

Adsorption of Rhodamine B onto Orange Peel Powder

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Abstract Adsorption studies of Rhodamine B (Rh B) on various raw materials and thermally modified biosorbent were carried out by batch experiments. The influence of major parameters governing the efficiency of the process such as, initial dye concentration, adsorbent dose, pH, contact time and temperature on the removal of process were explored. The linear regression coefficient R^2 was used to clarify the best adjustment isotherm model. All isotherm models, Langmuir, Temkin, Dubinin and Freundlich were found to be best adapting models. The monolayer adsorption capacities (q_m) vary between 10.101 to 10.172 mg/g for adsorbents PPOAT and PPOAS. The Lagergren pseudo-second order model best fits the kinetics of adsorption and the correlation coefficient R^2 for second order model has very high values of R^2 for the PPOAT, PPOAA, PPOAS ($R^2 = 0.999, 0.994$ and 0.979 respectively) and q_e (cal) values are in good harmony with q_e (exp). It shows that adsorption of Rh B on these orange peels powders activated thermally and chemically follow the kinetics second order and chemisorption playing role in speed determinant step. Adsorption of Rh B on adsorbents was found to decrease on increasing pH, increasing temperature and increasing adsorbent dose. Thermodynamic analysis proved that adsorption was exothermic, spontaneous physisorption, and decreased disorder at the interface of Rh B with biosorbents.

Keywords Adsorption isotherm, Kinetics, Orange peels powders, Rhodamine B, Thermodynamic parameters

1. Introduction

Textile industry uses wide capacity of water in hail treatment functioning and so, creates considerable quantities of wastewater containing large rising of dissolved dyestuffs and further products, such as dispersing agents, dye bath shippers, salts, emulsifiers, flattening agents and dull metals [1]. Majority of this dyes are artificial or synthetic and chemically and thermally stable, non-biodegradable. Colored dyestuffs are not only esthete, carcinogenic but also fetter light acumen and perturb period processes of living organisms in water [2]. Hence, the rapt of such colored agents from aqueous effluents is necessary. Rhodamine B (Rh B), a basic dye, is very used for the tincture of tissues, cotton, wool, silk, nylon, paper, leather, in color lasers and pigment in pharmaceutical and cosmetic preparation [3,4], etc., between all other dyes of its category. Indeed, Rhodamine B behaves to xanthene class of dyestuff. Hence, it is necessary to exclude these dyes from textile effluent before it is discarded into receiving water bodies [5]. The studies have been conducted in aim to put away color and other pollutions using various types of methods include

ozonation, addition of reducing agents, Fenton's method, membrane filtration, ion-exchange, and adsorption methods where their advantage and disadvantage are extensively discussed in literature [6-10], etc., in which adsorption is most useful due to its simplicity and efficacy. Although, activated carbon adsorption arises to be the one of the most used techniques for dye removal, but because of the relatively high cost and regeneration problems, researchers have developed many technics for alternate low cost adsorbents. The adsorbents were prepared from natural materials such as waste of coffee [11], waste of tea [12], straw of soybeans [13], fly ash [14], walnut shell [15], timber sawdust [16] used for removal of color. Several low cost materials were used for the manufacture of the modified biosorbent; in this research, a local waste, the orange peel powder, was used to produce thermally activated orange peel powder (PPOAT) and chemically activated orange peel powder using phosphorous acid (PPOAA) and sodium hydroxide (PPOAS) for adsorption of Rh B from wastewater.

2. Materials and Methods

2.1. Adsorbents

Adsorbents used in the present study are:

1. Orange peels powders thermally activated (PPOAT)
2. Orange peels powders activated to the soda (sodium hydroxide) (PPOAS)

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3. Orange peels powders activated to the acid (H_2SO_4) (PPOAA)

The materials from the above biosorbents were collected from Ngaoundere Adamawa region of Cameroon and thoroughly washed to remove foulness. Washed materials were dried in an etuve operated at 45°C and a solar energy overnight [17,18]. They were then pulverized and screened into a particle size lower or equal of 1 mm before; they were stored in an airtight container for subsequent use.

2.2. Synthetic Textile Dye Solution

Rhodamine B (Rh B) is a cationic basic dye with a molecular Formula $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$. It has a molecular weight of 479.01 g/mol and the structure is:

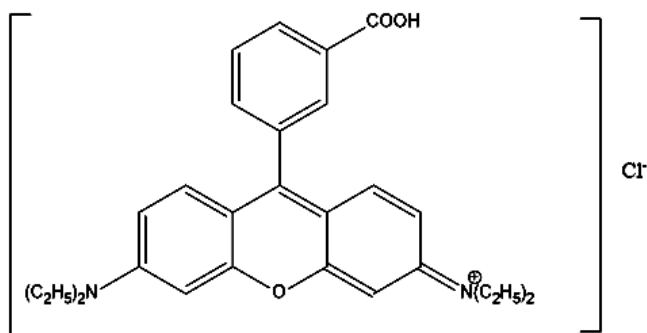


Figure 1. Chemical structure of Rhodamine B

The dye stock solution of Rh B 500 mg/L was prepared by dissolving an appropriate amount of Rh B in distilled water and a serial dilution was used in order to prepare lower Rh B concentrations from the stock solution.

