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ADSORPTION OF A CATIONIC DYE ONTO ZEA MAYS COBS: ISOTHERMS, KINETICS AND THERMODYNAMIC STUDIES

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ABSTRACT

Efficient adsorbent was prepared from the cobs of Zea mays (RZM). Various physicochemical characterization were determined for the RZM and its efficacy in the uptake of Rhodamine B (RhB) was investigated. Adsorption operational conditions were studied and adsorption data were tested using the five isotherm and four kinetics models. Optimum adsorption was obtained at pH 3. Adsorption data fitted best into the Freundlich adsorption isotherm, maximum monolayer adsorption capacity obtained is 500 mg/g. Pseudo second order best describe the kinetics of uptake of RhB onto RZM. The calculated adsorption energy obtained from D-R model was less than 8 kJ/mol suggesting that the uptake of RhB onto RZM was physical in nature.

Keywords: Biomass, Zea maize, BET, Isotherm, Kinetics and Thermodynamics.

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1. INTRODUCTION

Textile industries use huge volume of water in their various operations as well as discharges huge volume of wastewater hence contribute greatly to water pollution [1, 2]. The composition of their wastewater is complex with dyes being the most difficult constituent.

Dye laden wastewater generated from dye preparation, spent dye bath and washing processes constitute the largest portion of the total textile wastewater. Challenges posed by dye wastewater when released into water bodies vary from reduction in visibility, prevention of sunlight penetration to reduction in dissolved oxygen content of water bodies. Dyes are carcinogenic in nature. A widely used xanthene dye such as rhodamine B (RhB) causes human eye irritation and gastrointestinal disorder [3]. Hence effective treatment of RhB containing wastewater will preserve the water bodies and by extension prevent human exposure to hazardous materials that can affect human health.

Adsorption using activated carbon has been adjudged the best conventional method of wastewater treatment. It is simple to operate with high efficiency in the removal of very low concentration of both inorganic and organic pollutants [4]. The huge cost of precursors as well as preparation of activated carbon however makes adsorption using activated carbon an economically unfriendly wastewater treatment technique. Cheap and available material as alternative to activated carbon will address the economic disadvantage of adsorption technique.

Agricultural residues are carbonaceous and lignocellulosic in nature with numerous surface functional groups thus qualifies as alternative to activated carbon [5, 6].

Various crop residues have been widely used in the removal of dyes such as methylene blue [7, 8], Ramazol brilliant blue [9, 10, 11], Crystal Violet [12, 13], malachite green [14, 15], Congo red [16, 17] amidst others. RhB is widely used across dye utilizing industries because of its easy wet fastness and high solubility characteristics [18]. Its high solubility characteristic makes it difficult to deal with using conventional wastewater treatment technique [19]. Hence economically friendly techniques found effective in the removal of such subtle dyes will protect the water environment from its deteriorating effect.

The aim of this research work is to prepare a low cost adsorbent from a material that would have been a nuisance to us in the environment (Corn cobs) and investigate the efficiency of the adsorbent in the uptake of Rhodamine B (RhB). The kinetics, isotherm and thermodynamics of the adsorption process were studied and herein reported.

2. MATERIALS AND METHODS

All reagent used were of Analytical grade and were used without further purification. Deionized water was used throughout the experiment.

2.1. Adsorbate preparation

Analar grade of RhB was supplied by BDH. Its characteristics are as listed in Table 1. Stock solution of 1000 mg/L RhB was prepared, subsequently lower working concentration was prepared from the stock by serial dilution.

Table 1 Characteristics of Rhodamine B

Parameters	Values
Suggested name	Rhodamine B
C.I number	45170
C.I name	Basic violet 10
Class	Rhodamine
λmax	554nm
Molecular formular	C28H31N2O3Cl
Formular weight	479.02

2.2. Preparation of bioadsorbent (RZM)

Corncobs were collected from Landmark University teaching and research farm, it was washed properly to remove dirts and subsequently dried an oven operated at 55 ^{o}C overnight. Dried corn cobs was then pulverized and screened to a particle size of 150-250µm. RZM was stored in a airtight container for characterization and subsequent use.

2.3. Characterization of RZM

The surface area, pore volume and pore size were obtained using a micrometric Tristar II surface area and porosity analyser. pH point of zero charge (pHpzc) was done using previously reported method [19].

