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Equilibrium, kinetics and mechanism for the removal of Rhodamine B by adsorption on Okoume *(Aucoumea Klaineana)* sawdust from aqueous media

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ABSTRACT

The aim of the present work was to investigate the feasibility of Okoume *(Aucoumea Klaineana)* sawdust (OS) for Rhodamine B (RhB) adsorption from aqueous media. OS surface was characterized by the functional organic groups by the Boehm titration method, scanning electron microscopy (SEM) and isoelectric potential (pH_{ZPC}). The adsorption of RhB on OS material was studied as a function of solution pH 2–10, sodium chloride (0–5000 mg/L), solution temperature (25–45°C), contact time and initial concentration (5–30 mg/L). The influence of these parameters on the amount of RhB adsorbed was studied using the batch process. The results show that the increase of initial concentration, the temperature has a positive impact on the adsorption of RhB. However, the sodium chloride and pH have a negative effect to the dye removal, and a maximum adsorption was achieved at pH 3.0. Experimental kinetics data at different initial dye concentrations were analyzed using Lagergren pseudo-first-order, pseudo-second-order and Elovich models, and were found well described by the pseudo-second order model. The results for the mechanism adsorption, the intraparticle diffusion for all period was not the only rate-limiting step, it seems that other processes might implicate in control the rate. Equilibrium isotherm data at different temperatures (25–45°C) were analyzed according to Langmuir and Freundlich equations, and the adsorption isotherm was found to follow the Langmuir model. The monolayer adsorption capacity (q_m) was found to be 79.65 mg/g at 25°C. Furthermore, thermodynamic parameters such as ΔG°, ΔS° and ΔH° were calculated, and the results suggest that the adsorption is spontaneous, a physical process and endothermic in nature.

Keywords: Adsorption; Rhodamine B; Okoume sawdust; Kinetics; Isotherm; Modeling

1. Introduction

Color is the first contaminant to be recognized in water and has to be removed from wastewater before discharging it into water bodies. Residual dyes are the major contributors to color in wastewaters generated from textile and dye manufacturing industries, etc. [1]. Dyes are classified as follows: anionic-direct, acid and reactive dyes; basic dyes; non-ionic-disperse dyes [2]. Basic dyes have high brilliance and intensity of colors and are highly visible even in a very low concentration [3–5]. For industrial liquid effluents, color is the first indication of water pollution. Color impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has a tendency to chelate metal ions which result in micro-toxicity to fish and other organisms [6]. Most of the used dyes are stable to photo-degradation, bio-degradation and oxidizing agents. Currently, several physical or chemical processes such as fentons reagent, ozonation, photochemical, electrochemical, precipitation, reverse osmosis, ion exchange, and membrane filtration are used to treat dye-laden wastewaters [7]. However, these processes are costly and cannot be used effectively to treat the wide range of dye-laden wastewater [8].

The adsorption process is one of the efficient methods to remove dyes from effluent and has an advantage over the other methods due to the excellent adsorption efficiency of activated carbon for organic compounds even from dilute

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solutions available activated carbons are very expensive [9]. The study of adsorption which utilizing low cost natural materials or industrial and agricultural wastes is of great importance from an environmental point of view, as it can be considered as an alternative technique for removing toxic pollutants (dyes or heavy metals) from wastewaters. A number of studies in the last years focused on the bioadsorption of toxic polluants on sawdust of different woods: rubber wood [10], cedar [11], indian rosewood [12], pine [13], beech [14,15], neem [16] and okoume sawdust [17]. Recently, it appeared that the combining of anodic oxidation and adsorption onto sawdust constitute a very interesting technology [18].

Rhodamine B (RHB) was selected for the adsorption experiment due to its presence in the wastewaters of several industries (such as textile, leather, jute food industries). The OS is an exotic wood from equatorial West Africa (Gabon). It is mainly used for making panels, ply wood, interior carpentry and cigar boxes. Okoume sawdust has been used as an original low-cost adsorbent for the removal of mercury in our previous work [17]. So, the aim of the present study is to evaluate the applicability of the OS for the removal of toxic basic dye (RHB) from aqueous solutions in batch process. Batch experiments were performed to examine the effect of physico-chemical parameters, such as contact time, initial concentration of dye, temperature, initial pH solution and ionic strength. The kinetics approach of adsorption was studied by applying Lagergren pseudo-first-order, pseudo-second-order and Elovich models. In order to better understand the mechanism, the intraparticle diffusion and Boyd's model were applied [8,19]. Equilibrium isotherm data were analyzed according to Langmuir and Freundlich equations. The characteristic parameters for each model have been determined. Additionally, thermodynamic parameters such as ΔG°, ΔS° and ΔH° were determinated.

2. Materials and methods

2.1. Materials

Rhodamine B (abbreviation: RhB; C.I. Basic Violet 10; C.I. number: 45170; chemical class: xanthene; molecular formula: $C_{28}H3_1N_2O_3Cl$) was procured from Sigma-Aldrich. RhB (molecular weight: 479.01 g/mol); which is a highly water soluble, was used as a pollutant model. The molecular form of RhB is shown in Fig. 1. RhB solutions were prepared by dissolving requisite amount of the dye in distilled water (3000 mg/L). All other reagents used were of analytical grade. The pH of the solution was adjusted using HCl (0.1 N) and NaOH (0.1 N).