2.3. Adsorbent Characterization

2.3.1. Specific Surface Area

This method (model BET) consist to determinate the necessary amount of methylene blue (MB) to cover a monomolecular layer of the external and internal surfaces of the fine particles of a solid suspended in water.

2.3.2. Iodine Indices

Iodine number is used to measure the porosity of pores with diameters greater than 1nm. The iodine indices of adsorbents were determinated according to the protocole applied by Tchakala et al., in 2012 [19].

2.3.3. Point of Zero Charge

The point of zero charge (pH_{pzc}) was determined using the salt addition method [20]. The pH of solution of 0.01 M NaCl was adjusted between 2-12 by using HCl or NaOH then we add 0.2 g of the adsorbents. The containers were sealed and placed on a shaker for 48 hours at ambient temperature after which the final pH values were measured. The graph of final pH (pH_f) versus initial pH (pH_0) was used to determine the point at which initial pH and final pH of adsorbents solution were equal. At this point, (pH_{pzc}), the surface of

adsorbent is neutral.

2.3.4. pH Determination

The standard test method for determination of activated carbon pH ASTM D 3838-80 was used. About 1.0 g of the prepared adsorbent was weighed and transferred into a beaker; 100 cm^3 of distilled water was added and the mixture was stirred for 24 hours. The suspension was allowed to equilibrate and the pH was measured there after with a pH-meter (VOLTcraft).

2.4. Batch Adsorption Experiments

Batch experiment used in this study was generally carried out by mixing adsorbents (0.01 g) with Rh B solution (50 mL) of specific concentration in Erlenmeyer flasks and agitated at 250 rpm for a certain period of time at room ambient temperature. The concentration of the dye after agitation was analysed using UV-visible spectrophotometer (RAYLEIGH) at wavelength of 554 nm.

In this study, parameters such as contact time (0- 40 min), dosage (0.01–0.11 g), pH (2–10), initial concentration (5–35 mg L^{-1} Rh B) and temperature ($7\text{--}42^\circ\text{C}$) were measured in order to investigate their effects on the adsorption of Rh B onto adsorbent. The amount of dye adsorbed per gram of adsorbent at equilibrium, q_e (mg g^{-1}), is calculated using the following equation [21]:

$$q_e = \frac{C_0 - C_e}{m} V \quad (1)$$

Where C_0 is the initial dye concentration of Rh B (mg L^{-1}), C_e is the dye concentration at equilibrium (mg L^{-1}), V is the volume of dye solution used (L) and m is the mass of adsorbent used (g).

2.5. Methods

Standard solution (10 mg/L) of the Rh B was taken and absorbance was determined at different wavelengths using UV-visible spectrophotometer (RAYLEIGH) to obtain a plot of absorbance verses wavelength. The wavelength correspondent to the maximum absorbance ($\lambda_{\text{max}} = 554 \text{ nm}$) as identified from the plot. pH of solutions were adjusted using 0.1M HCl and 0.1M NaOH by VOLTcraft pH-meter.

The efficacy of adsorbents is estimated by leading laboratory batch mode studies. Specific quantity (0.01 g) of adsorbents were agitated in 50 mL aqueous solution of dye of variable concentration for different time periods at natural pH (7.12) and temperature (298K). At the end of determined time intervals, supernant was analyzed for the residual concentration of Rh B, spectrophotometrically at 554 nm wavelength. Even variation in pH, adsorbent dose, and temperature were studied.

2.5.1. Effect of Contact Time

0.01 g of adsorbent less than 200 μm size with 50 mL of dye solution was maintain constant for batch experiments with an initial dye concentration of 10 mg/L (for PPOAT,

PPOAA, PPOAS) were executed at 298K on a magnetic agitator at 250 rpm for 5, 10, 20, 30 and 40 minutes at pH = 7.12. Then optimum contact time was identified for facility batch experimental study.

2.5.2. Effect of Adsorbent Dosage

Initial dye concentration of 10 mg/L was used in combination with adsorbent dose of 0.01, 0.03, 0.05, 0.07, 0.09 and 0.11 g. Contact time, pH, and temperature of 10 and 20 minutes (PPOAT and PPOAA, PPOAS), 7.12, and 298K respectively were keep constant.

2.5.3. Effect of Initial Dye Concentration

Initial dye concentration of 5, 10, 15, 20, 25 and 30 mg/L were used in slip with adsorbent dose of 0.01 g. Contact time (10 minutes for PPOAT and 20 minutes for PPOAA, PPOAS), pH (7.12), and temperature (298K) were keep constant.

2.5.4. Effect of pH

Initial pH of dye solutions were adjusted to 3, 5, 7 and 11 for 10 mg/L concentration. Contact time, adsorbent dose, pH, temperature of 10 and 20 minutes (for PPOAT and PPOAA, PPOAS), 0.01 g, 7.12, and 298K respectively were keep constant.

2.5.5. Effect of Temperature

280K, 295K and 315K temperatures were used in conjunction with 10 mg/L dye concentration. Contact time, adsorbent dose, and pH of 10 and 20 minutes (PPOAT and PPOAA, PPOAS), 0.01 g and 7.12, respectively were keep constant.

