



Research Article

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## Adsorption of Rhodamine B from single, binary and ternary dye systems using Sawdust of *Parkia biglobosa* as adsorbent: Isotherm, kinetics and thermodynamics studies

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### ABSTRACT

This study investigates the use of sawdust of *Parkia biglobosa* for the removal of Rhodamine B from single, binary and ternary dye systems in aqueous solution so as to determine the effects of the composition of the solution on adsorption process. The sawdust was characterized using Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) spectrophotometry, X-Ray diffraction and pH point of zero charge. Batch adsorption experiments were carried out to investigate the isotherm, kinetics and thermodynamics of the adsorption processes. The adsorption process was described by Freundlich isotherm ( $R^2 > 0.99$ ) in single system, Langmuir isotherm ( $R^2 > 0.99$ ) in binary system and Temkin isotherm in ternary system. The adsorption process in the three systems investigated were described by pseudo second order kinetics and were all spontaneous (negative  $\Delta G$ ) but endothermic.

**Keywords:** wastewater, adsorption, rhodamine B, *Parkia biglobosa*, kinetics, isotherm, thermodynamics, ternary dye system, sawdust.

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### INTRODUCTION

In recent years, there has been a significant development in industrial sector which has left its impact on the environment [1]. The use of dye is found in every industry to give attractive colour to the products, while the residual and unspent dyes are discharged into water bodies [2]. It has been reported that the dye consumption in the textile industry alone is above 10,000 kg/year with an estimated 10 percent of this discharged into rivers and other water bodies as unspent [3]. The discharge of highly coloured effluents into natural water bodies is not only aesthetically displeasing, but also impedes light penetration, thereby affecting biological processes of the aquatic environment [4]. Dyes used in textile industry may be directly toxic to aquatic organisms and can be resistant to natural biological degradation. Hence, the removal of synthetic organic dyestuff from waste effluents becomes environmentally important [5]. Most of the dyes are also stable against photo degradation and oxidizing agents [6]. Many methods such as coagulation, membrane separation process, electrochemical, chemical oxidation, reverse osmosis, aerobic and anaerobic microbial degradation have been used to remove dyes from wastewaters but these methods have many restrictions and therefore, are not successful for complete colour removal from wastewaters [1,7]. Compared to other conventional physico-chemical methods for wastewater treatment, adsorption has proven to be more efficient, versatile, and easy to operate ([1,8,9]. But activated carbon which is widely used as adsorbents

is expensive and therefore uneconomical for wastewater treatment hence, the need to find low-cost and readily available materials such as agricultural wastes for preparing adsorbents.

Though many agricultural wastes have been investigated for their ability to remove different dyes especially in single systems, limited study has been reported on the adsorption of dye in multi-component systems. The aim of this study is to investigate the adsorption of rhodamine B in a competitive environment using the sawdust of locust bean tree (*Parkia biglobosa*)

## EXPERIMENTAL SECTION

### 2.1 PREPARATION OF ADSORBENT

A large quantity of sawdust of *Parkia biglobosa* was collected from a local saw mill industry in Ogbomoso, South-west Nigeria. Debris and other relatively big foreign materials were hand-picked from the collected sawdust, after which it was thoroughly washed with distilled water, dried at 105 °C for 15 hours. The dried material was then ground, sieved with 60-80 µm mesh and stored in an air-tight container as PSD.

### 2.2 CHARACTERIZATION OF ADSORBENT

The adsorbent was characterized using scanning electron microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction and pH point of zero charge ( $pH_{zpc}$ ). The Scanning electron microscope (Hitachi 2300 Scanning electron microscope) was used to study the surface morphology of the adsorbent prepared. The IR spectrum of RSD was recorded using Nicolet Avatar FT-IR within the range 4000  $cm^{-1}$  and 450  $cm^{-1}$  before and after adsorption. The X-ray diffraction was carried out using X-ray diffractometer (Philips Analytical) so as to determine the X-ray diffraction patterns of RSD. The pH point of zero charge determination ( $pH_{zpc}$ ) of the PSD was carried out by adding 0.1 g of PSD to 200 ml solution of 0.1 M NaCl whose initial pH has been measured and adjusted with 0.1 M NaOH or HCl in several flasks. The flasks were sealed and placed on a shaker for 24 hours after which the pH was measured using a Jenway pH meter. Change in pH values ( $pH_{initial}-pH_{final}$ ) were plotted against initial pH values and  $pH_{zpc}$  occurs where the plot crosses Change in pH values ( $pH_{initial}-pH_{final}$ ) were plotted against initial pH values and  $pH_{zpc}$  occurs where the plot crosses the horizontal axis [10].

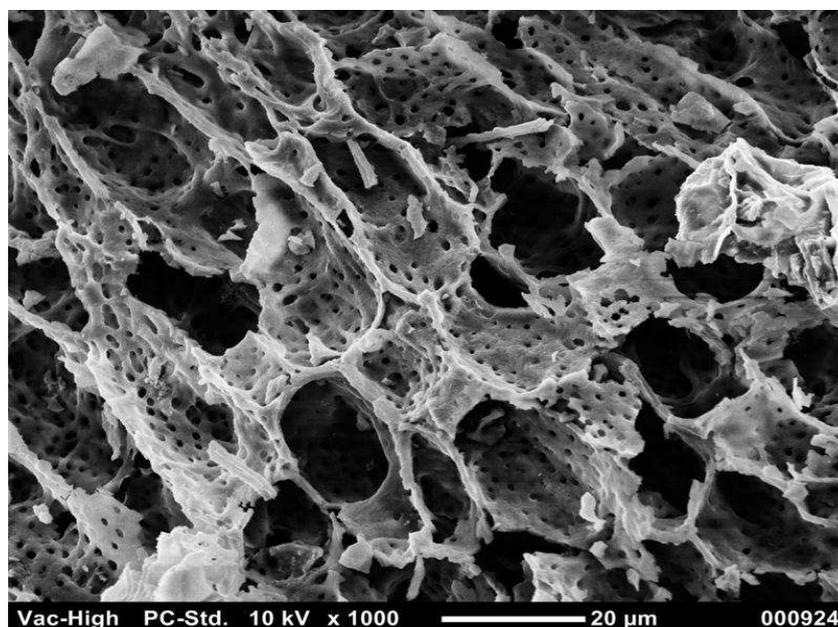


Fig. 1 Scanning electron microscope picture (\* 1000 magnification)