2.4. Kinetics and equilibrium adsorption studies

Various adsorption operational parameters such as initial solution pH, RhB concentration and contact time and adsorbent dosage were investigated. The initial solution pH was varied from 2 to 9, initial RhB concentration from 50 to 400 mg/L, and adsorbent dosage from 1 to 5 g/L. RhB solution pH was adjusted using 0.1 M HCl or 0.1 M NaOH. For each adsorption experiment, 0.1 g of the adsorbent (RZM) was added to 100 cm^3 samples of RhB solution of a specific concentration in a 250 cm^3 glass conical flask. The flask was agitated for a predetermined time in a thermostated water bath shaker operated at 26 $^{\circ}$C and 130 rpm to reach equilibrium. Then the adsorbent was separated from solution by centrifugation. The concentration of unadsorbed dye was determined using a Beckman Coulter Du 730 UV/Vis spectrophotometer at 554 nm. Quantity adsorbed at a given time t was calculated using equation 1 and percentage removal was obtained using equation 2:

$$\boldsymbol{q_t} = \frac{(\boldsymbol{C_i}-\boldsymbol{C_t})}{\boldsymbol{M}} \times \boldsymbol{V} \quad (1)$$

$$\%\,\boldsymbol{Removal} = \frac{(\boldsymbol{C_i}-\boldsymbol{C_t})}{\boldsymbol{C_t}} \times \mathbf{100} \quad (2)$$

Where C_i, C_t and C_f are the initial RhB concentration, the concentration of RhB at time t and final concentration of RhB respectively. V is the volume of RhB solution used for the adsorption studies in liter and M is the weight of the adsorbent in g.

2.5. Mathematical modeling

2.5.1. Isothermal studies

Isothermal studies gives insight into the equilibrium relationship of the amount of adsorbate uptake onto the adsorbent. Equilibrium adsorption data were analyzed using the Langmuir [20], Freundlich [21], Temkin [22], Dubinin–Radushkevich (D–R) [24] and Flory Huggins adsorption models.

Langmuir isotherm assumes a surface with homogeneous binding sites hence suggests that adsorption is onto a monolayer. Langmuir equation is expressed by equation 3 and the dimensionless factor R_L which suggests favourability of adsorption process is expressed by equation 3a;

The Freundlich isotherm well describe adsorption onto heterogeneous surface and it is expressed by equation 4;

Temkin isotherm ignores extremely low and very high concentration as it assumes linear rather than logarithm decrease of heat of adsorption. The linear form of Temkin adsorption isotherm equation is expressed by equation 5;

D-R explains adsorbent porosity and the energy of adsorption (E) viz-a-viz physical or chemical adsorption process. D-R isotherm linear equation is expressed by equation 6, Polanyi potential (Ɛ) and the mean energy of adsorption (E) can be obtained by equations 6a and 6b respectively;

Flory Huggins isotherm accounts for the degree of adsorbate surface coverage and it is expressed by equation (7)

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \quad (3)$$

$$R_L = \frac{1}{(1+K_L C_o)} \quad (3a)$$

$$\text{Log } q_e = \frac{1}{n} \log C_e + \log k_f \quad (4)$$

$$q_e = B\ln A + B\ln C_e \quad (5)$$

$$\ln q_e = \ln q_o - \beta Ɛ^2 \quad (6)$$

$$Ɛ = RT\ln\left(1 + \frac{1}{Ce}\right) \quad (6a)$$

$$E = \sqrt{1}/2\beta \quad (6b)$$

$$\log\left(\frac{\theta}{C_o}\right) = \log K_{FH} + n_{FH} log(1 - \theta) \quad (7)$$

Where C_e is the equilibrium concentration of RhB dye (mg/L), q_e is the quantity of RhB dye adsorbed onto the adsorbent at equilibrium (mg/g), q_{max} is the maximum monolayer adsorption capacity of adsorbent (mg/g) and K_L is the Langmuir adsorption constant (L/mg). K_f and n are Freundlich constants incorporating the factors affecting the adsorption capacity and adsorption intensity respectively. A is the Temkin isotherm constant (L/ g), from the value of Temkin constant B, b (J/mol) which is a constant related to the heat of absorption can be obtained from the expression B = RT/b, T is the temperature (K), R is the gas constant (8.314 J/mol K). β which is the activity coefficient. θ is the degree of surface coverage and it is defined by $\boldsymbol{\theta = 1 - \left(\frac{C_e}{C_o}\right)}$ n_{FH} and K_{FH} which can be obtained from slope and intercept of the linear plot of $\log\left(\frac{\theta}{C_o}\right)$ against log (1- θ) are Flory–Huggin's constants defined as the number of dye molecules occupying adsorption sites and the equilibrium constant of adsorption respectively.