2.2. Preparation and characterization of OS

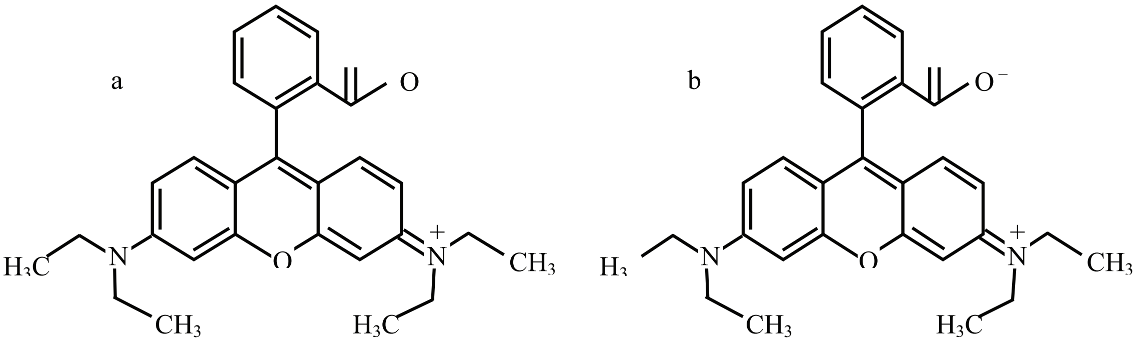
OS was washed, dried and sieved to desired mesh size (0.5–2 mm). Finally, the obtained material was then dried in an air circulating oven at 70°C for 3 d and stored in desiccators until use [17].

For analysis of OS surface, and detected the functional groups that might be involved in dye adsorption, the concentrations of acid and basic functional surface groups present on the OS were determined by the Boehm titration method [20]. In addition, the investigation of surface morphology of OS sample before and after adsorption dye was observed by scanning electron microscopy (SEM).

2.3. Adsorption procedures

The batch adsorption experiments were carried out in 100 mL flasks where 0.1 g of OS was added to 50 mL of the RhB solutions at initial concentrations that varied in the range of 5–30 mg/L. The flasks were placed in a thermostatic water bath to maintain a constant temperature (25°C) and were stirred at 300 rpm for 420 min to ensure that equilibrium was achieved. At predetermined intervals of time, samples filtrate of the mixture was withdrawn analyzed for the final concentration of RhB by using a UV Vis spectrophotometer (UV-6405, Jenway) set at a wavelength λ_{max} 553 nm, maximum absorbance in visible region. The flasks were placed in a thermostatic water bath in order to maintain a constant temperature at 25°C and stirring was provided at 300 rpm to ensure equilibrium was reached. Fig. 2 represents absorbance vs. concentration of RhB (Abs = f (c)).

The procedure of equilibrium experiments was basically identical to those of kinetic tests. The procedures of adsorption equilibrium experiments were carried out by adding a fixed amount of OS (0.06 g) into a number of sealed glass



Cationic form

Zwitterionic form

Fig. 1. Molecular form of RhB (cationic and zwitterionic form).

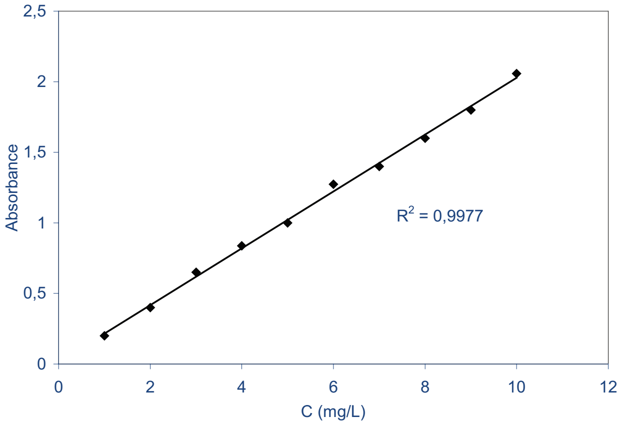


Fig. 2. Plot of absorbance vs. concentration of RhB.

flasks containing a definite volume (30 mL in each case) at different initial concentrations (30–400 mg/L) of RhB solution without changing pH. The flasks were placed in a thermostatic water bath in order to maintain a constant temperature (25, 35 and 45°C) and stirring was provided at 300 rpm for 15 h to ensure that equilibrium was reached for the higher concentrations. The amount of adsorption at any time q_t (mg/ g) and equilibrium q_e (mg/g) was calculated by [20]:

$$q_t = \frac{(C_0 - C_t)}{m} \times V \tag{1}$$

$$q_e = \frac{(C_0 - C_{et})}{m} \times V \tag{2}$$

where C_0, C_t and C_e (mg/ L) are the liquid phase concentrations of dye at initial, any time and equilibrium respectively, V (L) is the volume of the solution and m (g) is the mass of used adsorbent. All the experiments were carried out in duplicate, and the mean values are presented.

3. Results and discussion

3.1. Characterization of OS

The Fourier transform infrared analysis (FTIR) and the pHzpc of OS was previous study determinate [17] and for pHzpc was calculated using the addition solid method [20] and which was determined to be 5.64.

For the traditional Bohem titration, the results showed in Table 1. These results prove that several types of surface groups exist, i.e. lactonic, phenolic, carbonylic, etc. From acid groups, the carbonylic and quinonic and after phenolic groups were the dominant acidic oxygenated groups. Then, the result of the Boehm titration confirmed the nature of OS surface which enhanced the adsorption of RhB cationic ions from solution.