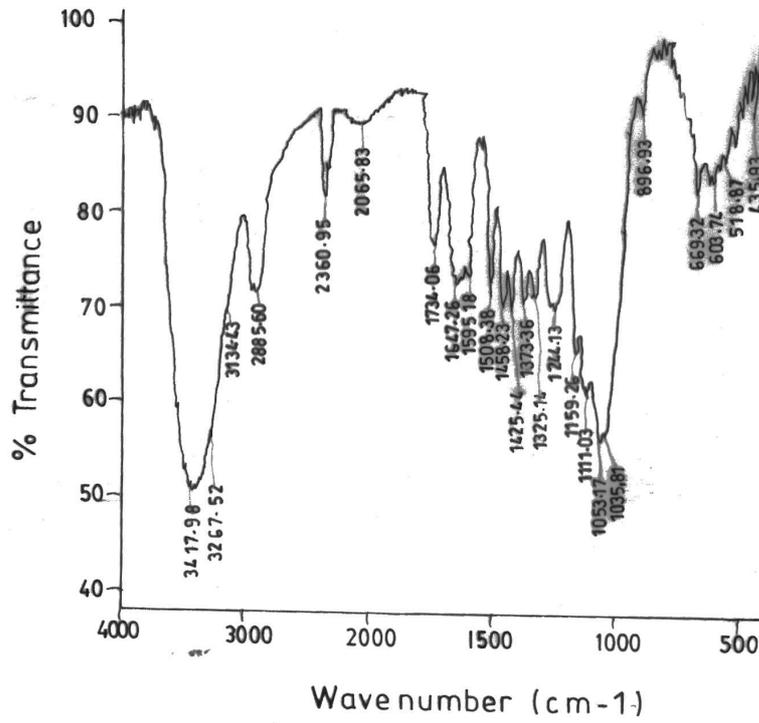


Fig. 2a FTIR spectra of PSD

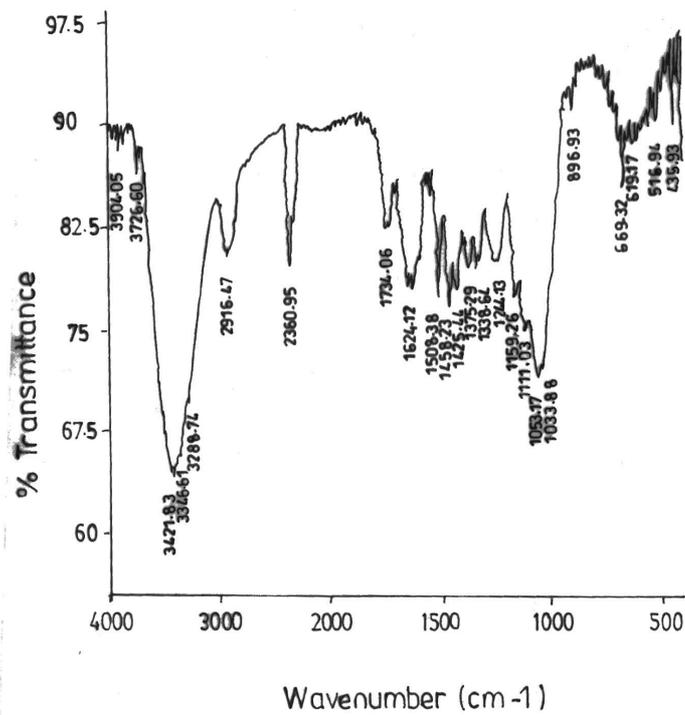
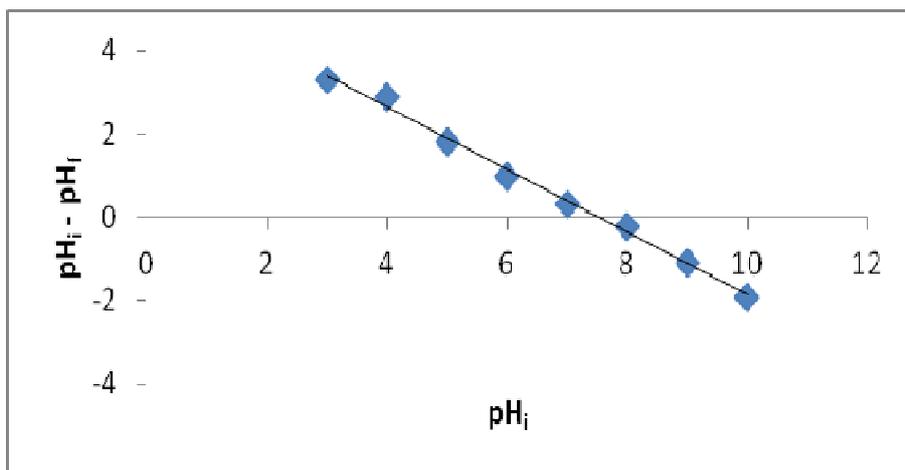


Fig. 2b FTIR spectra of PSD after adsorption of rhodamine B

Fig. 4 pH Point of zero charge (pH<sub>ZPC</sub>)

### 2.3 PREPARATION OF ADSORBATE

The main adsorbate used in this research is rhodamine B (RB), a basic (cationic) dye with molecular formula  $C_{28}H_{31}N_2O_3Cl$  and molecular weight =  $479.02 \text{ gmol}^{-1}$  (supplied by M & B Laboratory chemicals) in single, binary and ternary system with: methylene blue (supplied by M & B Laboratory chemicals) and acid blue in different mass ratios; their chemical structures are given in Figures 5-7.

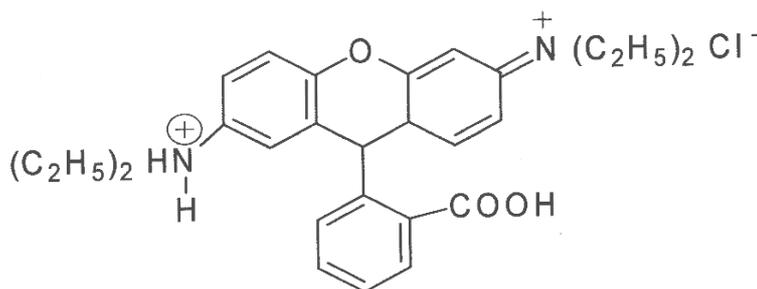


Fig. 5 Structure of Rhodamine B

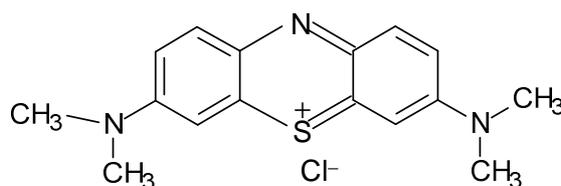


Fig. 6 Structure of Methylene blue

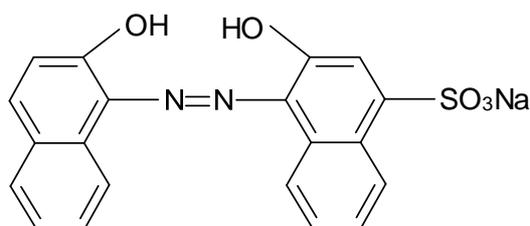


Fig. 7 Structure of Acid blue161

The stock solution of each dye was prepared by dissolving 1g of the dye in some distilled water in 1000 cm<sup>3</sup> (1dm<sup>3</sup>) volumetric flask and then made to the mark with distilled water. This gives 1000 mg/L of the solution. Working solutions were prepared from the stock solution by serial dilution.

#### 2.4 BATCH ADSORPTION STUDIES

Batch adsorption experiments were carried out in which 50 cm<sup>3</sup> of rhodamine B of different concentrations (10 -100 mg/L) was mixed with a definite mass (0.1-0.5g) of RSD in 150 cm<sup>3</sup> glass bottles and were agitated in a horizontal mechanical shaker (SM 101 by Sugarfriend medicals) at 120 rpm for predetermined periods of time and temperature at neutral pH. The mixture was filtered through whatman filter paper, and filtrate analyzed for residual dye content using Genesys 10 UV-Visible Scanning Spectrophotometer.

Mathematical quantitative evaluations were carried out by using the following equations:

$$q_e = \frac{(C_o - C_e)V}{W} \text{----- (1)}$$

$$q_t = \frac{(C_o - C_t)V}{W} \text{----- (2)}$$

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

Since adsorption is affected by physical and chemical variables, the influence of initial dye concentration, RSD dose, pH, temperature and contact time are investigated in this study.

## RESULTS AND DISCUSSION

### 3.1 CHARACTERIZATION OF RSD

The Scanning Electron Microscope (SEM) was used to study the surface morphology of the adsorbent. The surface textural structure of RSD is presented as scanning electron micrograph observed at  $\times 1000$  magnification (Fig. 1). The honey-comb like SEM image of RSD showed the irregular texture and porous nature of the surface of the adsorbent. Its seemingly high porosity is an indication of the presence of many active sites which enhances adsorption [11, 12].

The FTIR spectrum of RSD before adsorption (Fig. 2) displays a number of absorption peaks, indicating the complex nature of the material. The spectrum revealed a diagnostic band at 3417 cm<sup>-1</sup> representing bonded -OH in the oxygen containing functional groups. The positions of the C-H (2885 cm<sup>-1</sup>), aromatic C = C (1647 cm<sup>-1</sup>), and carbonyl (1734 cm<sup>-1</sup>) vibrations, contributed by those in the structure of cellulose, hemicelluloses and lignin, which are common components of plant materials, are indicated by spectrum of RSD. Thus, the FTIR spectrophotometric analysis indicates that the adsorbent has potential adsorption sites as represented by functional groups COOH, C = O, and C = C [12].