3. Results and Discussions

3.1. Characterisations of Adsorbent

Table 1. Depicts the values of specific area, iodine indices, pH determination and pH_{zpc}

Adsorbents	Specific Area (m ² g ⁻¹)	Iodine indice (mg g ⁻¹)	pH	pH _{zpc}
PPOAT	35.47	753.82 ± 10.77	7.93 ± 0.03	9.15
PPOAA	65.74	468.28 ± 5.38	5.59 ± 0.03	6.88
PPOAS	49.70	441.63 ± 0.00	4.80 ± 0.02	4.50

The values of Brunauer, Emmett and Teller (BET) surface area of the PPOAA have the high specific surface area per report at PPOAT and PPOAS. These values found shows that the adsorption properties are little influenced by their porous structure.

This increase of values of iodine indices is owed at the increase activation temperature [22,23]. The value of pH determination the adsorbent activated thermally is basic so that activated chemically are acid. This difference is owed the nature of activation the support.

According to the concept of point of zero charge, this value indicates the pH at which adsorbents surface is neutral. When adsorbent is subjected to higher pH, the surface would be predominately negative in charge due to the deprotonation of its functional group such as carboxyl group. While, in lower pH, the surface is predominately negative in charge due to the protonation of functional group such as amine group. This parameter is useful in the prediction at which pH the adsorbents can effectively adsorb the adsorbate in solutions.

3.2. Effect of Contact Time and Initial Concentration

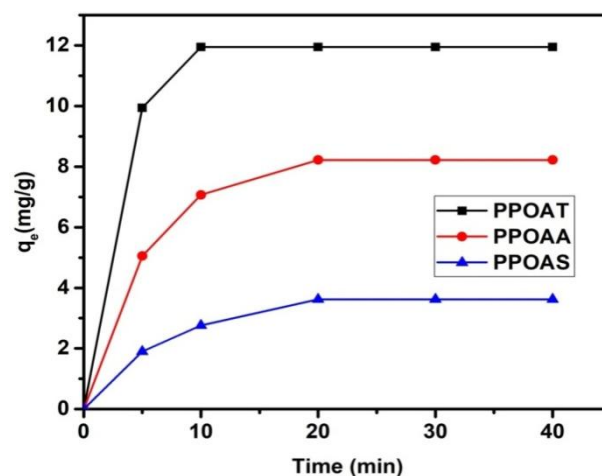


Figure 2. Effect of contact time on adsorption of Rh B

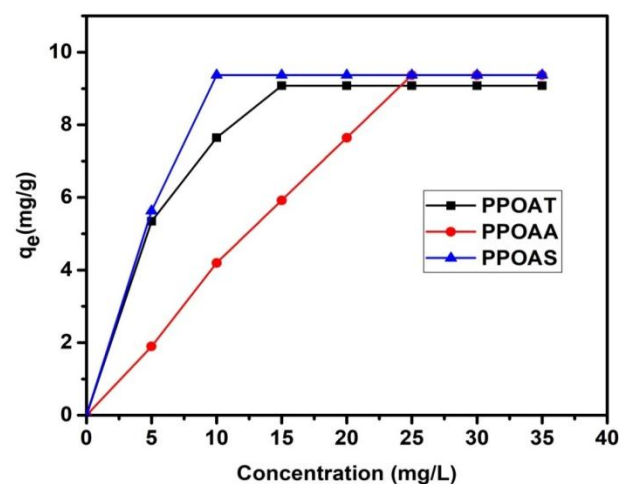


Figure 3. Effect of the initial dye concentration on adsorption of Rh B

Effect of contact time and initial concentration on adsorption of Rh B were presented in Figures 2 and 3. Uptake of Rh B was rapid in first minutes before of tender to saturation at 10 minutes for PPOAT and 20 minutes for PPOAA and PPOAS. The adsorption at different dye concentrations was rapid at the initial stages then stabilizes by forming a bearing. This rapid adsorption at the initial contact time can be attributed to a large number of surface sites are available for adsorption at the initial stages and after a lapse of time, the adsorption becomes less due to a slower

diffusion of the speckles dissolved through the pores of the adsorbent [9,24]. This increase in concentration is due to the increase of attraction forces of the concentration gradient [9,10,25,26]. For these author's, the effect of the initial concentration of dye factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface. There is also a possibility of transportation of the dye molecules within the pores of the active carbon; this can be attributed to a gradient increase of the driving force with the increase of the initial concentration dye.

3.3. Effect of Adsorbent Dosage

The adsorption capacity decreases with increase of adsorbent dose (0.01-1.11 g) hence the amount of adsorbed Rh B per unit mass decreases. This can be explained firstly by the interaction between the adsorbent molecules which leads to the desorption of Rh B molecules from the narrow sites of the adsorbent [27] and on the other hand the reduction of the specific surfaces due to the formation of an aggregation/agglomeration of the particles of adsorbents [9,10]. This decreases could also be explained by the unsaturation of the adsorption sites [28]. Similar result has been obtained by Domga *et al.*, 2015; Zheng *et al.*, 2009 [9,29]. These results show that for an increase in each adsorbent dosage, the adsorbent sites available upon the dye molecules also increase and consequently poor adsorption. Another consequence is the reduction of active sites at the surface of the adsorbents and also the matter rate transfer of the dye at the surface of the adsorbents, this means that the quantity of the dye adsorbed per unit mass of adsorbent has it limit with the adsorbent dosage.