2.5.2. Kinetics model

Kinetics studies that depends on the effects of contact time on RhB uptake onto the prepared adsorbents was well investigated. The kinetic of the adsorption systems were studied using the pseudo-first-order [25], pseudo-second-order [26] and Elovich [27] kinetic model. Intraparticle diffusion [28] and Bangham [29] model was employed in the investigation of the mechanism of adsorption.

Pseudo first-order, Pseudo-second-order and Elovich kinetic model is expressed by equation 8, 9 and 10.

Intraparticle diffusion model by Weber and Morris and the Bangham model are expressed by equation 11 and 12.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

$$t/q_t = 1/k_2q_e^2 + 1(t)/q_e \quad (9)$$

$$q_t = 1/\beta\ln(\alpha\beta) + 1/\beta\ln t \quad (10)$$

$$q_t = K_{diff}\, t^{1/2} + C \quad (11)$$

$$\text{Log log } (\frac{C_i}{C_i - q_t M}) = \log (\frac{K_j M}{2.303V}) + \alpha \log t \quad (12)$$

Where q_e is the quantity adsorbed at equilibrium (mg/g) and q_t is the quantity absorbed at time t (mg/g) and k_1 is the rate constant for the pseudo-first-order sorption min^{-1}. K_2 is the rate constant of the pseudo-second-order kinetic g/mg min^{-1}. α is a constant related to chemisorption rate and β is a constant which depicts the extent of surface coverage. The two constants (α and β) can be calculated from the intercept and slope of the plot of q_t versus lnt respectively. K_{diff} is the rate constant for intraparticle diffusion ($mgg^{-1}min^{-1/2}$). Insight into the thickness of the boundary layer can be obtained from the value of C, large intercept suggests great boundary layer effect. C_i is the initial concentration of dye solution (mg/L), V is the volume of dye solution in mL, M is the mass of adsorbent (g/L), q_t is the quantity of dye adsorbed at time t and α (< 1) and K_j are constants which can be obtained from slope and intercept respectively.

2.6. Validation of adsorption kinetics

Chi square and sum square of error expressed by equations 13 and 14, was used to validate the kinetics model.

$$X^2 = \sum_{i=1}^{n} \frac{(q_{exp} - q_{cal})2}{q_{cal}} \quad (13)$$

$$SSE = \sum_{i=1}^{n} \left(q_{cal} - q_{exp}\right)^2 \quad (14)$$

2.7. Thermodynamic studies

The spontaneity, feasibility and the nature of adsorbate-adsorbent interactions can be explained using the thermodynamic parameter ΔG^o. ΔG^o can be obtained from the mathematical expression 15;

$$\Delta G^o = -RT\ln K_o \quad (15)$$

Where T is the temperature in Kelvin, R is the gas constant and K_o can be obtained from q_e/C_e.

3. RESULTS AND DISCUSSION

3.1. Characteristics of RZM

The BET surface area of RZM was obtained to be 103.48 m^2/g^{-1}. Surface functional groups present in crop residue results in their low surface area [2]. RZM showed a low moisture content suggesting that weighed mass will be equal to utilized mass and moderate bulk density (Table 2) will enhance bioadsorbent equilibration with the adsorbate.

Table 2 Physicochemical properties of RZM

Parameters	Values
	RZM
pH	6.44
pHpzc	6.00
Bulk density/g cm-3	0.16
Moisture content/%	5.60
BET surface area/m2 g-1	103.48
Average pore diameter/nm	268.48

3.2. Effects of solution pH

Optimum RhB removal (81.82 %) was obtained at pH of 3 (Figure 1) and percentage biosorption subsequently dropped drastically afterwards and goes to equilibrium between pH 7 and 9. RhB usually exists in its zwitterionic form in solution pH above its pKa (3.7) hence attraction between the carboxyl and xanthenes groups of RhB monomers results in RhB dimer formation. RhB dimers being very large molecules may not be able to penetrate available pores in RZM hence subsequent decrease in RhB removal from pH and above. Optimum adsorption at pH of 3 were previously reported [29, 30].