The FTIR spectra of RSD after Adsorption of rhodamine B is shown in Fig. 3. There are remarkable changes in the position or occurrences of some diagnostic bands. A new band appeared at 3726 cm<sup>-1</sup> after the adsorption of rhodamine B. This can be assigned to O-H stretching vibration, possibly from water molecules from the dye. While some bands shifted. The shift in adsorption bands may be an evidence of some sort of chemical reaction between the adsorbent surface and the dye. There was a shift in the position of -OH band at 3417 cm<sup>-1</sup> before adsorption to 3421 cm<sup>-1</sup> after adsorption. Similarly, C=O band shifted from 1647 cm<sup>-1</sup> to 1624 cm<sup>-1</sup>. Also, C-H band shifted from 2885 cm<sup>-1</sup> to 2916 cm<sup>-1</sup>. These observations showed that adsorption of rhodamine B certainly occurred.

From Fig. 4, the point of zero charge pH is 7.83. At a pH below  $pH_{zpc}$  of the adsorbent, the surface of the adsorbent is positively charged and attracts anions. At pH above  $pH_{zpc}$  of the adsorbent, the surface of the adsorbent is negatively charged and attracts cations. [13].

### 3.2 EFFECTS OF ADSORBENT DOSE ON RHODAMINE B ADSORPTION

The adsorption capacity of PSD for RB decreases with increase in dose from 0.1 to 0.6 g for all the dye systems as shown in Figure 8. As dose increased from 0.1 to 0.6 g,  $q_e$  decreased from 16.84 to 3.89 mg/g in the RB single dye system, from 16.89 to 3.89 mg/g in the RB binary system of RB+MB, from 20.07 to 3.94 mg/g in the RB binary system RB+AB, from 16.51 to 3.26 mg/g in the ternary dye system.

The specific uptake of the dye decreased with increasing sawdust dose because at low doses, the active sites were effectively utilized. But, as the adsorbent dose was increased, a significant portion of the available active sites on the adsorbent overlapped which resulted in reduction in specific uptake [14]. Similar observations were reported [1,14 15, 16; 17].

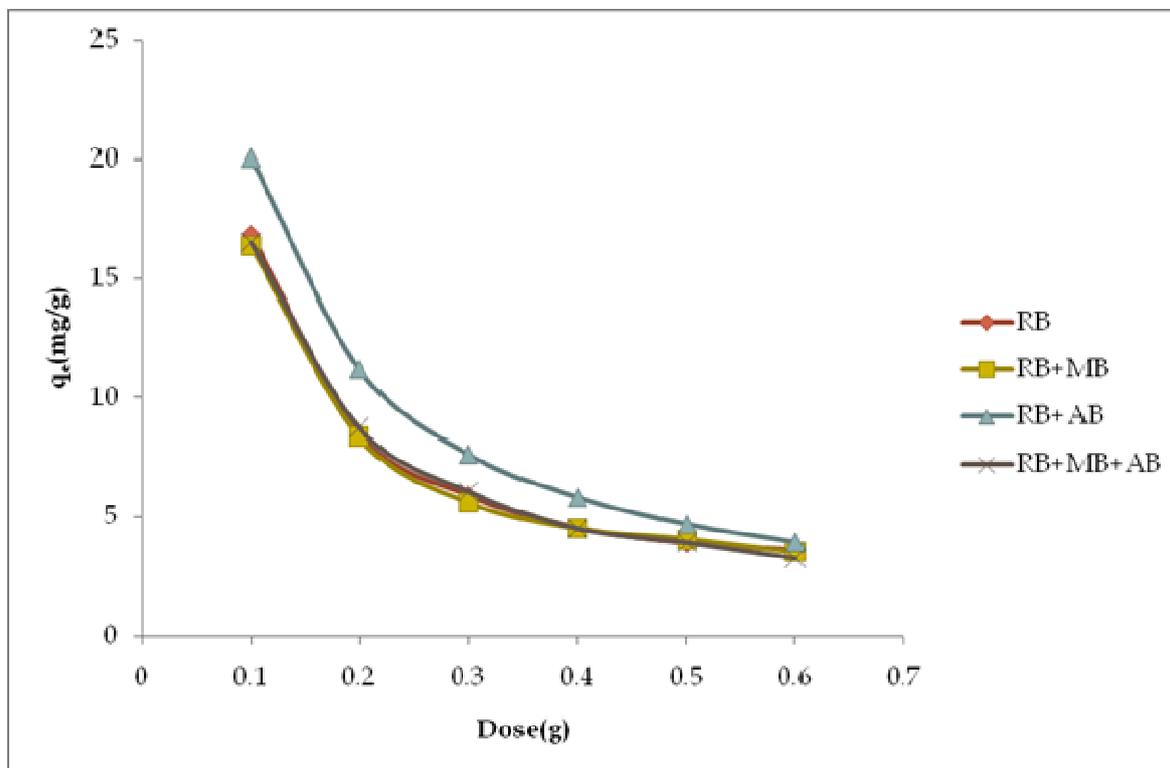


Fig. 8 Effects of adsorbent dose on adsorption of rhodamine B on PSD

### 3.3 EFFECTS OF SOLUTION pH ON ACID DYE ADSORPTION

The pH of an aqueous solution is an important parameter in wastewater treatment by adsorption technique. The pH controls the speciation and degree of ionization of the adsorbate. For the adsorption of rhodamine B, adsorption capacity,  $q_e$  (mg/g), increased with increasing pH from pH 1 (17.98 mg/g), reaching a maximum at pH 3.1 (19.41 mg/g) and then decreased afterwards (16.72 at pH. 10.07) as shown in Fig. 4.11. This is contrast to expectation for a basic dye. The observation may be due to the hydrolysis of the adsorbent in water which creates positive charged sites on the adsorbent [18]. Similar behavior of rhodamine B differing from expectation of basic dyes were reported in literature of adsorption of RB as pH 3.1 [19] and as pH 3.8 - 5.8 [18].

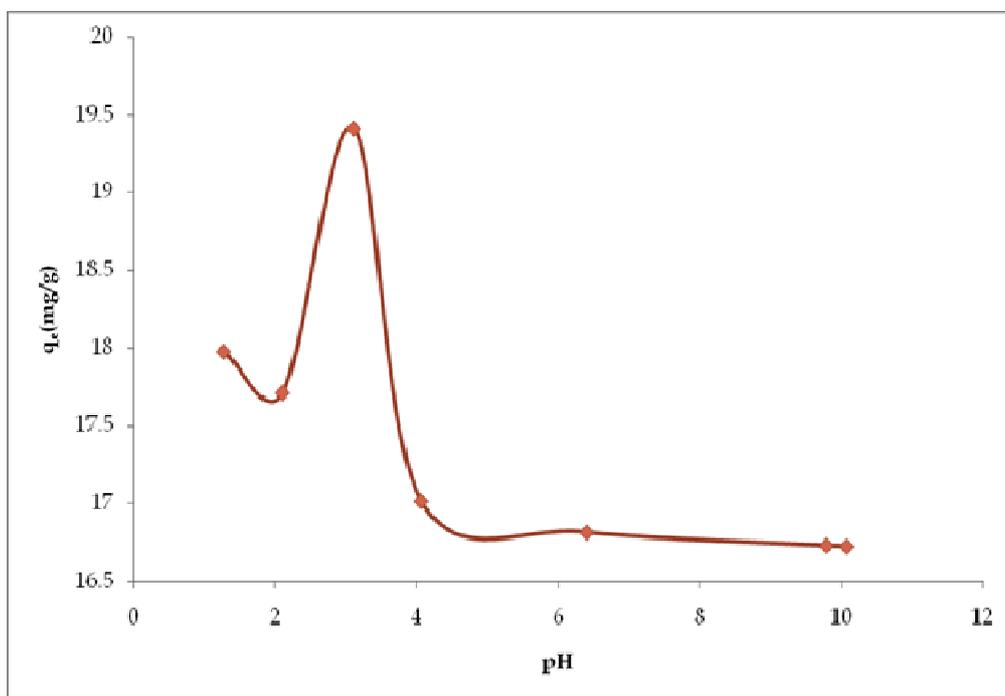


Fig. 9 Effects of pH on adsorption rhodamine B on PSD

#### 3.4. EFFECTS OF INITIAL DYE CONCENTRATIONS ON RHODAMINE B ADSORPTION

In investigating the effects of initial concentration of rhodamine B on its adsorption onto PSD, a total of six adsorbate systems were considered: (i) Rhodamine B only (single system) (ii) Rhodamine B together with 10 mg/L acid blue (RB+AB1; binary system) (iii) Rhodamine B together with 20 mg/L acid blue (RB+AB2; binary system) (iv) Rhodamine B together with 10 mg/L Methylene blue (RB+MB1; binary system) (v) Rhodamine B together with 20 mg/L Methylene blue (RB+MB2; binary system) (vi) A mixture of 50 mg/L of rhodamine B and 20 mg/L each of acid blue 161 and methylene blue (RB+MB+AB; ternary system) The uptake of rhodamine B (RB) per unit mass of PSD increased with increasing initial concentration of the dye for all the adsorbate- adsorbent systems i.e single, binary and ternary systems as shown in Fig 4.14. As the initial concentration increased from 10-100 mg/L,  $q_e$  increased from 4.02 to 41.49 mg/g in single dye system, from 3.49 to 41.48 mg/g in the RB binary system of RB+MB1, from 2.32 to 41.40 mg/g in the RB binary system of RB+MB2, from 4.10 to 41.40 mg/g in the RB binary system of RB+AB1, from 3.13 to 41.56 mg/g in the RB binary system RB+AB2, from 2.42 to 24.89 mg/g in the ternary dye system. The effect of varying compositions i.e different concentrations of other present dye(s) is not well defined.

