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Biosorption of Reactive Black 5 in Binary Dye Mixture onto Sawdust of *Parkia biglobosa*

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Abstract: The development and modification of existing processes for the abatement of pollutants in the environment is a continuous exercise. In this regard, the importance of wastewater treatment before its eventual discharge into the environment cannot be overemphasized. Adsorption process has been widely accepted as an efficient method and research is ongoing on the possible application of agricultural residues as adsorbents in wastewater treatment. This study investigates the potential of *Parkia biglobosa* sawdust in removing reactive black 5 dye from aqueous solutions in single and binary dye systems. Several works have been conducted on the adsorption of reactive dyes but reports on their adsorption as a component of a mixture of dyes is scanty. The sawdust, collected from a local sawmill was thoroughly washed, dried and characterized using Fourier Transform-Infrared (FT-IR) spectrophotometer and Scanning Electron Microscope (SEM). Batch adsorption experiments were conducted to determine the effects of adsorbent dose, initial concentration and pH of the dye solution. Five isotherm models were employed in the interpretation of the equilibrium experiments. Kinetics and thermodynamics of the adsorption processes were also studied. The results indicate the presence of functional groups which could be potential adsorption sites for interaction with the dye on the sawdust. The kinetics of the adsorption in both single and binary systems could best be described by the pseudo-second order model and Langmuir gave the best fit for the equilibrium adsorption data (R^2>0.94). The maximum monolayer adsorption capacity of the adsorbent for the dye was low (2.21 mg/G) with no significant difference in the 2 systems. The adsorption processes in all the systems were spontaneous with ΔG becoming increasingly more negative (-0.15-2.81 kJ/mol) as temperature increases. The enthalpy change (ΔH) for the sorption in both systems was positive, indicating that the process was endothermic, the change in entropy (ΔS) was also positive an indication of increased disorderliness on the surface of the adsorbent.

Key words: Reactive black, binary dye system, adsorption isotherm, adsorption kinetics, sawdust, *Parkia biglobosa*

INTRODUCTION

Dyes usually have synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade (Eren and Acar, 2006). Dye producers and consumers are interested in the stability and fastness of dyes and consequently are producing dyestuffs which are more difficult to degrade after being used (Seey and Kassim, 2012). There are more than 10,000 commercially available dyes with over 7×10^5 ton of dyestuff being produced annually across the world (Eren and Acar, 2006).

Textile, cosmetics, food, rubber, leather, pharmaceutical, paper and printing industries and dye houses, make use of dyes in their processes (Iscen *et al*., 2007). The total dye consumption of the textile industry worldwide is more than 10^7 kg/year and about 90% ends on fabrics (Seey and Kassim, 2012). It is estimated that 10-15 % of the dye is lost during the dyeing process and released with the effluent (Akceylan *et al*., 2009).

Reactive dyes are typically azo-based chromophores combined with different types of reactive groups (Eren and Acar, 2006). They differ from all other classes of

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dyes in that they bind to the textile fibres such as cotton to form covalent bonds (Aksu and Tezer, 2000). However, nearly 50% of reactive dyes may be lost in the effluent after the dyeing of cellulose fibres and are highly recalcitrant to conventional wastewater treatment processes (Vijayaraghavan and Yun, 2007). They are also known to have low adsorbability on a wider range of adsorbents (Rachakornkij *et al*., 2004). In this study, the biosorption of reactive black 5 (also known as remazol black B) in binary mixture with a model ionic dye, congo red, onto the sawdust of *Parkia biglobosa* was investigated.

MATERIALS AND METHODS

Preparation and characterization of adsorbent: Sawdust of *Parkia biglobosa* (Locust bean tree) was collected from a local sawmill in Ogbomoso metropolis, Nigeria. It was sorted, washed with distilled water, drained, oven dried and sieved into different particle sizes. It was washed again several times with large quantities of distilled water, so as to ensure the removal of any soluble component that may interfere with adsorption process. It was then oven-dried at 105°C and stored as Sawdust (SD) adsorbent. SD was characterized using scanning electron microscope fourier transform infrared spectroscopy, X-ray diffraction and pH point of zero charge (pH_{zpc}).