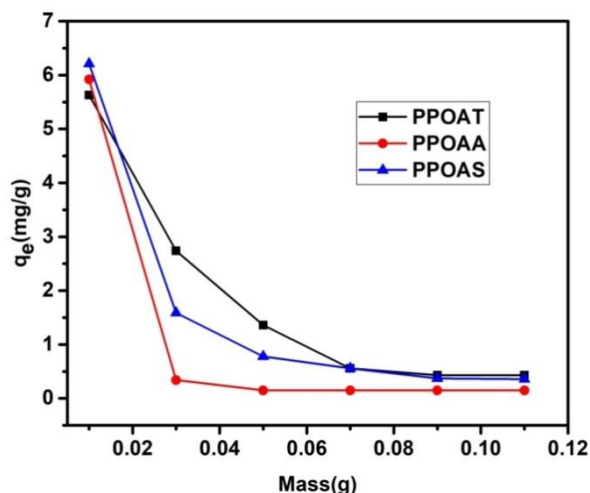


Figure 4. Effect of adsorbent dose on adsorption of Rhodamine B, [Rh B] = 10 mol. L⁻¹, T = 25°C, pH = 7.12

3.4. Effect of pH

pH is one of the important parameter in determining the adsorption efficiency since it affects the surface charge properties of the adsorbent and influences the behaviour of adsorbate ions into the solution [30]. Initial pH of dye

solutions were adjusted using sodium hydroxide (1 N). Uptake of Rh B from 10 mg/L concentration on given adsorbents was studied as a function of pH 3, 5, 7 and 11. The amount of dye adsorbed per unit mass of adsorbent at equilibrium (q_e) decreased with increased in pH with optimal uptake at pH = 3. At this pH optimal, the surface of our adsorbents is positively charged because when the pH < pHpzc, the adsorbent surface becomes positively charged and thus attracts the ionic form of RhB dye causing enhanced adsorption at pH lower than pHpzc value [31]. The decrease of the adsorbed quantity can be explained by the nature of the material used [32] and by the chemical functions presented on the surfaces of our materials. These results corroborate those obtained by Domga *et al.*, 2015 [9].

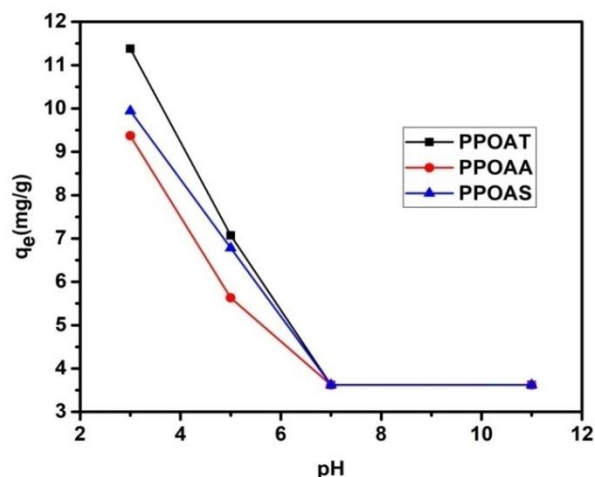


Figure 5. Effect of pH on adsorption of Rhodamine B

3.5. Effect of Temperature

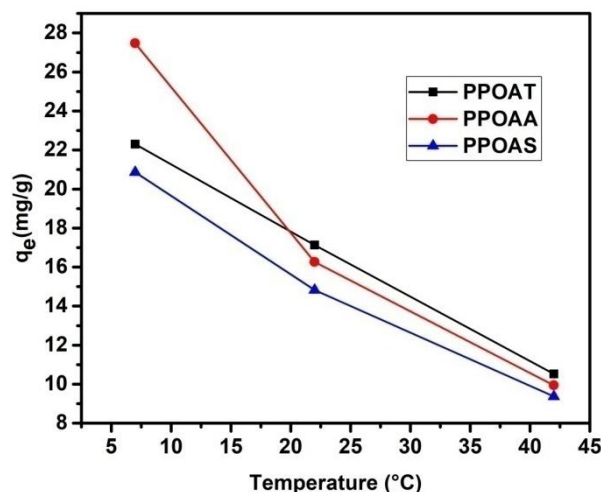


Figure 6. Effect of temperature on adsorption of Rhodamine B

Temperature has important factors on adsorption phenomena. Adsorption of Rh B at three different temperatures (280 K, 295 K and 315 K) onto biosorbents was studied for 10 mg/L initial Rh B concentration. The results showed that the quantity of Rhodamine B decreases with increasing temperature (figure 6). This may be explained that

the adsorption process is exothermic in nature. Similar result has been obtained by Boumchita *et al.*, 2016 [33] when removing methylene blue from potato peelings.

3.6. Kinetics of Adsorption

Three kinetics models [pseudo-first-order [34], pseudo-second-order [35] and Weber–Morris intraparticle diffusion [36] models] were used for characterising the kinetics data.