The observed increase in the dye specific uptake for the three dyes in single, binary and ternary systems with increasing initial dye concentration may be because at low concentrations, the number of dye molecules available is low, but at higher concentrations, the number of dye molecules available is high enough to overcome resistance to mass transfer. Similar observations were reported in the literature[12, 20].

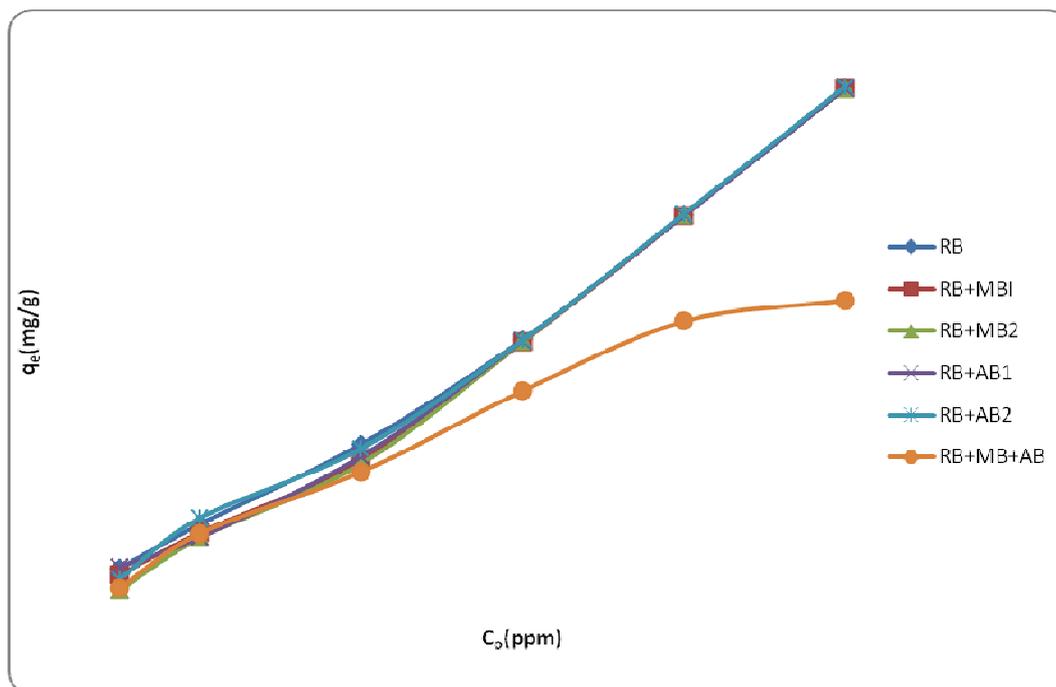


Fig. 10 Effects of initial dye concentration on adsorption of rhodamine B on RSD

### 3.5 EFFECTS OF CONTACT TIME AND KINETICS

The adsorption of RB in single, binary and ternary dye system as shown in Fig.4.17, adsorption increased with time and reached equilibrium within 45hrs after which no significant adsorption is observed. As time increased from 0 – 45 hrs,  $q_e$  (mg/g) increased from 0 – 11.92 for single system, from 0 – 11.88 for binary system RB+MB, from 0 – 12.072 for binary system RB+AB and 0 – 11.975 for ternary system RB+MB+AB. After 45 hrs,  $q_e$  remains constant for all the dye systems.

For the three dyes in single, binary and ternary system,  $q_e$  increased with time and then reached equilibrium at a point after which it becomes constant. This is because as time increases, the surface of the adsorbent has longer contact with the dye thereby attracting more dye molecules. But at equilibrium, the surface of the adsorbent has been occupied. Therefore after equilibrium,  $q_e$  becomes constant. Similar reports were given in the literature[5, 21].

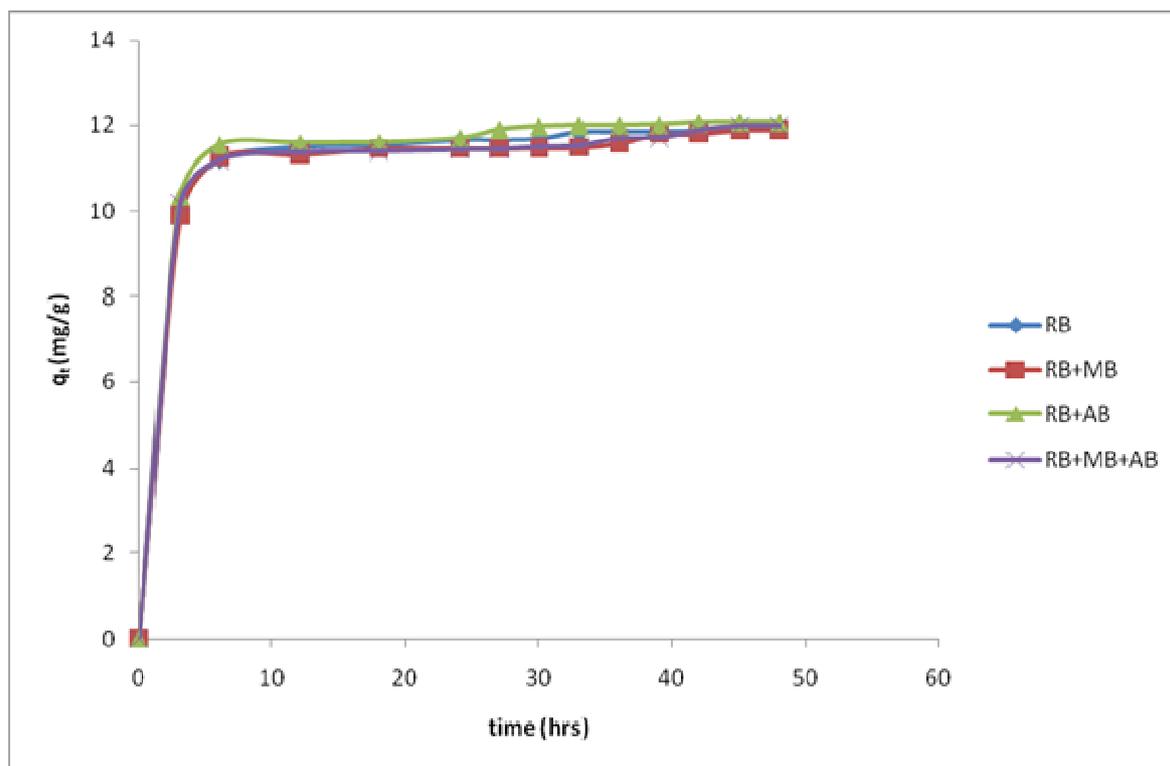


Fig. 11 Effects of contact time on adsorption of rhodamine B on PSD

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. Adsorption kinetics are analyzed using pseudo first order [22], pseudo second order [23], Elovich [24] and intraparticle diffusion [25, 26] Kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients ( $R^2$  values close or equal to 1). A relatively high  $R^2$  value indicates that the model successfully describes the kinetics of the adsorption. In this work, in order to examine the adsorption kinetics, two popular kinetic models: pseudo-first order and pseudo-second order were applied.