The scanning electron micrograph (SEM) of OS sample before and after adsorption RhB at bar length equivalent to 50 µm, working voltage 5 kV with 1500× magnification are shown in Fig. 3a and Fig. 3b, respectively. SEM reveals that the textural structure of surface OS (Fig. 3a) is heterogeneous, irregular and porous cell wall which proves the adsorption of RhB ions (Fig. 3b), because the morphology of OS was changed after RhB adsorption.

Table 1
Concentration of acid and basic groups on surface OS

Concentration groups	Value (mequiv·g^{-1})
Carboxylic	0.08
Lactonic	0.47
Phenolic	1.24
Carbonylic and quinonic	1.43
Acid	3.22
Basic	0.41
Total	3.65

3.2. Effect of operating conditions

3.2.1. Effect of initial pH

To study the effect of solution pH on RhB adsorption, the experiment was conducted at different pH values ranging from 2 to 10. Fig. 4 shows the results of the effect of initial pH. The experimental data illustrated that the amount was maximum (9.18 mg/g) of RhB at pH 3.0 and it has been observed that this value decreases with increase of pH. As shown, at pH 4.0 and 6.0 the amount was 8.98 mg/g and 8.16 mg/g, respectively, and at pH 10 the amount of RhB was 6.6 mg/g. It appears that a change in pH of the solution results in the formation of different ionic species of dye, and different adsorbent surface charge. The surface charge of the OS is positive at pH < pHzpc (5.64) causing a decrease in RhB cations uptake, and is negative at pH > pHzpc, and favors uptake of RhB cations. However, at pH values lower than 4 (pH < pKa = 3.7), the RhB ions are of cationic and monomeric molecular form (Fig. 1a) [21], thus RhB can diffuse into the pore structure. At a pH value higher than 4 (pH > pKa), the zwitterionic form of RhB in water (Fig. 1b) may increase the aggregation of RhB to form a larger molecular form (dimer) and become unable to enter into the pore. Similar result was observed for the adsorption of RhB on walnut shells [22].

3.2.2. Effect of sodium chloride

There is a number of studies showing the changing of the removal order of dye with the concentration of various electrolyte types in dye medium. The influence of ionic strength (salt concentration) on the removal of RhB on OS was investigated over the sodium chloride concentrations ranging from 0 to 5000 mg/L at naturel pH (around 4), with a constant initial concentration of 30 mg/L, OS mass of 0.10 g, solution volume of 50 mL and temperature of 25°C. Fig. 5 shows the effect of ionic strength on adsorbed quantity. It is clearly that in a low solution concentration NaCl had a larger uptake on the adsorption capacity, however, little uptake of RhB will be obtained at higher ionic strength.

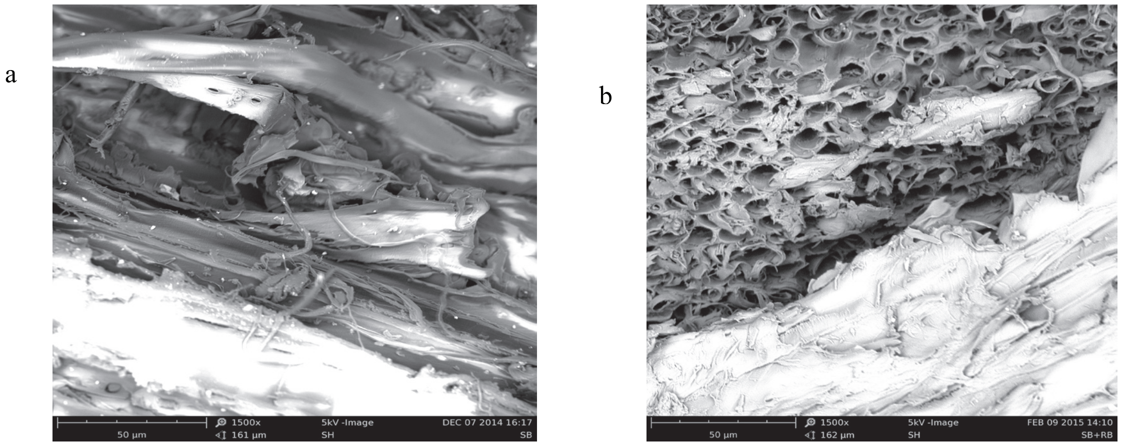


Fig. 3. SEM micrograph of OS before; (a) and after; (b) adsorption of RhB dye (×1500).

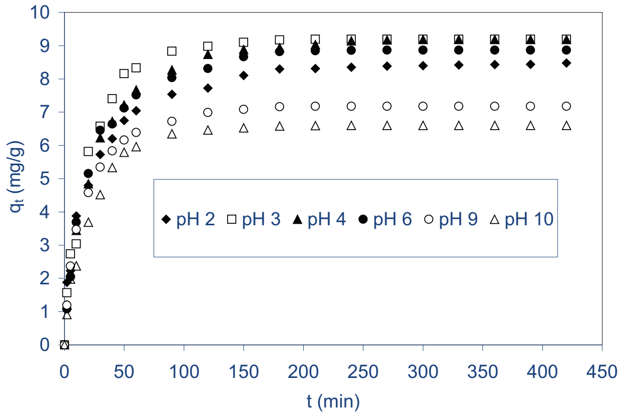


Fig. 4. Effect of initial pH of solution on the adsorption of RhB on OS.