The pseudo-first-order is typically expressed as:

$$\log (q_e - q_t) = \log q_e - \frac{t}{2.303} K_1 \quad (2)$$

Where q_t is the amount of adsorbate adsorbed per gram of adsorbent (mg g^{-1}) at time t , K_1 is the pseudo-first-order rate constant (min^{-1}) and t is the contact time (min).

The pseudo-second-order is commonly expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Where K_2 is the pseudo-second-order rate constant (g mg^{-1}

min^{-1}).

The Weber–Morris intraparticle diffusion model is expressed as:

$$q_t = k_3 t^{1/2} + C' \quad (4)$$

Where k_3 is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$) and C' is the intercept.

From Table 2 below that pattern of pseudo-first-order and intraparticle diffusion cannot be applied to explain the adsorption of Rh B because of their low values of correlation coefficients R^2 are less than 0.90. Only the pattern of pseudo-second-order best describes the adsorption. We also note that the calculated amounts adsorbed theoretically of the kinetic model of pseudo-second order are very close to the amounts obtained experimentally. This mechanism is done in two steps: the first step is the diffusion of Rhodamine B molecules to the surface of and the second step is the interaction of the Rhodamine B molecules to the surface of adsorbents.

Table 2. Pseudo-first order, pseudo-second and intra-particle diffusion kinetic parameters

Pseudo first order				Pseudo second order				Intra-particle diffusion		
Adsorbents	R^2	K_1 (min^{-1})	$q_{e_{cal}}$ (mg/g)	R^2	K_2 (mg/g.min)	$q_{e_{cal}}$ (mg/g)	$q_{e_{exp}}$ (mg/g)	R^2	K_3 ($\text{mg.g}^{-1}\text{min}^{-1/2}$)	C'
PPOAT	0.547	0.106	0.532	0.999	0.230	12.077	11.954	0.634	1.411	2.207
PPOAA	0.755	0.124	1.893	0.994	0.071	8.591	8.218	0.757	1.366	1.683
PPOAS	0.782	0.116	1.471	0.979	0.082	3.930	3.621	0.897	1.242	1.122

3.7. Adsorption Isotherms

In order to establish the relationship between the adsorption capacity and nature of adsorption for an adsorbate-adsorbent system since it explains the mechanism of adsorption and assists in optimizing the adsorption process. Four isothermal models were fitted to know: Langmuir and Freundlich. As per Langmuir, adsorption takes place at homogenous sites of adsorbent [37], while Freundlich presumes heterogeneous surface of adsorbent with non-uniform dissemination of heat of adsorption over the surface [38]. The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2 . Langmuir and Freundlich isothermal models are represented by equations (5) and (6). The Langmuir isotherm is:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L \cdot q_{max}} \quad (5)$$

Where C_e is the concentration of Rh B dye in the solution at equilibrium (mg L^{-1}), q_e is the concentration of Rh B dye on the adsorbent at equilibrium (mg g^{-1}), q_{max} is the monolayer adsorption capacity of adsorbent (mg g^{-1}) and K_L is the Langmuir adsorption constant (L mg^{-1}). The plot of C_e/q_e versus C_e should give a straight line with a slope $1/q_0$ and an intercept of $1/q_{max} \cdot K_L$. The favourability of the adsorption process was also confirmed by calculating the dimensionless equilibrium parameter (R_L) expressed by equation:

$$R_L = \frac{1}{1 + K_L \cdot C_0}$$

Where C_0 is the highest initial dye concentration in solution. The adsorption process is said to be favourable if R_L value falls between 0 and 1, that is to say ($0 < R_L < 1$), linear when $R_L = 1$, irreversible when $R_L = 0$ and unfavourable when $R_L > 1$.

The Freundlich equation was employed for the adsorption of Rhodamine B dye on the adsorbent. The Freundlich isotherm was represented by:

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

Where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (Rh B), K_F is the Freundlich constant related to adsorption capacity and n is the constant related to intensity of adsorption associated with heterogeneity factor. The plots of $\log q_e$ against $\log C_e$ should give a linear graph where the values of n and K_F can be obtained from the slope and intercept of the graph, respectively.

Temkin Isotherm Model

The Temkin isotherm, which can be expressed by equation contains a factor that takes into account the adsorbent-adsorbate interactions [39]

$$q_e = B \ln A + B \ln C_e \quad (7)$$

Where q_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}), C_e is equilibrium concentration of adsorbate (mg L^{-1}), B is a constant related to the heat of adsorption given as $B = RT/b$, b is the Temkin constant (J mol^{-1}), T is the absolute temperature (K), R is the gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$), and A is the Temkin isotherm constant (L g^{-1}). B and A can be calculated from the slope (B) and intercept ($B \ln A$) of the plot of q_e against $\ln C_e$.

Dubinin-Radushkevich Isotherm Model

The Dubinin-Radushkevich (D-R) model is a more general model that does not assume a homogenous surface or constant adsorption potential. The D-R model gives information about the sorption mechanism, whether chemisorption or physisorption [40], and it is expressed by equation 8:

$$\ln q_e = \ln q_0 - \beta \varepsilon^2 \quad (8)$$

Where q_e is the amount of Rh B adsorbed per unit mass of adsorbent (mg g^{-1}), q_0 is the maximum sorption capacity, β is the activity coefficient related to the mean sorption energy E (kJ mol^{-1}) and ε is the Polanyi potential. ε is expressed by equation 9:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (9)$$

Where R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) and T is the temperature (K). β ($\text{mol}^2 \text{J}^{-2}$) and q_0 can be obtained from the slope and the intercept of the plot of $\ln q_e$ against ε^2 , respectively. The adsorption parameters according to the Freundlich, Langmuir, Temkin and Dubinin equations are summarized in Table 3 below.