The linear forms of the models are given as:

$$\text{Pseudo-first-order equation: } \ln(q_e - q_t) = \ln(q_e) - K_1 t \quad (6)$$

$$\text{Pseudo-second-order equation: } \frac{t}{q_t} = \frac{1}{K_2 q_s^2} + \frac{1}{q_s} t \quad (7)$$

Where  $q_t$  is the adsorption capacity at time  $t$  ( $\text{mg g}^{-1}$ ),  $K_1$  is the rate constant of pseudo-first-order adsorption ( $\text{min}^{-1}$ ), and  $K_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the second-order-rate constant of adsorption.

The plots are shown in Fig. 25 and 26 and the constants calculated from the plots are given in table 2. From table 2,  $R^2$  values for Pseudo second order kinetics > pseudo – 1st-order kinetics. The adsorption capacity calculated,  $q_{e(\text{calc})}$ , for pseudo second order kinetics is closer to  $q_e$  experimented than  $q_e$  calculated for pseudo – 1st-order kinetics for the adsorption of acid blue 161 in single, binary and ternary dye system. Hence, these adsorption processes follow pseudo-2nd – order kinetic model which suggest a chemisorption process. Similar observations were reported in literature [15, 21, 27].

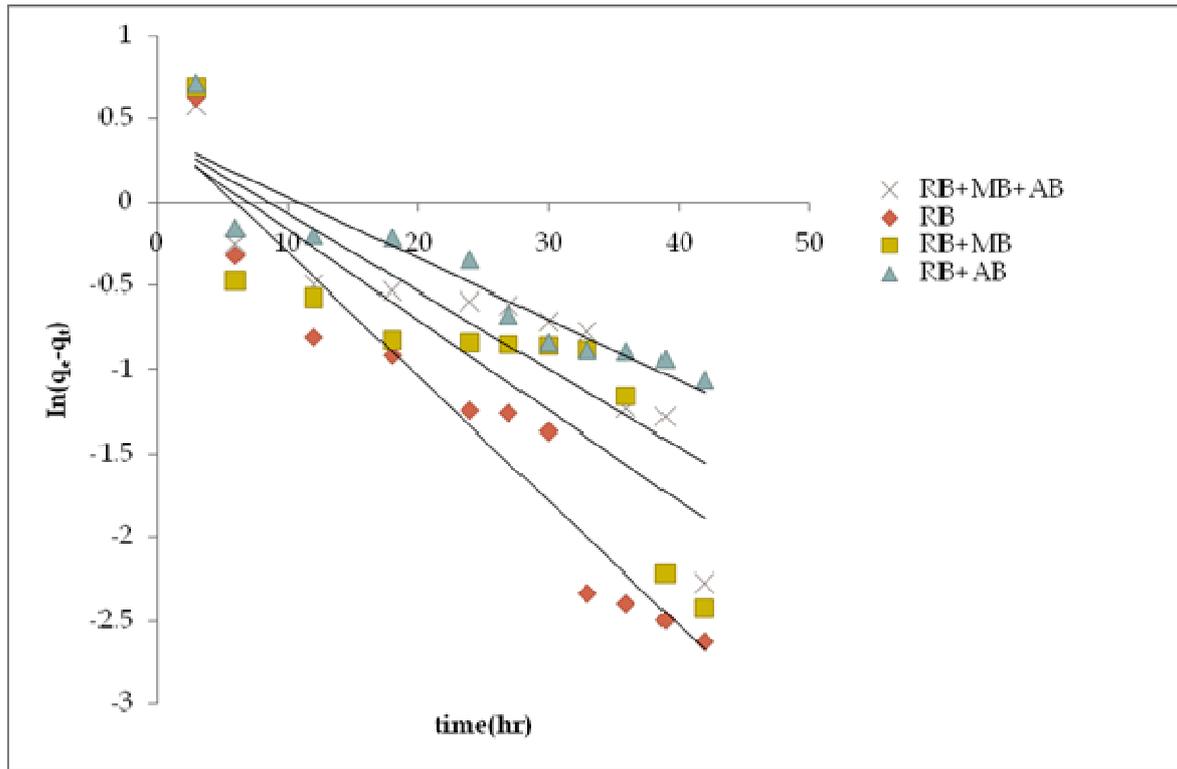


Fig. 25 Pseudo-first order kinetics plot for the adsorption of rhodamine B in single, binary and ternary system

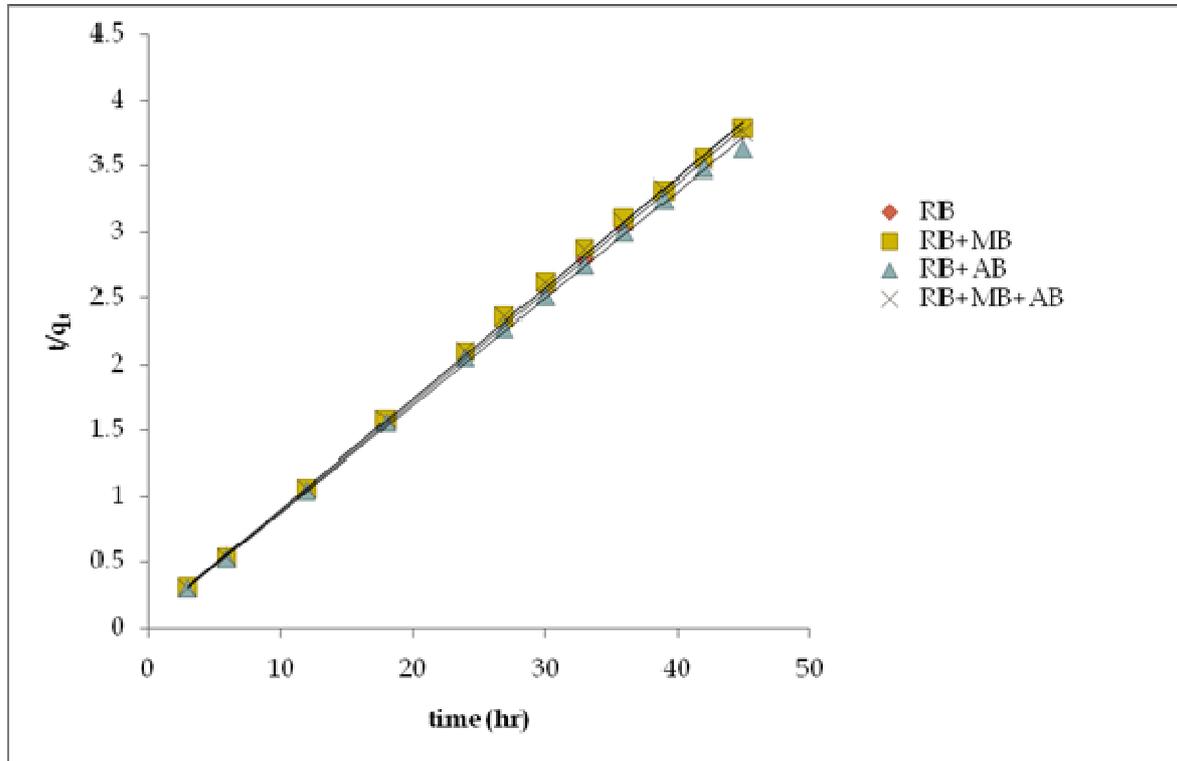


Fig. 26 Pseudo-second order kinetics plot for the adsorption of rhodamine B in single, binary and ternary system

Table 1: Kinetics Parameters for Adsorption of Rhodamine B onto PSD

ADSORBATE	$q_e(\text{exp})$	PSEUDO-1ST-ORDER			PSEUDO-2ND-ORDER			h
		$R^2$	$q_e(\text{calc})$	$K_1$	$R^2$	$q_e(\text{calc})$	$K_2$	
RB	11.93	0.923	1.06	0.074	0.999	12.05	0.128	18.52
RB+MB	11.88	0.739	1.06	0.054	0.999	11.90	0.116	16.39
RB+AB	12.40	0.860	1.07	0.036	0.999	12.35	0.098	14.93
RB+MB+AB	11.98	0.763	1.07	0.046	0.999	12.05	0.103	14.93

### 3.6 EFFECTS OF TEMPERATURE ON ADSORPTION OF DYES

The specific adsorption of rhodamine B increased with increasing temperature for all the adsorbate-adsorbent systems i.e single, binary and ternary systems as shown in Fig 4.20. As temperature increased from 303 K - 333 K,  $q_e$  for RB in single system increased from 16.77 - 22.05 mg/g. For RB binary system RB+MB,  $q_e$  increased from 16.72 - 21.13 mg/g. For RB binary system RB+AB,  $q_e$  increased from 16.61 - 21.86 mg/g. For RB ternary system,  $q_e$  increased from 16.62 - 21.29 mg/g.