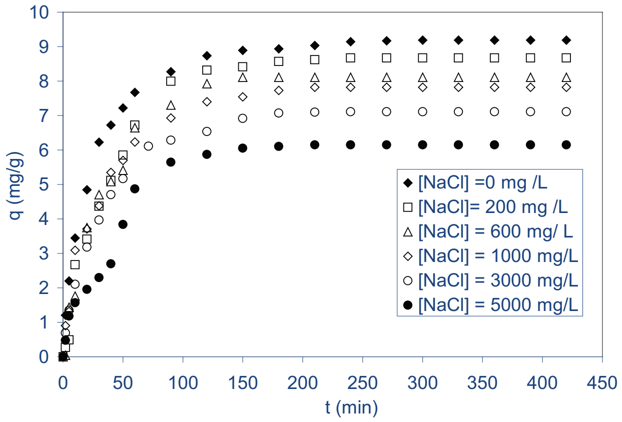


Fig. 5. Effect of sodium chloride (NaCl) on the adsorption of RhB on OS.

The variation of sodium chloride (NaCl) concentration exhibits a major effect on the extent of RhB adsorption. The reason for this is that Na^+ ions in the aqueous phase compete effectively with positively charged dye molecules for the same binding sites on the adsorbent surface. Similar results were reported using different adsorbents for the removal of basic dyes [23,24].

Know that after the adsorption pH of solution remains constant.

3.2.3. Effect of temperature

Temperature is a highly significant parameter in the adsorption processes. Fig. 6 shows the adsorption of RhB on OS. This shows the effect of temperature on the adsorption data as a function of contact time. The present data show that increasing temperature of dye solution from 25 to 45°C, causes a slight increase in the amount adsorbed at equilibrium. The fact that the adsorption of dye is in favor of temperature indicates that the process is endothermic. The amount of RhB increased from 9.18 to 9.45 mg/g while the temperature increases from 25 to 45°C, respectively. Similar results were found for the adsorption of dyes on different adsorbents [8,25].

3.2.4 Effect of initial RhB concentration and contact time

The effects of contact time and RhB initial concentration on the adsorption uptake using OS at 25°C and at natural pH are shown in Fig. 7. From this, it was shown that the adsorption of dye increased with an increase in initial dye concentration and this confirmed strong chemical interactions between RhB and OS. This is due to increasing concentration gradient, which acts as increasing driving force to overcome all mass transfer resistances between the aqueous solution and solid phase [26]. Furthermore, it can be seen that the adsorption of RhB at different concentrations is rapid in the initial stages and gradually decreases with the adsorption progress until the equilibrium is reached. The initial rate of adsorption was greater for higher initial RhB concentration, because the resistance to the dye uptake decreased as the mass transfer driving force increased. It was noticed that an increase in initial dye concentration led to an increase in the adsorption capacity of RhB on OS [20]. Fig. 7 reveals that at equilibrium, RhB adsorption increased from 1.30 to 9.18 mg/g with increase in the initial RhB concentration from 5 to 30 mg/L, respectively. Also, the neces-

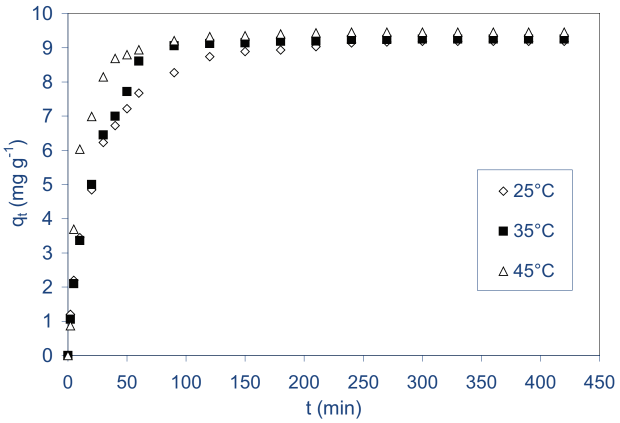


Fig. 6. Effect of temperature of solution on the adsorption of RhB on OS.

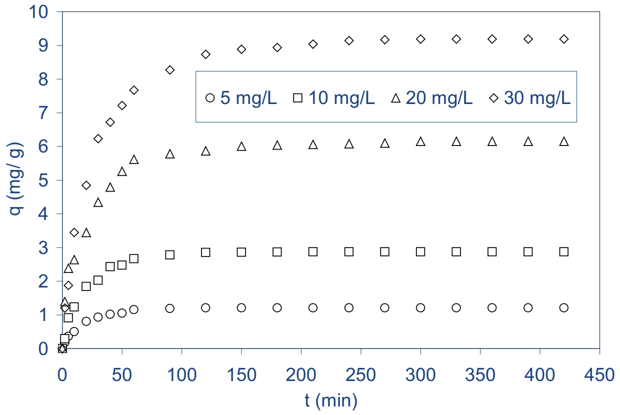


Fig. 7. Effect of initial concentrations vs. the contact time on the adsorption of RhB on OS.

sary time to reach equilibrium is variable according to the initial concentration of dye: about 50 min for C_0 = 5 mg/L, 60 min for C_0 = 10 mg /L, 90 min for 20 mg/L and 150 min 30 mg/L. Similar trend were observed for the adsorption of some dyes on others sawdust [27,28].