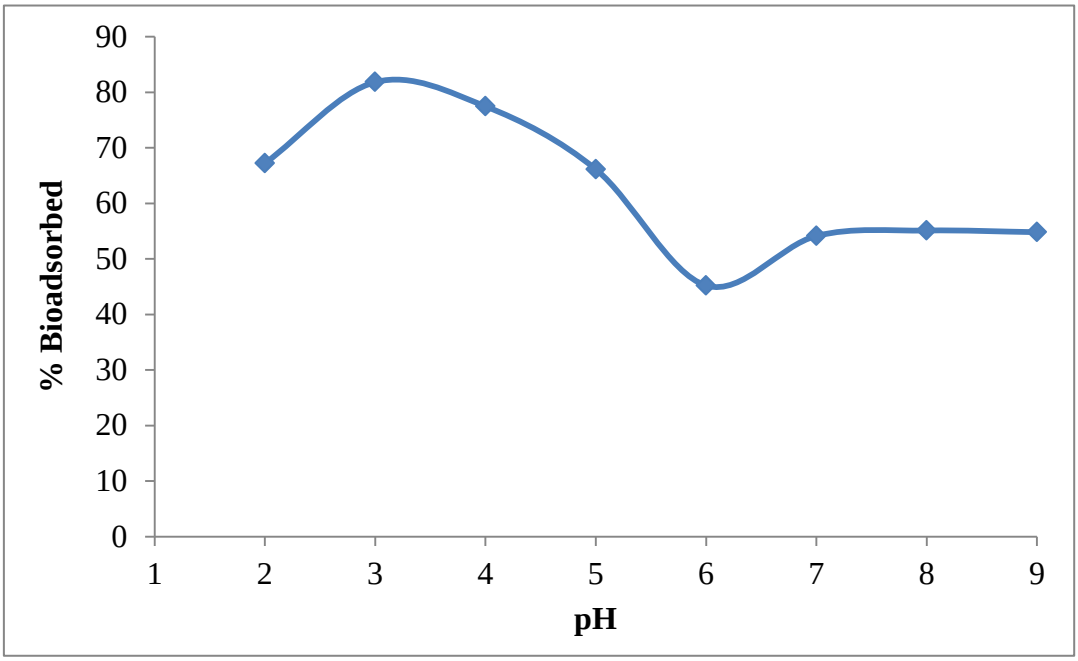

Figure 1 pH effects on the percentage removal RhB uptake by RZM

[Dosage (1g/L), agitation speed (130 rpm), agitation time (30 minutes), Temperature (27 ^{o}C), initial Adsorbate concentration (100 mg/L)].

3.3. Effects of adsorbent dosage

Percentage RhB uptake was observed to increase as adsorbent dosage increased. Percentage RhB adsorbed increased from 75 to 87.5 % as adsorbent dosage increased from 1 g/L to 5 g/L, subsequently no further increase was observed in percentage removal as adsorbent dosage increased from 5 g/L to 7 g/L. Increased available adsorption sites results into increase in percentage adsorption as the adsorbent dosage increased from 1 g/L to 5 g/L (Figure 2) [31]. Agglomeration and saturation of adsorption site results into equilibrium after dosage of 5 g/L [32].