Preparation of adsorbate: The adsorbate consists of reactive black 5 (Color Index (C.I), 52015; λ_{max}, 598 nm; molecular weight, M and B laboratory chemicals) singly and in binary mixture with congo red (Color Index (C.I.), 22120; λ_{max}, 500 nm; molecular weight, 696.66, M and B laboratory chemicals). Stock solutions of the two dyes of concentration 1000 mg/L were prepared separately in distilled. Appropriate working solutions were prepared from the stock solutions by accurate dilution with distilled water. Experimental solutions of both single and binary dye mixture of desired concentrations were prepared by mixing appropriate volumes of the stock solutions and accurately diluting it with distilled water (Fig. 1).

Batch adsorption studies: Batch adsorption experiments were conducted to study the effects of SD dose, initial concentration and pH of the adsorbate (the dye) temperature and contact time. The isotherm, kinetics and thermodynamics of the process were also studied. These were carried out by shaking desired doses of the adsorbent with fixed volume of the dye solutions of the known initial concentration solution at predetermined temperature and contact time in a horizontal shaker (SM 101 by Surgafriend Medicals). The mixture was filtered and the residual concentration of the dye determined using UV-VIS scanning spectrophotometer, genesys 10. Changes in the initial pH of the solutions were effected

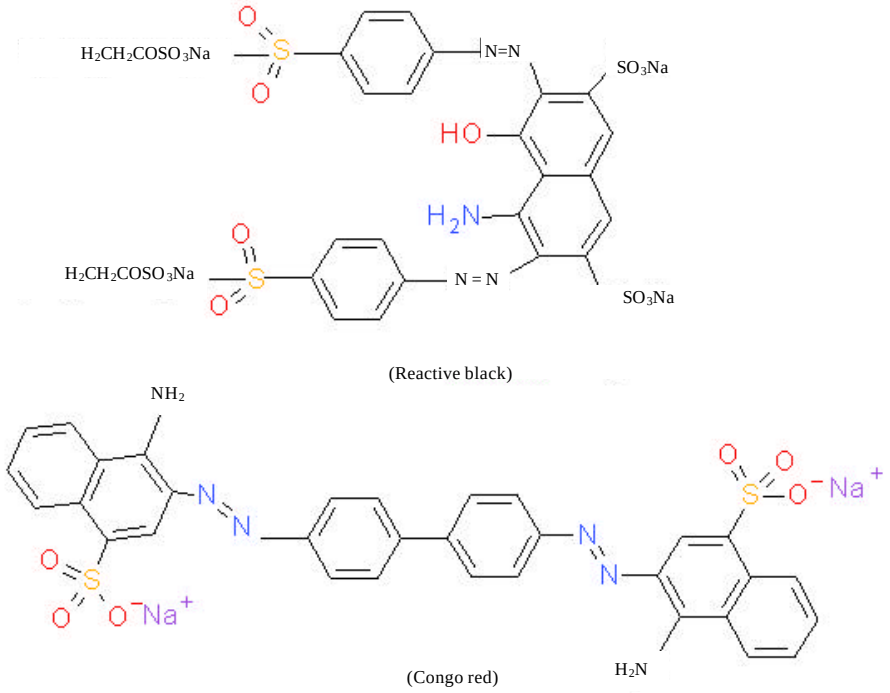

Fig. 1: Structural formula of reactive black and congo red

with 0.1M HCl or 0.1M NaOH solutions to attain the desired pH values. The amount of dye removed was evaluated using the following Eq. 1 and 2:

$$q_e = \frac{(c_o - c_e)v}{w} \quad (1)$$

$$q_t = \frac{(c_o - c_t)v}{w} \quad (2)$$

Where:

q_e and q_t = The amount of dye adsorbed (mg/g) at equilibrium and at time t, respectively

C_o and C_t (mg/L) = The initial concentration of dye (at t = 0) and its concentration at time t = t, respectively

V = The volume of the solution (l) and W is the mass of RSD (g)

RESULTS AND DISCUSSION

Characterization of SD: The FTIR spectrum of SD is presented as Fig. 2. It shows some absorption peaks that revealed the complexity of the sawdust. There are 2 broad bands at 3417 and 3335 cm^{-1} representing bonded-OH of the oxygen-containing functional groups. The positions of the C-H (2918 and 2937 cm^{-1}), aliphatic C-C (1244 cm^{-1}), aromatic C = C (1620 cm^{-1}) and carboxyl/carbonyl (1735 cm^{-1}) vibrations also triple bond C = C/C = N (2142 cm^{-1}) contributed by those in the structure of cellulose, hemicellulose and lignin are indicated by the spectrum of SD. Thus, the FTIR analysis indicates that the SD is represented by functional groups such as COOH, C = O, C = C, C = C and C = N that could be potential adsorption sites for interaction with the dye .