3.3. Adsorption kinetics studies

A study of kinetics of adsorption is popular as it provides information about the mechanism of adsorption, which is important for the efficiency of the process. The applicability of the Lagergren pseudo-first order, the pseudo second-order and the Elovich model was tested for the experimental results for different initial dye concentrations RhB adsorption on OS.

3.3.1. Lagergren pseudo-first-order model

Lagergren equation was used to investigate the suitability of pseudo-first-order kinetic model and obtain rate constants .This equation can be written as [29]:

$$\ln\frac{q_e - q}{q_e} = -K_1 t \tag{3}$$

where q_e (mg/ g) and q_t (mg/g) are the amount of dye adsorbed at equilibrium and at any time t, respectively, and k_1 (min^{-1}) is the rate constant for Lagergren-first-order adsorption.

The straight line plots of ln ($q_e - q_t$) against t of Eq. (3) were made at different initial dye concentrations. The plot of ln ($q_e - q_t$) vs. t gives a straight line for the Lagergren pseudo-first-order adsorption kinetics (figure not shown). The values of the Lagergren pseudo-first-order rate constant k_1 were obtained from the slopes of the straight lines. The parameters of Lagergren pseudo-first-order are given in Table 2. As seen that the correlation coefficient (r) values have varying in the range of 0.966 and 0.989. Also, the experimental $q_{e,exp}$ values were not agree with the calculated $q_{e,cal}$ values obtained from the linear plots. These results have shown that the experimental data do not agree with the pseudo-first-order kinetic model. In many cases the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes.

3.3.2. Pseudo-second-order model

Pseudo-second-order kinetic model can be expressed as follows [30]:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where k_2 (min g/mg) is the rate constant for the pseudo-second-order adsorption kinetics and $h = k_2 q_e^2$, where h is the initial adsorption rate (min mg/g). The pseudo-second-order rate constant (k_2) and the equilibrium adsorption capacity (q_e) can be determined experimentally from the slope and intercept of the plot of t/q_t vs. t. The parameters of the pseudo-second-order are illustrated in Table 2. As seen in this Table that the correlation coefficient values for RhB adsorption on OS has changed in the range of 0.996 and 0.999. And, the experimental $q_{e,exp}$ values were agree with the calculated $q_{e,cal}$ values obtained from the linear plots (Fig. 8) .

3.3.3 Elovich model

The Elovich equation is useful in describing adsorption on highly heterogeneous adsorbents [31]. Recently, this model has been used for the description of the bioadsorption of pollutants from aqueous solutions on materials [32–34]. The linearized form of this equation is written as follows:

$$q_t = \frac{1}{\beta}\ln(\alpha \cdot \beta) + \frac{1}{\beta}\ln(t) \tag{5}$$

where q_t is the adsorption capacity at time t (mg/g), α is the initial adsorption rate (mg/g min) and β is the desorption constant (g/mg) during any one experiment.

The Elovich kinetic constants could be deduced from the slopes and the intercepts of the linear plots of q_t vs. ln(t) (fig-

Table 2
Parameters of the kinetic models for the adsorption of RhB on OS

Kinetics models	Initial concentration C_0 of RhB (mg/L)			
	5	10	20	30
Lagergren pseudo-first-order				
$q_{e',exp}$ (mg/g)	1.20	2.37	6.81	9.18
$q_{e,cal}$ (mg/g)	8.32	1.23	18.53	34.66
k_1 (min^{-1})	0.169	1.111	0.052	0.067
r	0.989	0.978	0.988	0.966
Pseudo-second-order				
$q_{e,cal}$ (mg/g)	1.29	2.67	6.08	9.75
k_2 (g/mg min)	0.031	0.049	0.053	0.065
h (mg/g min)	0.28	1.16	3.46	7.26
r	0.999	0.998	0.999	0.996
Elovich				
α (mg/g min)	1.33	3.79	9.64	11.32
β (g/ mg)	0.128	0.752	0.630	0.503
r	0.959	0.973	0.968	0.956

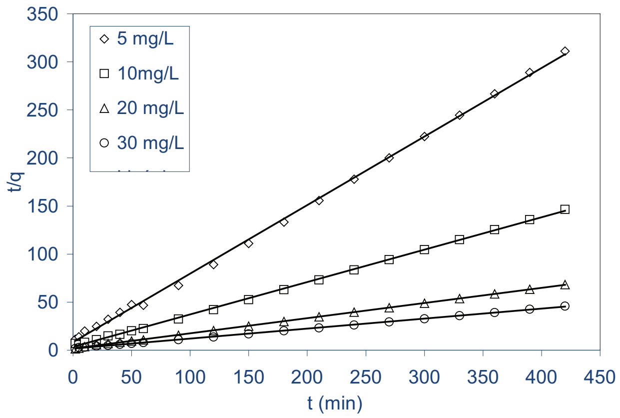


Fig. 8. Modeling of adsorption kinetics by pseudo-second order model.

ure not shown) and the values of Elovich parameters were regrouped in Table 2. It was observed that Elovich equation represent a poor fit with the experimental data because all concentrations studied, the linear regression correlation coefficients, r, values were found to be lower.

Subsequently, these prove the applicability of the second pseudo-order equation nature of the adsorption process. Similar kinetic results were already reported by some authors in basic dyes on various adsorbents [20,22,35].