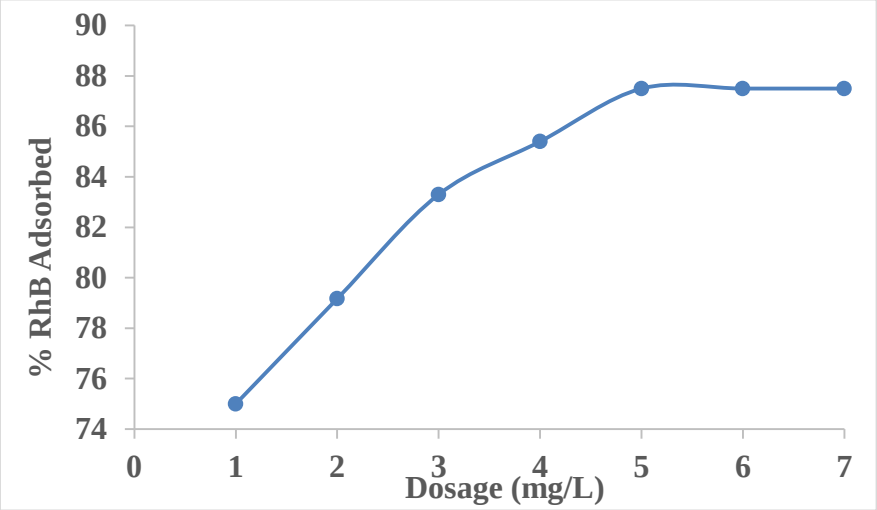

Figure 2 Effects of adsorbent dosage on RhB adsorption onto RZM

[agitation speed (130 rpm), Initial concentration (100 mg/L), Temperature (27 ^{o}C), pH (3)].

3.4. Effects of contact time/concentration

Quantity of RhB adsorbed was observed to increase with increased concentration (Figure 3). High concentration usually provide effective driving force to overcome the mass transfer barrier between solid and liquid phase hence facilitating adsorption. Adsorption of RhB onto RZM was observed to be very rapid reaching equilibrium within the first 20 minutes. Continuous bombardment of the adsorbate on the sorption site also facilitates increased adsorption as time increased. Crop residue surface is known to contain numerous functional groups hence ready contact of the surface functional groups with adsorbate molecule may have resulted into rapid uptake of the adsorbates.

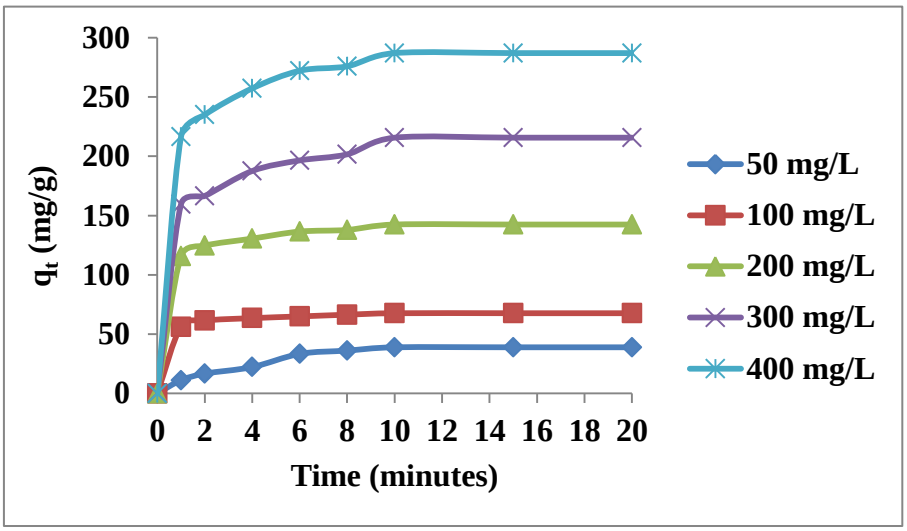

Figure 3 Effects of contact time and initial dye concentration on RhB adsorption onto RZM

[Dosage (1 g/L), agitation speed (130 rpm), Temperature (27 ^{o}C), pH (3)].

3.5. Isothermal studies

Adsorption data fitted best into the Freundlich adsorption isotherm suggesting that RhB uptake was onto a multiple site. The feasibility of the adsorption process was validated by the values of R_L and n which were less than 1 and greater than 1 respectively (Table 2). Correlation coefficient of Langmuir isotherm was obtained to be 0.9190 and the maximum monolayer sorption capacity (q_{max}) was 500 mg/g. The energy of adsorption obtained from the D-R model was obtained to be 7.07 $kJmol^{-1}$ suggesting that adsorption mode was physical in nature. Adsorption data fitted the isotherms used in the order Freundlich>Langmuir> Florry-Huggins>Temkin>D-R models.

Table 2 List of calculated parameters from the Langmuir, Freundlich, Temkin, D-R and Florry-Huggins sorption isotherm models.