Table 3. Parameters for the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms for the uptake of Rh B onto PPOAT, PPOAA, PPOAS

Isotherms	Constants	PPOAT	PPOAA	PPOAS
Langmuir	q_{\max} (mg/g)	10.172	42.918	10.101
	K_L (L/mg)	0.368	0.011	0.588
	R^2	0.993	0.537	0.991
Freundlich	n	3.710	1.097	2.216
	K_F (mg/g)	4.031	0.513	0.335
	R^2	0.845	0.979	0.983
Temkin	B	-76.625	-69.018	-79.308
	b	-32.333	-35.897	-31.239
	A	0.091	0.087	0.092
	R^2	0.997	0.995	0.997
Dubinin-Radushkevich	q_0	9.46×10^{-12}	0.133	1.757
	B	-0.001	-0.0007	0.001
	R^2	0.982	0.955	0.969

The results obtained show that the Langmuir model better describes the phenomenon of adsorption of Rh B by the PPOAT and PPOAS whereas for PPOAA it is Freundlich model. This shows that the adsorption is done in a monolayer where the molecules have the same activation energy for PPOAT and PPOAS and Temkin this confirm that; while the distribution is heterogeneous in adsorption sites as well as

the heat is non-uniform for PPOAA. The value of n of the Freundlich between 1 and 2 for PPOAA shows that the equilibrium of Rh B adsorption is moderately difficult.

3.8. Thermodynamics Parameters

Thermodynamics parameters, namely free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) are important in determining the feasibility, spontaneity and the nature of adsorbate-adsorbent interactions can be obtained by using the following mathematical relations:

$$\Delta G^\circ = -RT \ln K_c \quad (10)$$

$$K_c = \frac{q_e}{C_e} \quad (11)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

Where K_c is the equilibrium constant, q_e and C_e are amount adsorbed (mg/g) and concentration of solution (mg/L) at equilibrium respectively. R is the universal gas constant (8.314 J/mol/K) and T is the temperature (K). ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot $\ln K_c$ vs. $1/T$, respectively (From equation 12), ΔG° were determined using $\ln K_c$ values for different temperatures. The Results were summarized in Table 4.

Table 4. Thermodynamics parameters for the adsorption of RhB

Adsorbents	ΔH° (KJ/mol)	ΔS° (KJ/mol)	R^2	ΔG° (KJ/mol)		
				280	295	315
PPOAT	-10.099	-0.030	0.994	-1.407	-1.019	-0.325
PPOAA	-14.381	-0.045	0.979	-1.827	-0.937	-0.245
PPOAS	-10.346	-0.032	0.995	-1.289	-0.880	-0.161

The thermodynamic parameters, the standard enthalpy (ΔH°), standard Gibbs energy (ΔG°) and entropy (ΔS°) for Rh B at various temperatures are shown in Table 4. As shown in Table 4, the negative enthalpy (ΔH°) values obtained for the uptake of Rh B onto PPOAT, PPOAA and PPOAS indicate that the sorption process is exothermic in nature. The negative values between -20 and 0 KJ/mol of the standard Gibbs energy (ΔG°) indicate that the adsorption reaction is spontaneous physical type and the feasibility of adsorption decreases at high temperature. The negative values of (ΔS°) (Table 4) suggest a decrease of the mess at the adsorbent/solution interface during the adsorption to give a well-organized distribution of dye molecules at adsorption sites [33].

4. Conclusions

The objective of this study was used of different natural materials as adsorbents for the removal of Rhodamine B. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich were found to the better adjustment models with respect to R^2 values. The monolayer (maximum) adsorption capacities (q_m) were found to be 10.101 to 10.172 mg/g for adsorbents

PPOAT and PPOAS. Lagergen pseudo-second order model best fits the kinetics of adsorption. The correlation coefficient R^2 for second order model has very high values of R^2 for the PPOAT, PPOAA, PPOAS ($R^2 = 0.999, 0.994$ and 0.979 respectively) and $q_e(\text{cal})$ values are in good harmony with $q_e(\text{exp})$ indicated that pseudo second order adsorption equation of Lagergen fit much with whole interval of contact time. Intra-particle diffusion plot indicated limit layer effect and greatest intercepts indicates greater contribution of area sorption in rate determining step. Adsorption of Rh B on adsorbents was found to decrease on increasing pH, increasing temperature and increasing adsorbent dose. The values of thermodynamic parameters, the standard enthalpy (ΔH°), standard Gibbs energy (ΔG°) and entropy (ΔS°) showed exothermic, spontaneous physisorption and decreased disorder at the interface of Rh B with biosorbents. Adsorption capacities of different adsorbents towards Rh B were found to be of the order in function of contact time: PPOAT > PPOAA > PPOAS; adsorbent dose: PPOAS > PPOAA > PPOAT; pH: PPOAT > PPOAS > PPOAA; initial concentration: PPOAS > PPOAT > PPOAA; temperature: PPOAA > PPOAT > PPOAS.