For the three dyes in single, binary and ternary system, adsorption capacity,  $q_e$  increased with increasing temperature. This may be due to an increase in the number of molecules that become mobile and acquire sufficient energy to undergo an interaction with active sites at the surface. In addition, an increase in temperature may produce a swelling effect with the internal structure of the adsorbent enabling large dyes to penetrate further [28]. Similar report was given in the literature [2].

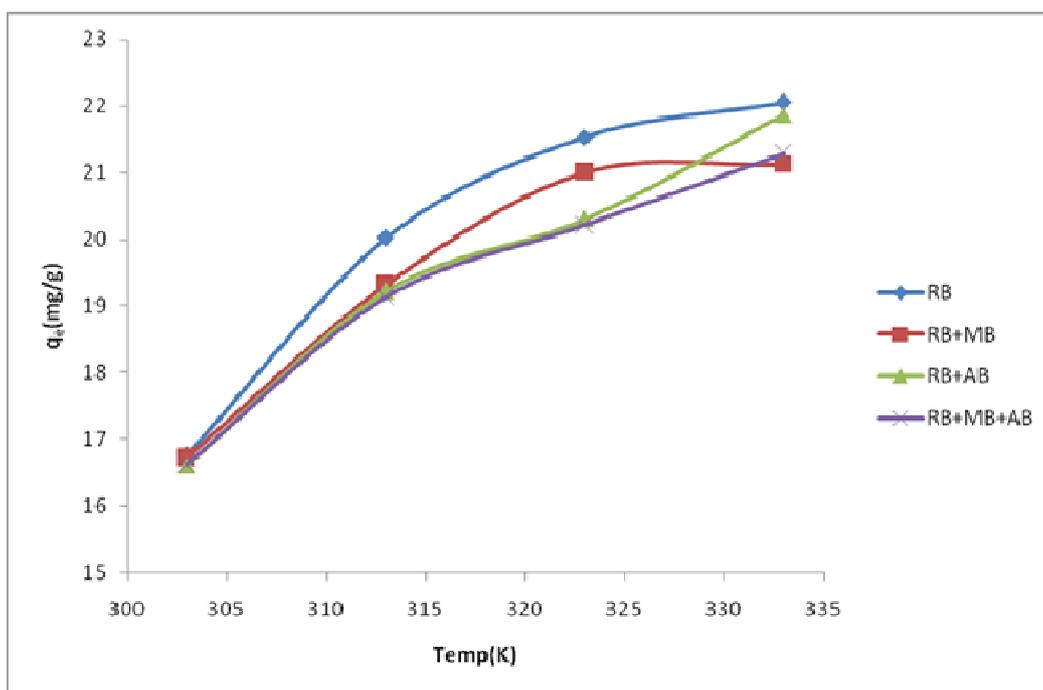


Fig. 12 Effects of temperature on adsorption of rhodamine B on P

### 3.7 ADSORPTION ISOTHERMS

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of equilibrium adsorption data by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purposes [29]. Adsorption isotherm study is carried out on three well-known isotherms, Langmuir and Freundlich. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [30]. The Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [30] while the Temkin isotherm assumed that because of the adsorbate – adsorbent

interactions, the energy of adsorption will decrease linearly with coverage [31]. The applicability of the isotherm equation is compared by judging the correlation coefficients,  $R^2$  [20].

### 2.5.1 Langmuir isotherm

The linear form of Langmuir's isotherm model is given by the equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \left(\frac{1}{Q_0}\right) C_e \quad (3)$$

Where  $C_e$  is the equilibrium concentration of adsorbate (mg/l)

$q_e$  is the amount of adsorbate absorbed per unit mass of adsorbate ( $\text{mg g}^{-1}$ ).

$Q_0$  and  $b$  are Langmuir constants related to monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively [20].

### 2.5.2 Freundlich isotherm

The well-known logarithmic form of Freundlich isotherm model is given by the following equation:

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

$K_f$  is rough indicator of the adsorption capacity related to the bond energy and  $\frac{1}{n}$  is the adsorption intensity of dye onto the adsorbent or surface heterogeneity [32].

### 2.5.3 Temkin isotherm

The Temkin model is expressed as

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (5)$$

$q_e$  is the amount adsorbed at equilibrium ( $\text{mg/g}$ )

$C_e$  is the equilibrium concentration of the adsorbate

$A_T$  and  $b_T$  are Temkin constants

$R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )

$T$  is the temperature in Kelvin [14, 33].

The isotherm plots of Langmuir, Freundlich and Temkin for adsorption of rhodamine B (RB) in single, binary and ternary dye systems are shown in Figures 13 – 24. Isothermal parameters are calculated and presented in Table 4.6. The Co-efficient of correlation,  $R^2$  values, in Table 4.6 for the adsorption of RB in single system follows Freundlich > Temkin > Langmuir Isotherm. Hence, adsorption of RB in single system onto PSD follows Freundlich isotherm, which suggests multilayer adsorption. Adsorption of rhodamine B in binary systems of RB+MB and RB+AB, has  $R^2$  values of Langmuir > Freundlich > Temkin Isotherm. Hence, adsorption of RB in binary systems onto PSD follows Langmuir isotherm which suggests monolayer adsorption. Adsorption of rhodamine B in ternary dye system has  $R^2$  values of Temkin isotherm greater than Freundlich isotherm which is also greater than Langmuir isotherm. Hence, adsorption of RB from its ternary mixture onto PSD follows Temkin isotherm which implies that the energy of the coverage decreased linearly with coverage.

The monolayer adsorption capacity ( $q_0$ ) of PSD differs for each dye system; it is highest for RB single system, followed by its ternary system, then by binary system RB+AB and least for binary system of RB+MB. The affinity of PSD ( $b$ ) towards rhodamine B is highest for the binary system RB+AB, followed by the ternary system, then the

binary system RB+MB and least for the single system. The adsorption capacity related to bond energy ( $K_f$ ) is highest for binary system RB+AB, followed by single system, then by its ternary system and least for binary system of RB+MB. Considering the values of  $1/n$ , the adsorption of rhodamine B is favorable for all the dye systems as all the values are lesser than 1.