The surface textural structure of SD is presented as scanning electron micrograph Fig. 3 showing the rough texture and porous nature of the surface of the adsorbent. A rough surface is generally an indication of high surface area which enhances adsorption (Demirbas *et al*., 2004).

Effect of initial RB5 concentration on its adsorption: The effect of the initial concentration of RB5 dye on its adsorption by SD is shown in Fig. 4. Adsorption capacity (q_e) increases with increasing initial concentration of RB5 dye. From the Fig. 3 an increase in the initial concentration of the RB5 dye from 10-100 mg/L led to an increase in adsorption capacity (q_e) from 0.234-2.043 mg/g. Similar

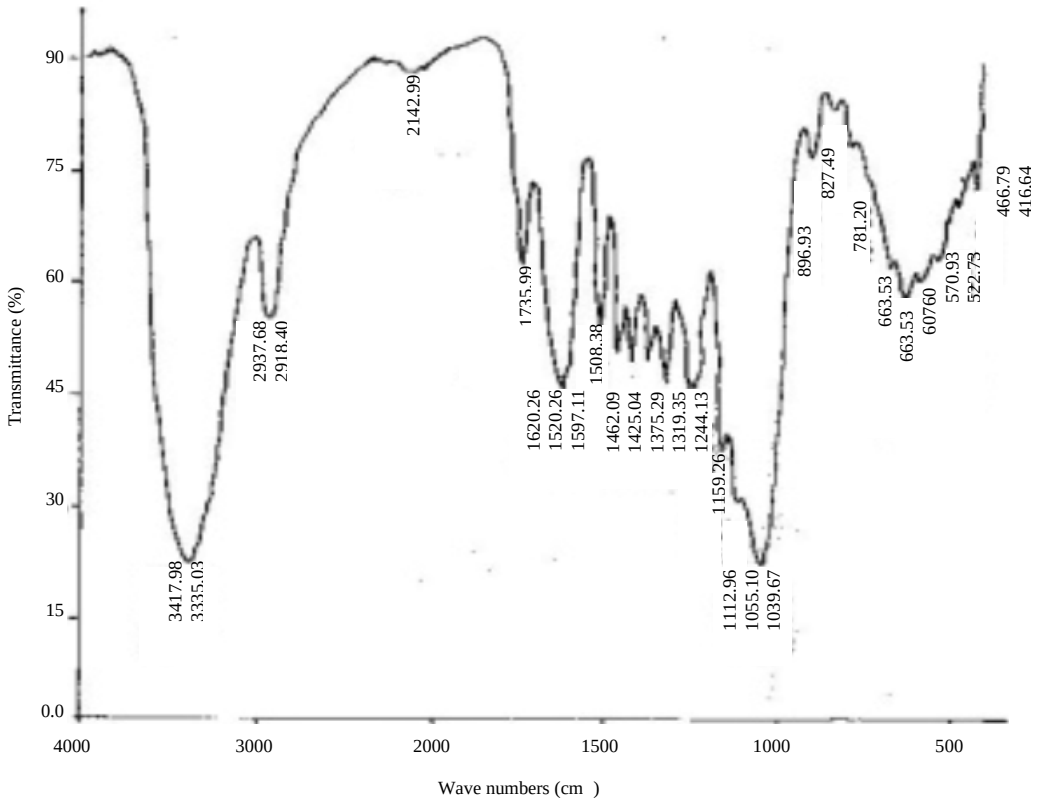

Fig. 2: FTIR spectrum of Sawdust (SD)

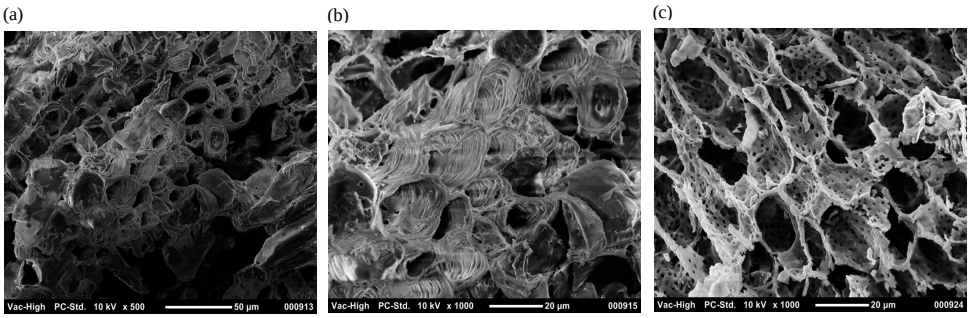

Fig. 3: SEM images of SD at different magnifications: a) ×100; b) ×500 and c) ×1000

