) pH point of zero charge (pH_{zpc}) plot, and (c) X-ray diffraction patterns of RSD.

of wastewater. The effect of pH on the adsorption of Acid Blue 161 on RSD is presented in Figure 5. The adsorption capacity, q_e , was relatively high in the acidic pH region, attaining its maximum at around 3 and reducing with increasing pH afterwards. This may be due to the increase in OH^- ions competing with the anion groups on the dye for adsorption sites on RSD, with an increase in pH. Also, at pH below pH_{zpc} of the adsorbent, the surface of the adsorbent is positively charged and thereby electrostatically attracts anionic dyes [29]; and this enhances the adsorption of Acid Blue 161. Similar observations on high adsorption capacity of acid dye at acidic pH values have been reported by Hameed et al. [30] and Yang et al. [32].

3.4. Effects of Initial Dye Concentrations on Acid Blue 161 Adsorption. In investigating the effects of initial concentration of Acid Blue 161 on its adsorption onto RSD, a total of six different adsorbate systems were considered, with the series of initial concentrations of Acid Blue 161 being the same in all: (i) Acid Blue 161 only (single system), (ii) Acid Blue 161 together with 10 mg/L Methylene Blue (AB + MB₁, binary system), (iii) Acid Blue 161 together with 20 mg/L Methylene Blue (AB + MB₂, binary system), (iv) Acid Blue 161 together with 10 mg/L Rhodamine B (AB + RB₁, binary system), (v) Acid Blue 161 together with 20 mg/L Rhodamine B (AB + RB₂, binary system), and (vi) a mixture of Acid Blue 161 and

20 mg/L of Methylene Blue and 20 mg/L of Rhodamine B (AB + MB + RB).

The adsorption capacity of RSD for Acid Blue 161 (i.e., adsorption of Acid Blue 161 per unit mass of RSD) increased with increasing initial concentration of Acid Blue 161 for all the adsorbate-adsorbent systems whether single, binary, or ternary system, as shown in Figure 6. As the initial concentration of Acid Blue 161 increased from 10 mg/L to 100 mg/L, q_e increased from 4.48 to 20.61 mg/g in the AB single dye system, from 4.32 to 28.60 mg/g in AB + MB₁ binary system, from 3.96 to 22.81 mg/g in AB + MB₂ binary system, from 4.39 to 21.87 mg/g in AB + RB₁ binary system, from 4.35 to 20.76 mg/g in AB + RB₂ binary system, and from 4.24 to 19.71 mg/g in the ternary dye system. The observed increase in the specific uptake of the dye with increasing initial dye concentration in all the systems may be because, at low concentrations, the number of dye molecules available is low, but, at higher concentrations, the number of dye molecules available is high enough to overcome resistance to mass transfer. Bello et al. [33] and Giwa et al. [26] reported similar observations.

At low but equal initial concentrations of Acid Blue 161 dye, there were marginal increases in adsorption capacity with decreasing concentration of the competing dye. For example, at 10 mg/L initial Acid Blue 161 concentration, adsorption capacity of RSD for the dye was 4.48, 4.32, 4.39, and 4.35 mg/g for single, AB + MB₁, AB + RB₂, AB + RB₁,

TABLE 1: Kinetics parameters for adsorption of Acid Blue 161 onto raw sawdust.

Adsorbate system	$q_{e,exp}$	R^2	Pseudo-1st order			Pseudo-2nd order		
			$q_{e,calc}$	k_1	R^2	$q_{e,calc}$	k_2	h
AB	10.38	0.866	3.55	0.159	0.998	11.11	0.055	6.76
AB + MB	11.31	0.976	1.10	0.119	0.999	11.49	0.216	28.57
AB + RB	10.97	0.980	0.51	0.046	0.999	11.11	0.219	27.03
AB + MB + RB	11.51	0.701	1.08	0.087	0.998	11.90	0.118	16.67

FIGURE 4: Effects of RSD dose on adsorption of Acid Blue 161 on raw sawdust.

and AB + RB₂ systems, respectively. This may be due to the competitive nature of the adsorption processes.