3.4. Adsorption mechanism

3.4.1. Intraparticle diffusion model

The prediction of the rate-limiting step is an important factor to be considered in adsorption process. For solid–liquid adsorption process, the solute transfer process was generally considered by intraparticle diffusion or external (boundary layer) diffusion (Boyd) or both. Intraparticle diffusion model is characterized by the relationship between specific adsorption and the square root of time, according to the following equation [36]:

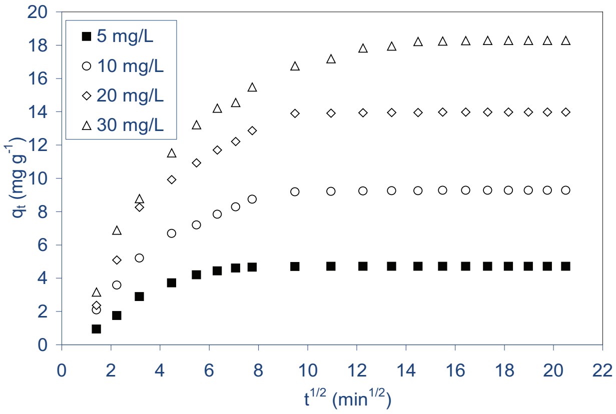


Fig. 9. Modeling of adsorption kinetics by intraparticle diffusion model of RhB on OS.

$$q_t = k_i t^{1/2} + C \tag{6}$$

where q_t is the amount adsorbed at any time (mg/g), k_i is intraparticular diffusion rate constant (mg/g min$^{1/2}$), $t^{1/2}$ is the square root of time (min$^{1/2}$) and C is the intercept, which represents the resistance to mass transfer in the external liquid film. If the regression of q_t vs. $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the lone rate-limiting step. From Fig. 9, it is clear that the plots were multilinears; containing three consecutive linear steps with different slopes during the adsorption of RhB on OS, indicating the different periods in adsorption. The first linear period represents (1) the instantaneous adsorption, followed by (2) the second linear period is the progressive adsorption period where intraparticle diffusion is the rate limiting and (3) the third period is the final equilibrium period. In brief, it is confirmed that for a short time period (the first linear segment) represents film-diffusion (or chemical reaction), and at longer adsorption times (second segment) represent pore-diffusion and equilibrium [37].

Consequently, at all initial concentrations and all period (Fig. 9) the intraparticle diffusion was not only rate controlling step but other processes might implicate in control the rate of adsorption as chemical reaction.

3.4.2 Boyd model

Boyd's model or external diffusion determines if the main resistance to mass transfer is in the thin film (boundary layer) surrounding the adsorbent particle, or in the resistance to diffusion inside the pores.

The adsorption data kinetic were further analyzed by Boyd's model and can be expressed as follows [9]:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \tag{7}$$

where F is the fraction of solute adsorbed at different time t and Bt is a mathematical function of F and given by:

$$F = \frac{q_t}{q_e} \tag{8}$$

Eq. (7) could be transformed to obtain the approximations given in Eqs. (8) and (9) [38]:

$$(\text{for } F > 0.85)\ \ Bt = -0.4977 - \ln(1 - F) \tag{9}$$

$$(\text{for } F < 0.85)\ \ Bt = (\sqrt{\pi} - \sqrt{\pi^2 F / 3})^2 \tag{10}$$

Boyd state that if the plot is linear and passes through the origin then pore diffusion controls the rate of mass transfer. If the plot is nonlinear or linear but does not pass through the origin, then it is concluded that the transport is extraparticulaire (external diffusion). From Fig. 10 it was observed that the plots at all initial concentrations were linear ($R^2 \geq 0.9849$), but did not pass through the origin, indicating that, for the studied dye concentration range, external mass transport (transport extraparticulaire) control the rate-limiting process or chemical reaction control the adsorption rate.

3.5. Adsorption isotherms studies

An adsorption isotherm describes the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium.

Various isotherm models have been used to describe the equilibrium data nature of adsorption. For this purpose, the adsorption equilibrium data on OS were modelled by Langmuir [39] and Freundlich [40,41]. The linear forms of these four isotherm models were simplified and represented as follows:

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{b \cdot q_m} + \frac{1}{q_m} \times C_e \tag{11}$$

$$\text{Freundlich: } \ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \tag{12}$$

where q_m is maximum biosorption capacity (mg/g), b is Langmuir constant (L/mg), K_F ($mg^{1-\frac{1}{n}} L^{\frac{1}{n}} / g$) is Freundlich biosorbent capacity, $1/n_F$ is heterogeneity factor (if $n_F > 1$, the adsorption is a favorable physical process).