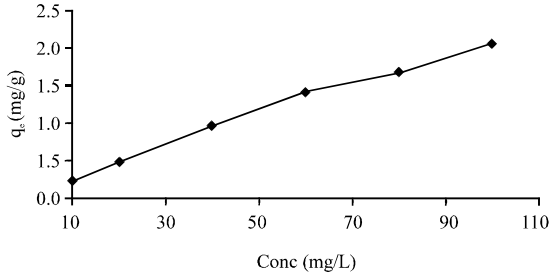

Fig. 4: Effect of initial RB5 concentration on SD adsorption

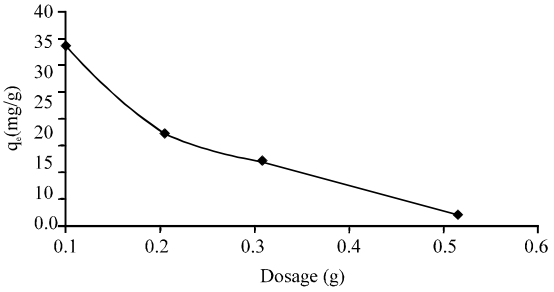

Fig. 5: Effect of SD dose on the adsorption of reactive black 5

observation where increasing initial concentration of sorbate resulted in increased adsorption capacity has been reported in the literature (Handan, 2011). The increase in the initial concentration of the dye enhances the interaction between the RB5 dye molecules and the surface of the adsorbent. Also, at low initial concentrations the amount of dye molecules available is low but at higher concentrations the amount available is high enough to overcome the resistance to mass transfer. This was also reported by other researchers.

Effect of SD dose on the adsorption of reactive black 5: Dose of SD was varied from 0.20-1.00 g in 25 mL of 50 mg/L reactive black 5 solution. The adsorption capacity, q_e that is the mass of reactive black adsorbed by 1 g of SD decreased with increasing dose of the adsorbent. It reduced from 3.33 mg/g at 0.1 g SD dose to 0.83 mg/g at a dose of 1.00 g (Fig. 5). Similar trend was also observed in the adsorption of RB5 on loquat seed (Handan, 2011).

Effect of pH on RB5 adsorption: The adsorption of RB5 by SD was studied at various pH values of the solution (volume 50 mL, concentration 50 mg/L) obtained by adding appropriate amounts of 0.1 M HCl or 0.1 M NaOH. The effect of pH on RB5 adsorption arose apparently from the charge properties of both RB5 and SD. It is

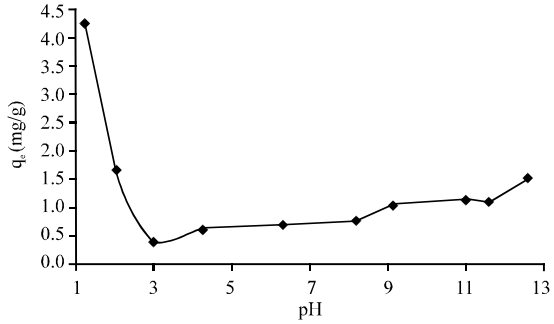

Fig. 6: Effect of pH on RB5 adsorption

attraction between the surface of SD and RB5 dye resulting in high adsorption capacity. Low adsorption capacity of RB5 observed at basic pH is a result of competition between the excess hydroxyl ions and the negatively charged dye ions for the adsorption sites (Iscen *et al.*, 2007). Figure 6 reveals that an increase in pH from 1-3 decreases RB5 adsorption by SD; The adsorption recognized that the surface of SD is protonated and acquire a net positive charge with diminishing solution pH. This causes a significantly high electrostatic capacity decreased from 4.4 -0.5 mg/g and then rises gradually at a very slow rate from 4-11. Similar results have been reported in the literature (Iscen *et al.*, 2007, Vijayaraghavan and Yun, 2007).