Isotherms		**Constants**	**RZM**
Langmuir		q_{max} (mg/g)	500.00
		K_L ($L.mg^{-1}$)	0.0075
		R_L	0.2495
		R^2	0.9190
Freundlich		K_F	4.8978
		n	1.1765
		R^2	0.9960
Temkin		B	103.20
		A (L/g)	0.0843
		b (J/mol)	24.17
		R^2	0.8340
D-R		q_o (mg/g)	238.89
		$\beta(mol^2.kJ^{-2})$	0.0100
		E ($kJmol^{-1}$)	7.0700
		R^2	0.7910
Florry-Huggins		n_{FH}	7.9740
		K_{FH}	56.49
		R^2	0.8510

3.6. Kinetics studies

For the pseudo second order kinetics, close agreement exist between the q experimental and the q calculated, correlation coefficient was close to unity and low values were obtained for SSE and X^2 hence RhB-RZM system was best described by the pseudo second order kinetics model. β_{El} which is related to extent of surface coverage was found to decrease as initial dye concentration increased from 100 mg/L to 400 mg/L (Table 3) suggesting that surface functional must have played a significant role in RhB uptake onto RZM [2]. Multiple adsorption mechanism occurred in the RhB-RZM adsorption system. The Bangham model gives better correlation coefficient than the intraparticle diffusion suggesting that some level of pore diffusion occurred in the uptake of RhB onto RZM. Linearity of Bangham plot (Figure not shown) however suggests that pore diffusion is not the only rate controlling step.

Table 3 Comparison of Pseudo-first-order, Pseudo-second-order, Elovich, Bangham and intra particle diffusion kinetic model parameters for the adsorption of RhB onto RZM

Constants	**Initial concentration**				
	RZM				
	50	100	200	300	400
$q_{e\ experimental}$ (mg/L)	38.89	67.65	142.44	215.69	287.03
Pseudo first order					
$q_{e\ calculated}$ (mg/L)	45.17	13.37	31.77	69.29	89.28
K_1 X 10^{-2} (min^{-1})	33.7	28.83	25.49	20.64	27.36
R^2	0.9586	0.9735	0.9795	0.9887	0.9855
SSE	39.41328	2945.776	12247.85	21435.36	39104.90
X^2	0.872554	220.3273	385.5162	309.3572	438.003
Pseudo second order					
$q_{e\ calculated}$ (mg/L)	46.51	68.49	144.93	222.22	294.12
K_2 X 10^{-3} ($gmg^{-1}min^{-1}$)	6.9	5.61	2.07	0.698	0.77
R^2	0.9834	0.999	0.9998	0.9992	0.9997
SSE	58.03392	0.714025	6.2001	42.53388	50.27377
X^2	1.247773	0.010425	0.04278	0.191404	0.170929
Elovich	42.82	69.19	145.81	221.59	296.66
α_{El} (mg/g.min)	29.75	14.35 x 10^6	25.03x10^5	33.18 x 10^3	13.86 x 10^4
β_{El} (g/mg)	0.094	0.2621	0.1062	0.04666	0.03908
R^2	0.928	0.928	0.954	0.9555	0.952
SSE	15.42918	2.387025	11.3569	34.71331	92.7446
X^2	0.360327	0.0345	0.077888	0.156656	0.312629
Bangham					
α	0.66	0.104	0.13	0.19	0.18
K_i (g)	26.93	86.36	88.78	74.52	80.04
R^2	0.9340	0.9280	0.9550	0.9560	0.9530
Intra particle diffusion					
C X 10^2 (mgg^{-1})	0.066	0.56	1.14	1.48	2.11
K_{diff} ($mgg^{-1}min^{-1/2}$)	8.63	3.01	7.55	17.63	20.48
R^2	0.8321	0.7903	0.838	0.8822	0.8328

3.7. Thermodynamics studies

Calculated Gibbs free energy (ΔG^o) usually explains the feasibility and spontaneity of sorption process. Negative ΔG^o value was obtained (-10.06 kJ/mol) suggesting that the sorption process was spontaneous and feasible.

4. CONCLUSION

Prepared adsorbent (RZM) was found to be effective in the uptake of RhB. Optimum sorption was obtained at pH 3, RhB percentage removal rose up to 87.50 % for adsorbent dosage of 5 g/L. Thus, this dosage may effectively reduce the concentration of RhB in a moderately polluted effluent to an acceptable discharge limit. Freundlich isotherm best describe the sorption of RhB onto RZM suggesting that adsorption was onto a multiple site. Maximum monolayer adsorption capacity was obtained to be 500 mg/g. Adsorption energy (E) suggest that the uptake of RhB onto RH was physical in nature. Elovich and Bangham models suggest that more than one mechanism was involved in the uptake of RhB onto RZM.

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