Fig. 11 shows the plotted models including the fitted models at different temperatures and the result parameters isotherm studies were summarized in Table 3. The results indicate that the Freundlich parameters increase with an increase of temperature; the obtained value $n_F > 1$, indicates that the adsorption is a favorable physical process, and the correlation coefficients obtained are higher and varies between 0.996 and 0.997, but they are lower than those obtained from Langmuir model ($0.997<r<0.999$). So, the experimental data for the adsorption isotherms of basic dye, RhB, on OS can be better explained by Langmuir model which shows involves a homogeneous surface with equal energy and equally available sites for adsorption. The maximum adsorption capacity (q_m) of Langmuir model were from 79.65 to 85.14 mg/g while the temperature varied from 25°C to 45°C, respectively. Table 4 lists the adsorption capacity for RhB on OS compared with other adsorbents. This study presents a relatively large

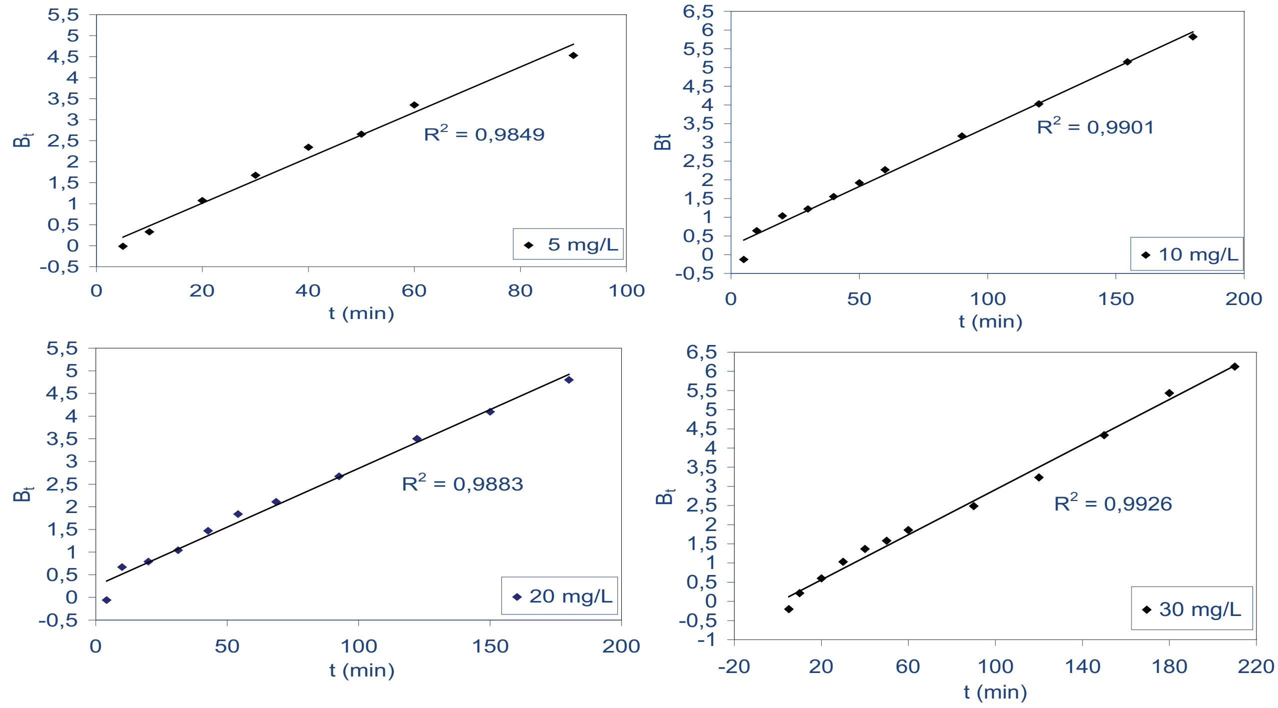


Fig. 10. Boyd plots for RhB adsorption on OS at different initial concentrations.

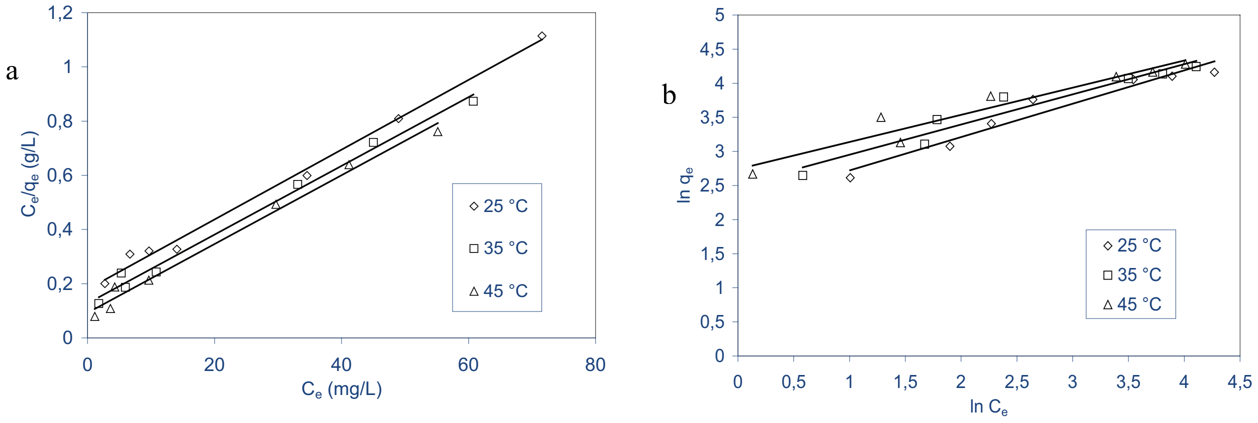


Fig. 11. Langmuir (a) and Freundlich (b) isotherms for the adsorption of RhB on OS.