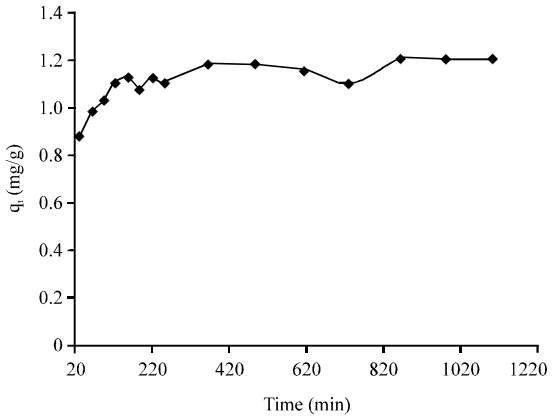

Fig. 7: Effect of contact time on the adsorption of RB5 on SD

Effect of contact time on the adsorption of RB5 on SD: A plot of quantity (qt) adsorbed against time (t) depicts a typical contact time for the removal of RB5 by SD (Fig. 7). The initial rapid phase may be due to the large number of vacant active adsorption sites available at the initial period of the sorption (Wong *et al*., 2009) this makes the concentration gradient to be high thereby enhancing the sorption process (El-Nemr *et al*., 2005). The observed initial rapid sorption of the dye can also be connected with ion exchange on the functional groups on the surface of SD (Ho and Ofomaja, 2006). The increase in quantity adsorbed continued at a slower rate until a quasi-static point was reached at about 480 min. This decrease in adsorption rate has been attributed to the reduction in concentration gradient which is the driving force (Vilar *et al*., 2008) and the gradual uptake of the dye on the inner surface of SD (Ho and Ofomaja, 2006). The enhanced adsorption with increasing contact time can be attributed to the decreasing boundary layer resistance to mass transfer in the bulk solution with time (Horsfall and Abia, 2003).

Kinetics of RB5 adsorption onto SD: The kinetic data was fitted into four models and the kinetic parameters are presented in Table 1. Pseudo-first order model, Pseudo-second order model and Elovich model. Weber-Morris model was also used to know if the diffusion is the only rate determining step.

In the single system in which RB5 only was present, the R^2 value for pseudo-first order model, Pseudo-second order model and Elovich model were 0.368, 0.998 and 0.806 respectively. From the R^2 value, the kinetics followed pseudo-second order model. The low value of SSE (9.04×10^{-4}) for this model confirmed the findings. In the binary system in which RB5 was adsorbed in the presence of 5 ppm CR, the high R^2 value of pseudo-second order model (0.999) makes it the best fit for the kinetics process. The value of SSE which is the lowest for all the models Table 1 further supports these findings.

Table 1: Comparison of rate constants and other parameters for various kinetic models for RB5 in single and binary systems

Parameters	R×B5	Adsorbate system	Values
	RB5 only	RB5+5CR	RB5+10CR
q_e (expt)	1.20	1.19	1.15
Pseudo-first order			
R^2	0.368	0.914	0.882
K_1	2.07×10^{-3}	3.45×10^{-3}	3.45×10^{-3}
q_e (cal)	0.159	0.245	0.252
SSE (%)	0.30	0.27	0.25
Pseudo-second order			
R^2	0.998	0.999	0.999
K_2	5.06×10^{-2}	3.98×10^{-2}	3.70×10^{-2}
q_e (cal)	1.20	1.21	1.17
H	0.0733	0.0581	0.0506
SSE (%)	9.04×10^{-4}	2.14×10^{-3}	4.96×10^{-3}
Elovich model			
R^2	0.806	0.953	0.916
A	33.04	18.57	10.79
B	13.18	11.71	10.79
SSE(%)	0.0588	0.0397	0.0185
Morris-weber			
R^2	0.653	0.843	0.813
K_{id}	0.0083	0.0098	0.0106
X_i	0.955	0.910	0.846
SSE (%)	0.078	3.98	0.333

Table 2: Isotherm model parameters for adsorption of RB5 onto SD

Model/Parameters	RB5 only	RB5+5 ppm congo red	RB5+10 ppm congo red
Langmuir			
R^2	0.959	0.981	0.949
Q_m	2.280	2.290	2.720
K_a	0.310	0.330	0.230
Freundlich			
R^2	0.815	0.763	0.879
1/n	0.513	0.423	0.613
K_f	0.518	0.641	0.491
Temkin			
R^2	0.951	0.904	0.959
β	0.466	0.488	0.559
K_T	3.89	3.60	2.920
D-R			
R2	0.948	0.932	0.872
β	3×10^{-7}	6×10^{-7}	3×10^{-7}
Xm	1.739	1.923	1.587
Harkin-Jura			
R^2	0.427	0.421	0.570
A	0.137	0.414	0.108
B	1.029	1.173	0.879