3.5. Effects of Contact Time and Kinetics. Adsorption of Acid Blue 161 in single, binary, and ternary dye systems increased as contact time increased (Figure 7) until equilibrium was attained. Equilibrium was reached relatively faster in binary and ternary systems than in the single dye system. This may be due to the contribution of concentration to the rate of the reactions. Though the initial concentration of Acid Blue 161 which is the focus of the study was the same in all the systems, the total concentrations of dyes in the mixture systems were higher than in the single system (AB only) as a result of the presence of the other dyes (Rhodamine B and/or Methylene Blue) in the mixture (AB + MB, AB + RB, and AB + MB + RB).

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of the adsorption of Acid Blue 161 were examined using the pseudo-first-order model [34] and pseudo-second-order equation by Ho et al. [35]. The linear forms of the models are given as follows.

FIGURE 5: Effects of pH on adsorption of Acid Blue 161 on raw sawdust.

The pseudo-first-order equation is given as follows:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t. \quad (2)$$

The pseudo-second-order equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (3)$$

where q_t is the adsorption capacity at time t ($\text{mg} \cdot \text{g}^{-1}$), k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}), and k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the pseudo-second-order rate constant.

The linear plots of the two equations are shown in Figure 8, and the rate parameters obtained thereof are given in Table 1. The kinetics of adsorption for all the four adsorbate systems (one single system, two binary systems, and one ternary system) are best described by the pseudo-second-order rate model. They all have high R^2 values >0.99 . In addition to this, there is a better agreement between the experimental and calculated values of q_e for pseudo-second-order model than for pseudo-first-order model (Table 1). The conformation of the kinetics of the sorption processes to pseudo-second-order equation suggests a rate limiting step involving chemisorption [36, 37]. The pseudo-second-order overall rate constant, k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$), and the initial rate constant, h , are both higher for the dye mixtures than for the single Acid Blue 161 dye system.

TABLE 2: Isotherm parameters for the adsorption of Acid Blue 161 onto raw sawdust.

Adsorbate system	Langmuir			Freundlich			Temkin and Pyzhev		
	R^2	q_m	K_a	R^2	K_F	$1/n$	R^2	A_T	b_T
AB	0.991	40.0	0.02	0.998	1.48	0.651	0.924	4.12	0.351
AB + MB	0.982	100	0.5	0.983	13.84	0.284	0.999	417.79	1.22
AB + RB	0.964	100	0.25	0.991	10.09	0.213	0.855	133.05	1.92
AB + MB + RB	0.954	94.3	0.28	0.904	3.69	0.237	0.848	10.41	1.77

FIGURE 6: Effects of initial dye concentration on adsorption of Acid Blue 161 on RSD.

3.6. Adsorption Isotherm Modelling. The adsorption equilibrium isotherm gives the relationship between the adsorbates in the liquid phase and on the surface of the adsorbent at equilibrium at constant temperature. In this study, the equilibrium concentrations of the residual Acid Blue 161 dye solution (C_e) and the various amounts of the dye adsorbed on the surface of RSD (q_e) for single, binary, and ternary systems were modelled after the linear forms of Langmuir (1918) [38], Freundlich (1906) [39], and Temkin and Pyzhev (1940) [40] isotherm equations so as to describe the equilibrium relationship at constant temperature. Comparative applicability of the isotherm models was determined using the correlation coefficients, R^2 , of the linear plots. The linear forms of the equations applied in this study are given below.

Langmuir model is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{C_e}{q_m}. \quad (4)$$

Freundlich isotherm is given as follows:

$$\log q_e = \log K_F + \log C_e. \quad (5)$$

FIGURE 7: Effects of contact time on the adsorption of Acid Blue 161 on raw sawdust.

Temkin and Pyzhev model is given as follows:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e, \quad (6)$$

where C_e is the equilibrium concentration of adsorbate (mg/L); q_e is the amount of adsorbate absorbed per unit mass of adsorbate ($\text{m} \cdot \text{g}^{-1}$); q_m and K_a are Langmuir constants related to monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively; K_F is the Freundlich constant which is an indicator of the adsorption capacity related to bond energy and is the adsorption intensity on the adsorbent or surface heterogeneity; A_T and b_T are Temkin and Pyzhev constants; R is the universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$); and T is the temperature in kelvin [31, 41, 42].

The equilibrium isotherm parameters obtained from the linear plots of the linearized isotherm equations together with their respective correlation coefficients for the adsorption processes are given in Table 2.

The coefficients of correlation, R^2 , presented in Table 2 are high for the three isotherm models, implying that the adsorption processes exhibit different characteristics at different stages, which influenced the final mechanism. This is an indication that the adsorption of Acid Blue 161 is a complex process.