Table 3
Parameters of the Langmuir and Freundlich models obtained using the linear expression

Model T (°C)	Parameters	25	35	45
Langmuir	q_m (mg/g)	79.65	83.97	85.14
	b ($\times 10^2$ L/mg)	6.85	7.1	9.75
	r	0.999	0.997	0.998
Freundlich	$K_F\ (mg^{1-\frac{1}{n}}\ L^{\frac{1}{n}}\ /g)$	12.93	16.34	21.09
	n_F	2.02	2.81	3.04
	r	0.996	0.997	0.997

Table 4
Comparison of the adsorption capacity for RhB by different low cost adsorbents reported in literature

Adsorbent	Initial concentration range (mg/L)	T (°C)	q_m (mg/g)	Reference
Coir pith	10–60	32	2.6	[42]
Industrial solid waste	10–40	30	16.1	[43]
Treated parthenium biomass	50–250	36	59.2	[44]
Fly ash	–	30	4.5	[45]
Surface modified tannery waste	–	30	213	[35]
Walnut shell	10	–	2.29	[22]
Chemically treated A. nilotica leaves	25–200	27	22.37	[46]
AC of Bagasse pit	200	20	93.1	[9]
Cedar cone	25–400	25	20.41	[8]
Okoume sawdut	30–400	25	79.65	This study

maximum monolayer adsorption capacity at natural pH and room temperature (25°C). On this basis, we can conclude that, OS that has been proposed in this study might be considered an effective material as compared with reported low cost adsorbents for the elimination of RhB from aqueous media.

3.6. Thermodynamic parameters

The thermodynamic parameters that must be considered to determine the process as changes in enthalpy ($\Delta H°$), entropy ($\Delta S°$) and free energy ($\Delta G°$) are calculated using the following equations:

$$\Delta G^o = -RT\ln b \tag{13}$$

In which T (K) is the absolute temperature, R (kJ/ mol K) is the gas constant and b (L/ mol) is the Langmuir equilibrium constant (calculated).

$\Delta G°$ (kJ mol^{-1}) is the function of change in enthalpy of adsorption, $\Delta H°$ (kJ/mol) as well as change in standard entropy, $\Delta S°$ (J/mol K):

$$\Delta G° = \Delta H° - T\Delta S° \tag{14}$$

The values of Gibbs free energy change ($\Delta G°$) were obtained according to Eq. (12) at different temperatures. From the slope and the intercept of the plot of $\Delta G°$ vs. T as presented in Fig. 12, $\Delta H°$ and $\Delta S°$ values were estimated.

The calculated thermodynamic parameters using the above equations at different temperatures are collected in Table 5. The negative values of $\Delta G°$ (–5.81, –6.08 and –6.35 kJ/mol) at 25, 35 and 45°C, respectively, demonstrate the feasibility of the process and the spontaneous nature for the adsorption. The lower and positive value of $\Delta S°$ (26.8 J/mol K) indicates that may imply that no remarkable change in entropy occurred during the adsorption of RhB. The positive value of enthalpy change (2.18 kJ/mol) indicated the endothermic nature of the adsorption interaction.

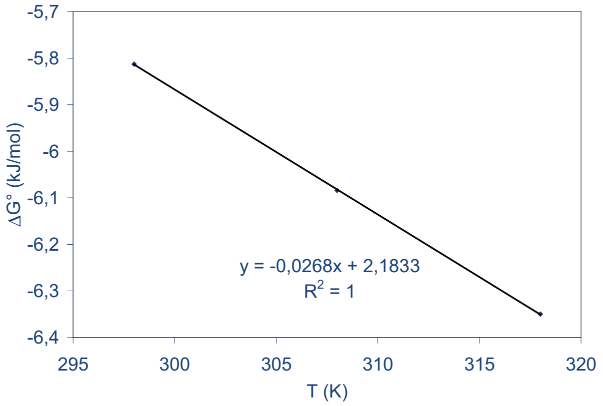


Fig. 12. Plot of $\Delta G°$ vs. T for estimation of thermodynamic parameters.

Table 5
Thermodynamic parameters for the adsorption of RhB on OS

T (°C)	$\Delta H°$ (kJ/mol)	$-\Delta G°$ (kJ/mol)	$\Delta S°$ (J/mol K)
25	2.18	5.81	26.8
35		6.08	
45		6.35	

4. Conclusions

The results obtained in this work indicate that OS can be successfully used for the removal of hazardous dye, from aqueous phase. The results of analysis for OS surface (morphology and the concentrations of acid and basic groups) improve the adsorption of RhB.

The amount of dye adsorbed was found to increase with increase of contact time, initial dye concentrations and temperature. The contact time required to reach the equilibrium at initial concentrations from 5 to 30 mg L^{-1} is from 50 to 150 min, respectively. But, the amount of RhB adsorbed decreases with the increase of sodium chloride and pH, with a maximum adsorption obtained (9.18 mg/g) at pH 3.0. The adsorption kinetics approach of the RhB on OS is well described by the pseudo-second order model, and the intraparticle diffusion was not the only rate-limiting step, other processes might implicate in control the rate of adsorption. Equilibrium data at different temperature (25–45°C) were best described by Langmuir isotherm model, confirming the monolayer adsorption capacity of dye on OS with q_m of 79.65 mg/g. The data obtained from adsorption isotherms at these three temperatures were used to determine thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$. The results imply that the adsorption is spontaneous and endothermic in nature.

Consequently, The OS was found to be both effective as adsorbent and economically (waste) viable.

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