In the binary system in which RB5 was adsorbed in the presence of 10 ppm CR, the kinetics followed the same trend as that of the first binary system whereby it followed the pseudo-second order model as evident from the high R^2 value and low SSE value Table 1. In all the systems, the diffusion is not the only rate determining step in the process. Similar results were obtained in literature (Iscen *et al*., 2007 and Handan, 2011).

Isotherm of RB5 adsorption onto SD: The 5 different models of isotherm were used to explain the adsorption of RB5 onto SD in single and binary systems. The equilibrium data were fitted into five models and the isotherm parameters are presented in Table 2.

Table 3: Thermodynamics parameters for the adsorption of reactive black 5 in single and binary systems on SD

	Single system (RB5 only)			Binary system (RB5+5 CR)			Binary system (RB5+10 CR)		
Temp (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
303	-0.15			-2.04	-0.15				
313	-2.11	+39.10	+0.13	-3.49	-50.44	+0.17	-1.38	-30.59	+0.10
323	-2.81			-5.51			-2.28		

In the single system, the Langmuir Model described the equilibrium data best having a high R^2 of 0.959 as opposed to that of Temkin (0.951) Dubinin-Radush Kevich (0.948) Freundlich (0.815) and Harkin-Jura (0.427). Also, in the binary system in which RB5 was adsorbed in the presesnce of 5 ppm congo red, the Langmuir Model gave the best fit as evidently seen from the high R^2 (0.981).

The order of fitness of the other 4 models is: Dubinin-Radush Kevich >Temkin >Freundlich >Harkin-Jura. But for the adsorption of RB5 in binary system in which RB5 was adsorbed in the presence of 10 ppm CR, Temkin gave the best fit having an high R^2 of 0.959 followed by Langmuir (R^2 = 0.99) Freundlich (R^2 = 0.879) Dubinin-Radush Kevich (R^2 = 0.870) and Harkin-Jura (R^2 = 0.570). On the overall, Langmuir seems to explain the adsorption on the 2 systems (single and binary) proposing that the adsorption of RB5 onto SD may be physisorption and monolayer. Similar reports was observed in literature (Vijayaraghavan and Yun, 2007).

Thermodynamics of adsorption of RB5 onto SD: A plot of $\ln K_C$ versus 1/T for the adsorption of RB5 onto SD for all the systems and the thermodynamic parameters (ΔG, ΔH and ΔS) are shown in Table 3. In the single system, ΔG is negative indicating the feasibility and spontaneity of the adsorption process at low temperatures. ΔH is positive showing that the process is endothermic and heat can be applied to speed up the rate of the reaction and ΔS is positive indicating good affinity between RB5 and SD and that there is increased randomness in the sorption process on the surface of SD. But in the binary system whereby RB5 was adsorbed in the presence of 5 ppm CR, although the process was feasible as seen from the ΔG being negative but the process was exothermic judging from the fact that ΔH is negative and the ΔS is positive like that of the single system. This implies that in the presence of another adsorbate, heat might not be needed to speed up the rate of reaction. The binary system of RB5 in the presence of 10 ppm congo red followed the same trend as that of the previous binary system.

CONCLUSION

The study investigated the potential of sawdust, a well-known waste in agroforestry for removing Reactive Black 5 (RB5) from aqueous solution in single and binary systems.

The equilibrium time for the sorption of RB5 was 840 min and the optimum dose was 0.800 G. The kinetics of the adsorption of RB5 in both systems could best be described by the pseudo-sec order model.

Temkin, Dubinin-Radushkevich and Freundlich isotherms had high coefficients of determination than that of Harkin-Jura isotherm but it seems Langmuir explained RB5 isotherm better as evidently seen from its higher regression coefficient. Thermodynamically, the sorption of RB5 is feasible as well as spontaneous seeing that its ΔG is negative. Also, the sorption process is endothermic as its ΔH is positive for the single system and one of the binary system but in the binary system comprising of RB5 and 5 ppm congo red, the ΔH is negative. In conclusion, raw sawdust is a very potential adsorbent capable of abating the level of dye residue in wastewaters.

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