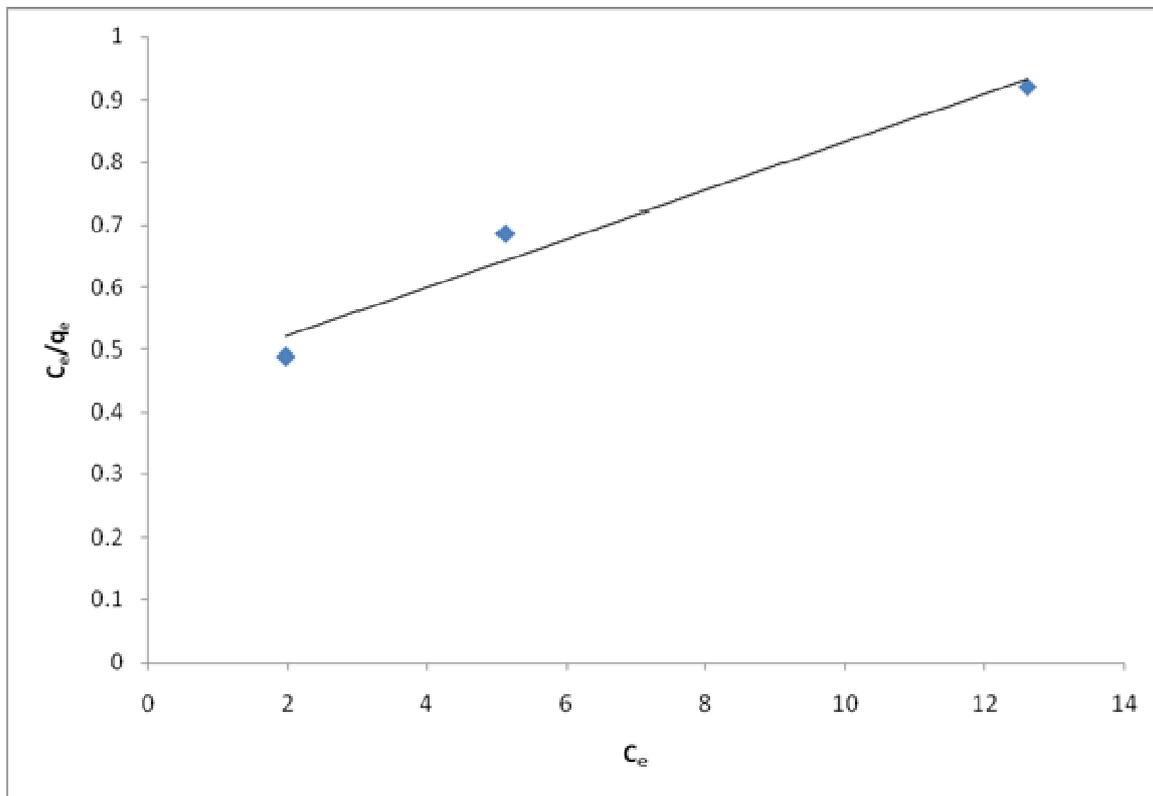


Fig. 4.33 Langmuir isotherm plot for the adsorption of rhodamine B on PSD

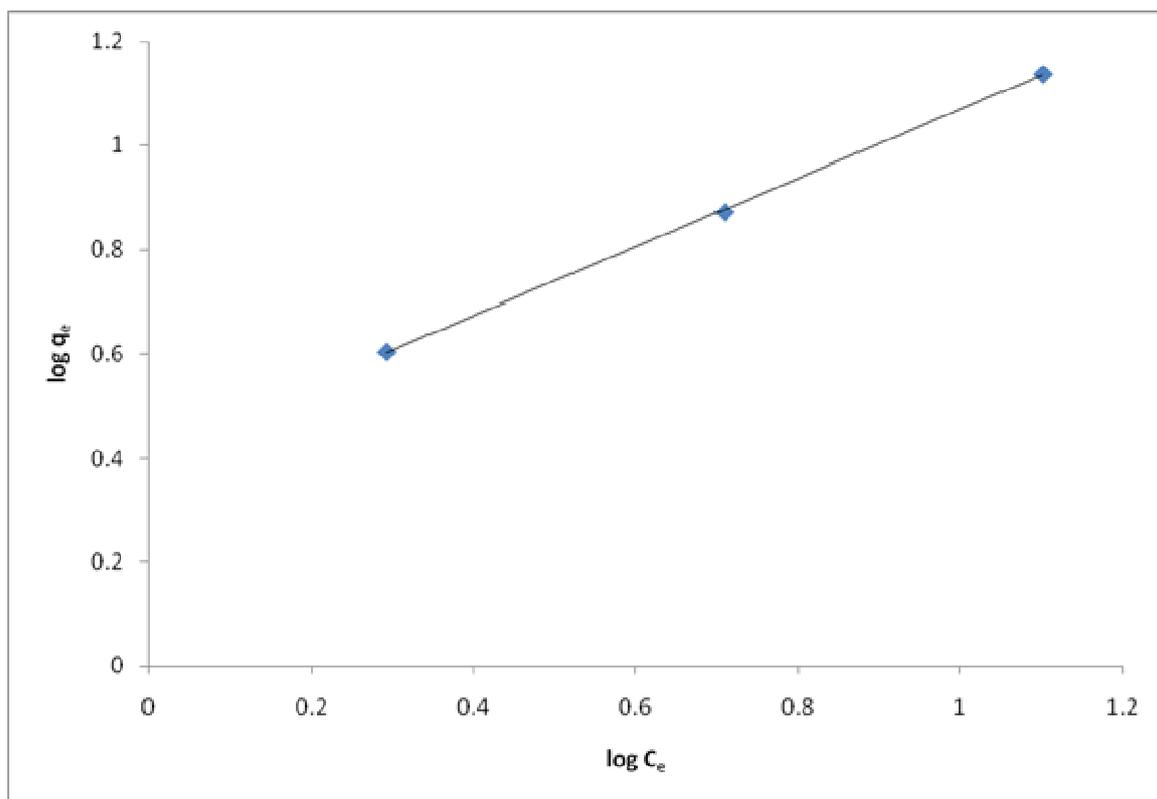


Fig. 4.46 Freundlich isotherm plot for the adsorption of rhodamine B on PSD

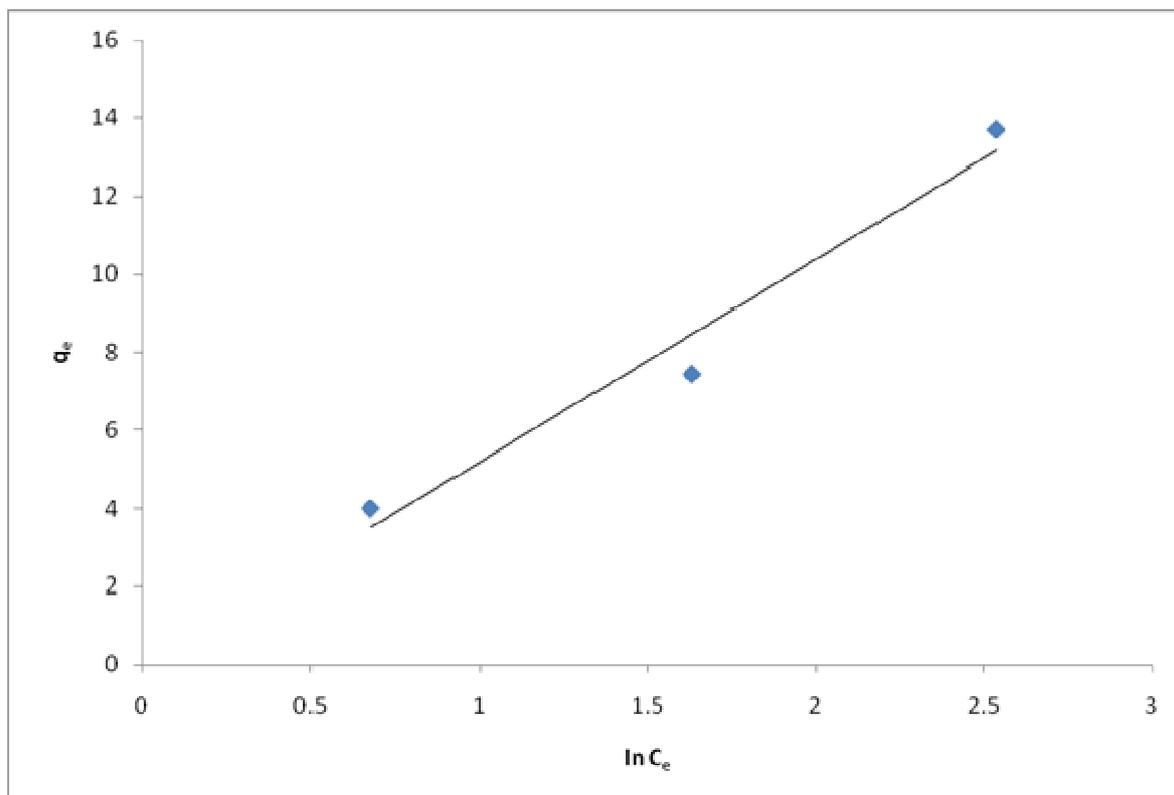


Fig. 4.47 Temkin isotherm plot for the adsorption of rhodamine B on PSD