FIGURE 8: Plots of (a) pseudo-first-order and (b) pseudo-second-order kinetics for adsorption of Acid Blue 161 onto RSD in single and mixture systems.

Langmuir isotherm model assumes monolayer adsorption onto a finite number of adsorption sites on the surface of an adsorbent and with no transmigration of adsorbate in the plane of surface [43]. The Langmuir maximum monolayer coverage, q_m , for the adsorption processes in this study was relatively low (40 mg/g) for the single Acid Blue 161 adsorbate system when compared with the two binary and ternary systems which have values of 100 mg/g and 94.34 mg/g, respectively (Table 2). This shows that, with respect to the monolayer adsorption capacity, the presence of Rhodamine B and Methylene Blue dyes in the system has a synergetic effect on the adsorption of Acid Blue 161. This, however, is contrary to the report on the adsorption of Methylene Blue on melon husk in single and ternary dye systems with two acid dyes where the monolayer capacity was higher in single system than in ternary dye system [22]. The Langmuir constant, K_a , a measure of the affinity between adsorbate and adsorbent which is related to free energy of adsorption [44], was higher in mixture systems than in the single system (0.018 L/g) (Table 2). The synergetic effect was more pronounced with Methylene Blue (0.5 L/g) than with Rhodamine B (0.25 L/g). Though both dyes are classified as basic, Rhodamine B can behave in an "amphoteric" manner depending on the medium. This is also evident in the ternary system where the value for the Langmuir constant (0.275 L/g) was between those of Methylene Blue and Rhodamine B binary systems, respectively (Table 2).

As for the Freundlich model, R^2 values for the adsorption processes are high (0.904–0.998) (Table 2), suggesting possible heterogeneous nature of the RSD surface and the possibility of multilayer adsorption on it. The Freundlich constant, K_F , is an empirical constant, which indicates the sorption

capacity of adsorbents in mg/g. This constant is higher in binary and ternary dye mixture than in the single Acid Blue 161 system (Table 2). A high K_F value may also indicate that the rate of adsorbate removal is high [45]. Again, the binary dye system with Methylene Blue gave the highest K_F value, in agreement with the results obtained from Langmuir model (Table 2). The values of $1/n$, another Freundlich constant which is a measure of adsorption intensity or surface heterogeneity, are below 1 for all the adsorption processes under investigation. This implies favourable adsorption processes [44].

The Temkin and Pyzhev isotherm is considered so as to investigate the energy relationship in the Acid Blue 161 and RSD interaction. Since R^2 values obtained from the plots of the isotherm equation are also high, the model is suitable for the processes involved. It can, therefore, be deduced that the energy associated with the adsorption of Acid Blue 161 dye in all the systems decreases linearly with coverage as assumed by the Temkin and Pyzhev isotherm model [46]. This also suggests that there were adsorbate-adsorbate interactions in the processes of the adsorption under study (Table 2). Values obtained for Temkin and Pyzhev parameter A_T , which is a measure of the adsorption potential, are higher in the mixture systems than in single Acid Blue 161 system. This follows the same trend as recorded for the Langmuir isotherm (Table 2). The constant b_T , which relates to energy of adsorption, has its values between 0.35 and 1.92 kJ/mol. This is lower than the range 8–16 kJ/mol associated with bonding energy for ion-exchange mechanism in adsorption [34]. This implies that the association between Acid Blue 161 and RSD adsorbent in all the four adsorbate-adsorbent systems under study might not involve an ion-exchange mechanism but may be

FIGURE 9: Effects of temperature (a) and thermodynamics (b) of adsorption of Acid Blue 161 on RSD.

physiosorption. However, this assertion does not rule out the possibility of chemisorption, as not all chemical interactions are by ion-exchange mechanism. The conformation of the adsorption processes to pseudo-second-order rate model, as stated earlier, suggests an element of chemisorptions in the process, particularly in the rate determining step. Positive value of b_T implies that the adsorption processes were endothermic.