REFERENCES

- [1] Ndi, J. N., Ketcha, J. M., (2013) The adsorption efficiency of chemically prepared activated carbon from cola nut shells by ZnCl₂ on methylene blue, *Journal of chemistry*, ID469170, 7.
- [2] Rangabhashiyam S. and Anu N., Selvaraju., "Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents" *J. Environ.Chem. Eng.* 1: 629–641, 2013.
- [3] Gargetal, V. K. R., Gupta, T., "Removal of a Basic Dye (Rhodamine-B) From Aqueous Solution by Adsorption Using Timber Industry Waste", *Chem. Biochem. Eng.* 19(1): 75-80, 2005.
- [4] Santhi, T., Prasad, A. L. and Manonmani, S., "A comparative study of microwave and chemically treated Acacia nilotica leaf as an eco friendly adsorbent for the removal of Rhodamine B dye from aqueous solution", *Arabian Journal of Chemistry*. 7(4): 494–503, 2014.
- [5] Arivoli, S., Thenkuzhali, M. and Martin Deva Prasath P., "Adsorption of Rhodamine B by acid activated carbon – kinetic, thermodynamic and equilibrium Studies", *E-Journal of Chemistry*. 1(2): 138-155, 2009.
- [6] Xue, X., Hanna, K., Denga, K., *J. Hazard. Mater.* 166: 407–414, 2009.
- [7] Medien, H. A. A., Khalil, S. M. E., *J. King Saud Univ. (Science)*. 22(3): 147–153, 2010.
- [8] Crini G. "Non-conventional low-cost adsorbents for dye removal: a review", *Bioresource Technology*. 97(9): 1061-1085, 2006.
- [9] Domga, R., Harouna, M., Tcheka, C., Tchatchueng, J.B., Tsafam, A., Domga., Kobbe Dama, N., Dangwang, D., "Batch Equilibrium, Kinetic and Thermodynamic Studies on the Adsorption of Methylene Blue in Aqueous Solution onto Activated Carbon Prepared from Bos Indicus Gudali Bones", *chemistry journal*. 1(6): 172-181, 2015.
- [10] Domga, R., Tcheka, C., Arnaud, G., Anombogo, M., Kobbe Dama, N., Domga., Tchatchueng, J.B., Tchigo, A., Tsafam, A., (). Batch equilibrium adsorption of methyl orange from aqueous solution using animal activated carbon from gudali bones. *International Journal of Innovation Sciences and Research*. 5(07): 798-805, 2016.
- [11] Mi-Hwa, B., Christianah, O.I., Se-Jin, O., Dong-Su, Kim. "Removal of Malachite Green from aqueous solution using degreased coffee bean", *Journal of Hazardous Materials* 176: 820–828, 2010.
- [12] Amarasinghe, B.M.W.P.K., Williams R.A., "Tea waste as a low cost adsorbent for the removal of Cu²⁺ and Pb²⁺ from wastewater", *Chemical Engineering Journal*. 132 (1-3): 299-309, 2007. <https://doi.org/10.1016/j.cej.2007.01.016>.
- [13] Bo, Z., Tongxiang, F., Di, Z., "Adsorption of copper ions from aqueous solution by citric acid modified soybean straw", *Journal of Hazardous Materials*. 153 (1-2): 300-308, 2008. <https://doi.org/10.1016/j.jhazmat.2007.08.050>.
- [14] Vimal., Srivastava, C., Mahadeva., Swamy, M., Indra., MallBasheswar, D., Prasad, I., Mishra, M., "Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 272 (1–2): 89-104, 2006. <https://doi.org/10.1016/j.colsurfa.2005.07.016>.
- [15] Xiu-guo, L. and Yi-ting, G., "Removal of Pb (II) from aqueous solution by sulfur-functionalized walnut shell, " *Environmental Science and Pollution Research* " 10.1007/s11356-019-04753-7, 2019.
- [16] Rafatullah, M., Sulaiman, O., Hashim, R., Ahmad, A., "Adsorption of methylene blue on low-cost adsorbents: A review", *Journal of Hazardous Materials*. 177(1–3): 70-80, 2010. <https://doi.org/10.1016/j.jhazmat.2009.12.047>.
- [17] Uslu, Ayla., Faaij, André. P.C Bergman, P.C.A., "Pre-treatment technologies and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation", *Energy*. 33(8): 1206-1223, 2008. <https://doi.org/10.1016/j.enery.2008.03.007>.
- [18] Benaïssa, H., Elouchdi, M.A., "Biosorption of copper (II) ions from synthetic aqueous solutions by drying bed activated sludge", *Journal of Hazardous Materials*. 194: 69-78, 2011. <https://doi.org/10.1016/j.jhazmat.2011.07.063>.
- [19] Tchakala, I., Bawa, L. M., Djaneye-Boundjou, G., Doni, K. S., Pnambo., "Optimization of the process for the preparation of chemically active carbons (H₃PO₄) from shea cakes and cottonseed cakes", *J. Biol. Chem. Sci.* 6(1): 461-478, 2012.
- [20] Mahmood, T., Saddique, M.T., Naeem, A., Westerhoff, P., Mustafa, S. and Alum, A., (). "Comparison of different methods for the point of zero charge determination of NiO," *Industrial Engineering Chemistry Research*. 50(17): 10017–10023, 2011.
- [21] Limousin, G., Gaudet, J.P., Charlet, L., Szenknet, S., Barthèse, V., Krimissa, M., "Sorption isotherms: a review on physical