3.7. Thermodynamics of Adsorption of Acid Blue 161 Dye on RSD. The effects of temperature on the adsorptive removal of Acid Blue 161 in single and mixture systems were investigated by performing batch adsorption experiments at four different temperatures: 303, 313, 323, and 333 K. The results are depicted in Figure 9. As clearly shown in the figure, the adsorption capacity, q_e , of RSD for Acid Blue 161 dye increased with increasing temperature in the single, binary, and ternary dye systems. The effect was, however, more pronounced in the ternary mixture than in others. With the increase in temperature, more dye molecules gained additional energy to overcome the energy barrier in chemisorption processes. Also, the increase in temperature must have resulted in a change in the morphology of the RSD adsorbent, leading to increased pore sizes and thereby allowing easier penetration of dye molecules [47].

The changes in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) of the adsorption processes were the thermodynamic parameters evaluated from the data obtained from batch adsorption experiments conducted at the different temperatures. The following equations were employed:

$$\Delta G = -RT \ln K_o,$$

$$K_o = \frac{q_e}{C_e},$$

$$\Delta G = \Delta H - T\Delta S. \quad (7)$$

Therefore,

$$\Delta H - T\Delta S = -RT \ln K_o. \quad (8)$$

In linear form,

$$\ln K_o = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \quad (9)$$

where K_o 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, and ΔS ($\text{K}\cdot\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$) is the entropy change.

Figure 9(b) shows the plots of $\ln K_o$ versus $1/T$ for the adsorption of Acid Blue 161 in single and mixture adsorbate systems at different temperatures. The corresponding enthalpy change, ΔH , and entropy change, ΔS , obtained from the slopes and intercepts and the free energy changes, ΔG , evaluated using (9) are presented in Table 3.

The change in Gibbs free energy, ΔG , for the adsorption of the dye in all the four systems investigated is negative, ranging from -0.72 to -5.36 kJ/mol. This is an indication that the sorption processes were spontaneous and thermodynamically feasible. In each system, the adsorption process became more feasible with increasing temperature (Table 3). Similarly, all the adsorption processes in the adsorbate systems studied were endothermic as the enthalpy change, ΔH , for

TABLE 3: Thermodynamic parameters for adsorption of Acid Blue 161 in single, binary, and ternary mixture on RSD.

Temp.	Single system		Binary system (AB + MB)			Binary system (AB + RB)			Ternary system (AB + MB + RB)		
	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔH (KJ/mol)	ΔS (J/molK)	ΔG (kJ/mol)	ΔH (KJ/mol)	ΔS (J/molK)	ΔG (kJ/mol)	ΔH (KJ/mol)	ΔS (J/molK)
303	-0.89		-0.72			-1.62			-2.29		
313	-1.62	15.91	-2.20	19.60	68.19	-2.31	11.37	43.17	-3.09	26.31	93.78
323	-1.82		-2.60			-2.51			-3.41		
333	-2.68		-2.80			-2.98			-5.36		

AB: Acid Blue 161; MB: Methylene Blue; RB: Rhodamine B.

each of them is positive. This explains why the spontaneity of the processes increased with an increase in temperature as heat was absorbed in the course of the interaction between the dye and the surface of the adsorbent. The change in entropy, ΔS , was positive for the four adsorption processes (Table 3). These positive values of ΔS portray increased randomness at the interface between RSD and the dye(s) in both the single and the mixture systems. Increased randomness after adsorption processes has also been reported in several studies [22–24, 48, 49]. This suggests a significant alteration to the internal structure of the adsorbent resulting from these adsorption processes [44].

4. Conclusion

This present study shows that sawdust of *Parkia biglobosa* adsorbent was able to remove Acid Blue 161 from aqueous solutions in single and mixture adsorbate systems. The adsorption processes were all described by pseudo-second-order kinetics while the three isotherm models (Freundlich, Langmuir, and Temkin and Pyzhev) have high correlation coefficients (>0.9) in some cases, implying that at different stages the adsorption processes exhibit different characteristics which influenced the final mechanism. The Langmuir maximum monolayer coverage, Q_o , for the adsorption of Acid Blue 161 dye was lower in the single adsorbate system (40.00 mg/g) than in the two binary and ternary systems which have values of 100.00 mg/g and 94.34 mg/g, respectively; hence, the mixture had a synergetic effect on the adsorption process. All the adsorption processes investigated were spontaneous and thermodynamically feasible as evident from negative ΔG values (ranging from -0.72 to -5.36 kJ/mol). They were endothermic (ΔH range: 11.37–26.31 kJ/mol) and accompanied with increased randomness with ΔS values range of 43.17–93.78 J/mol·K.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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