- bases, modelling and measurement”, *Appl. Geochem.* 22: 249-275, 2007.
- [22] Badie, S., Girgis., Abdel-Nasser, A., El-Hendawy., “Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid”, *Microporous and Mesoporous Materials.* 52(2): 105-117, 2002. [https://doi.org/10.1016/S1387-1811\(01\)00481-4](https://doi.org/10.1016/S1387-1811(01)00481-4).
- [23] Monneyron, P., Faur-Brasquet, C., Sakoda, A., Suzuki, M. and Le Cloirec, P., “Competitive Adsorption of Organic Micropollutants in the Aqueous Phase onto Activated Carbon Cloth: Comparison of the IAS Model and Neural Networks in Modeling Data”, *Langmuir.* 18 (13): 5163-5169, 2002. DOI: 10.1021/la020023m.
- [24] Graindorge, J. and Landot, E., “The quality of drinking water, techniques and responsibilities”, *Territorial Editions.* 2007.
- [25] Sultan, S., Hasnain, S., “Reduction of toxic hexavalent chromium by *Ochrobactrum* intermedium strain SDCr-5 stimulated by heavy metals”, *Bioresource Technology.* 98(2): 340-344, 2007. <https://doi.org/10.1016/j.biortech.2005.12.025>.
- [26] Özacar, M. and Şengil, İ. A., “Application of kinetic models to the sorption of disperse dyes onto alunite”, *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 242: 105–113, 2004.
- [27] ManoharK, D.M., Anoop Krishnan., Anirudhan, T.S., “Removal of mercury(II) from aqueous solutions and chlor-alkali industry wastewater using 2-mercaptobenzimidazole-clay”, *Water Research.* 36(6): 1609-1619, 2002. [https://doi.org/10.1016/S0043-1354\(01\)00362-1](https://doi.org/10.1016/S0043-1354(01)00362-1).
- [28] Lobo, V., Patil, A., Phatak, A., Chandra, N., “Free radicals, antioxidants and functional foods: Impact on human health”, *Pharmacogn Rev.* 4(8): 118–126. 2010. doi: 10.4103/0973-7847.70902.
- [29] Zheng, H., Donghong, L., Yan, Z., Shuping, L., Zhe, L., “Sorption isotherm and kinetic modeling of aniline on Cr-bentonite”, *Journal of Hazardous Materials.* 1-7, 2000.
- [30] Soltani, T., Entezari, M.H., “Sono-synthesis of bismuth ferrite nanoparticles with high photocatalytic activity in degradation of Rhodamine B under solar light irradiation”, *Chem. Eng. J.* 223: 145-154, 2013. <http://dx.doi.org/10.1016/j.cej.2013.02.124>.
- [31] Maurya, N.S., Mittal, A.K., Cornel, P., Rother, E., “Biosorption of dyes using dead macro fungi: effect of dye structure, ionic strength and pH”, *Bioresour. Technol.* 97: 512-521, 2006. <http://dx.doi.org/10.1016/j.biortech.2005.02.045>.
- [32] Mohammad, A. R., Ruhul Amin, S. M., Shafiqul Alam, A. M., “Removal of Methylene Blue from Waste Water Using Activated Carbon Prepared from Rice Husk Dhaka”, *Univ. J. Sci.* 60 (2): 185-189, 2012.
- [33] Boumchita, S., Lahrichi, A., Benjelloun, Y., Mater, J., “Elimination of methylene blue onto potato peeling”, *Environ. Sci.* 7(1): 73- 84, 2016.
- [34] Lagergren, S. and Svenska, B.K., “On the theory of so-called adsorption of materials”, R. Swed. *Acad. Sci. Doc., Band.* 24: 1–13, 1898.
- [35] Ho, Y.S and McKay, G., “A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents”, *Proc. Saf. Environ. Protec.* 76: 332–340, 1998.
- [36] Weber, W.J. and Morris, J.C., “Kinetics of adsorption on carbon from solution”, *J. Sanitary Eng. Div. Am. Soc. Civil Eng.* 89: 31–59, 1963.
- [37] Langmuir, I., “The Adsorption of Gases on plane surface of Glass, Mica and Platinum”, *J. Am. Chem. Soc.* 40: 1361–1403, 1918.
- [38] Freundlich, H. M. H., “Over the adsorption in solution”, *Journal of Physical Chemistry.* 57: 384, 1906.
- [39] Temkin, M.I. and Pyzhev, V., “Kinetics of ammonia synthesis on promoted iron catalyst”, *Acta Phys. Chim. USSR.* 12: 327–356, 1940.
- [40] Dubinin, M. M. and Radushkevich, L.V., “Equation of the characteristic curve of activated charcoal”, *Proc. Acad. Sci. Phys. Chem. USSR.* 55: 331–333, 1947.