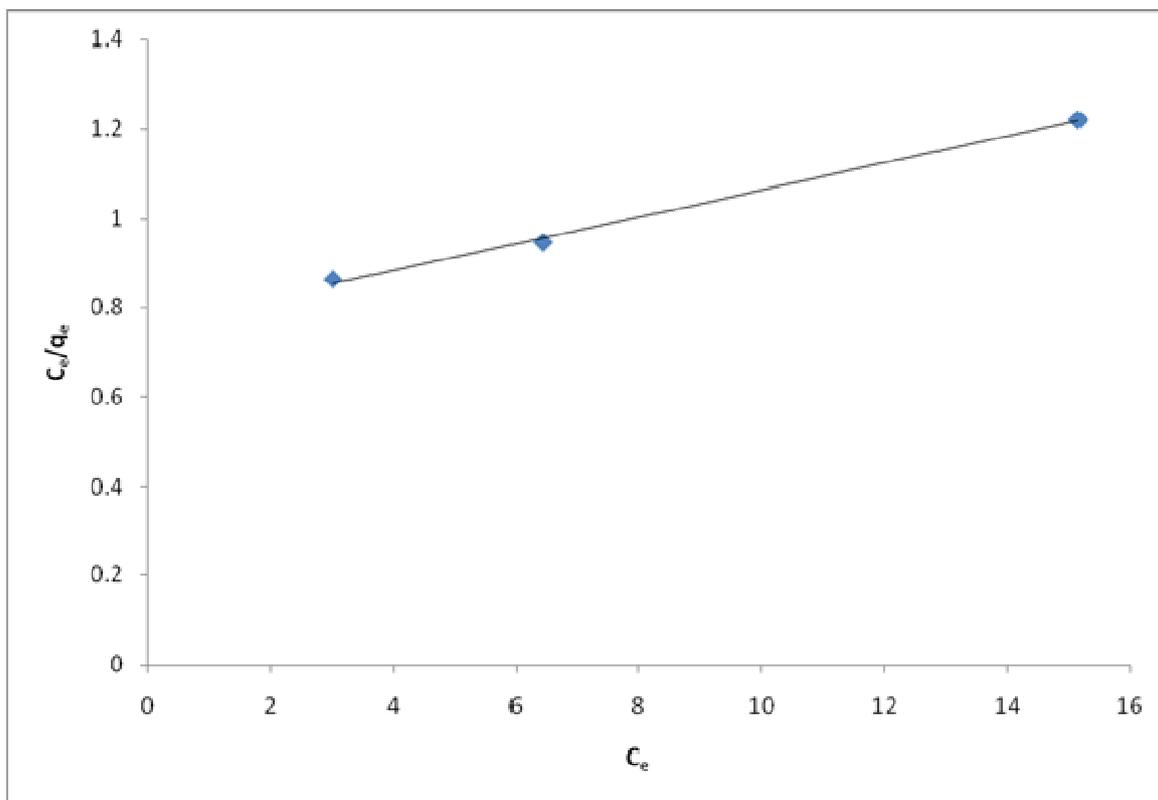


Fig. 4.48 Langmuir isotherm plot for the adsorption of rhodamine B from RB+MB system on PSD

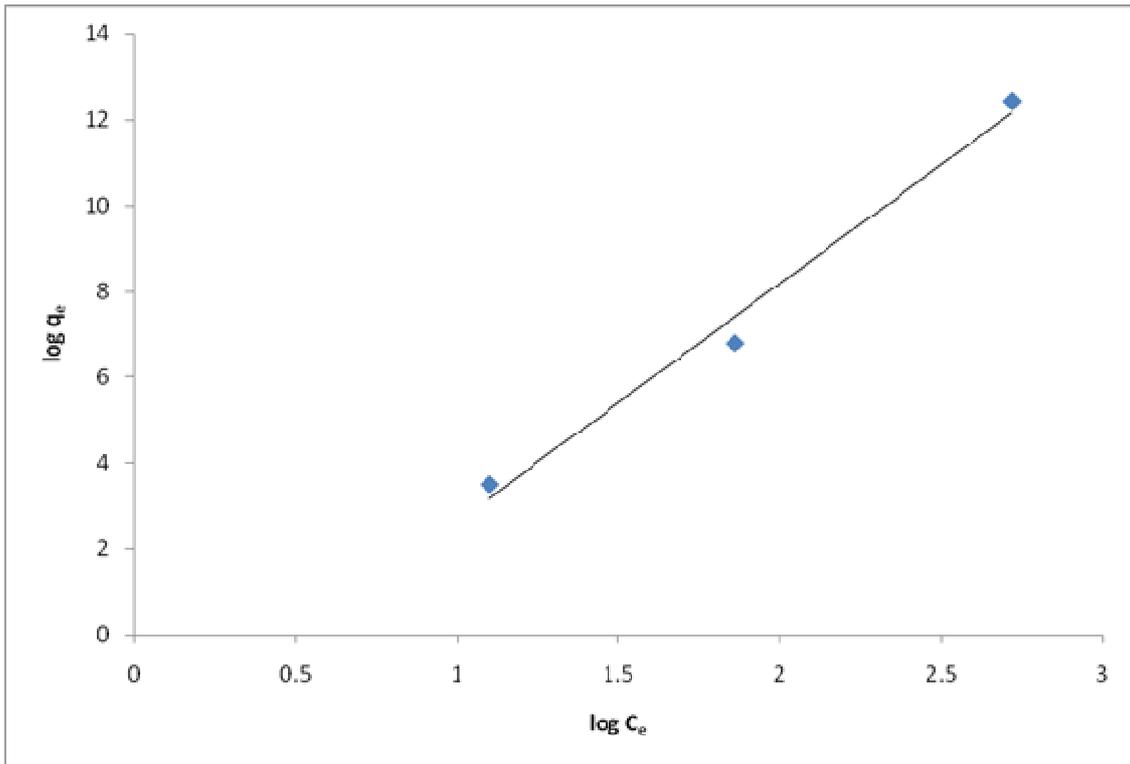


Fig. 4.49 Freundlich isotherm plot for the adsorption of rhodamine B from RB+MB system on PSD

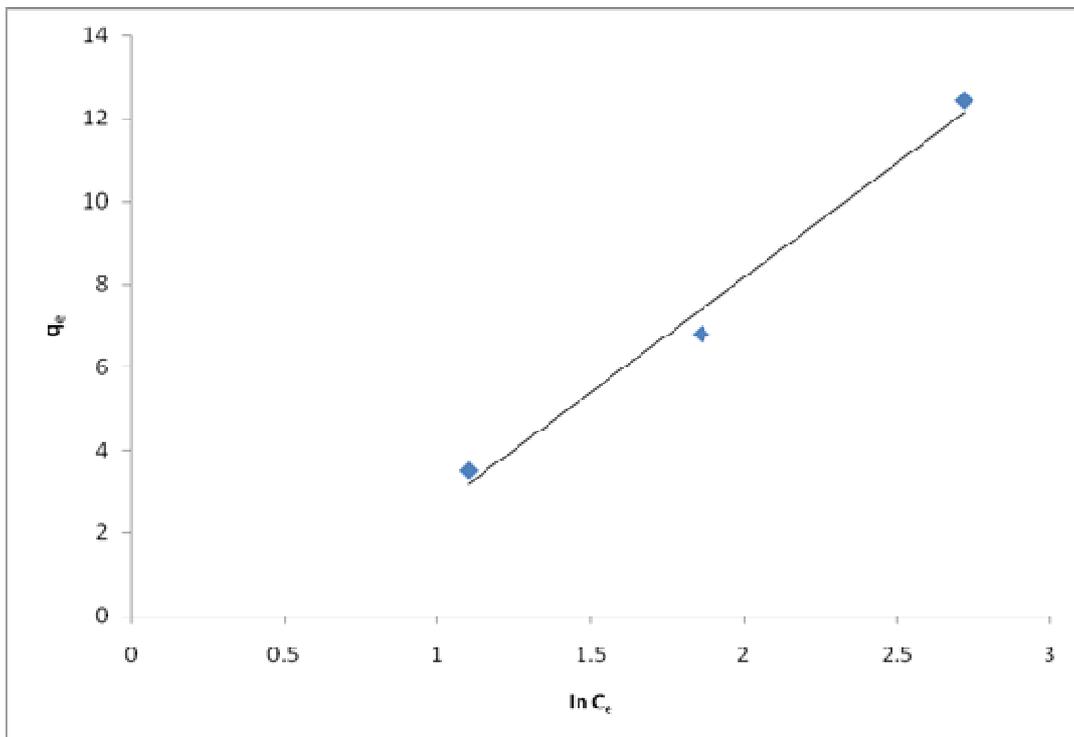


Fig. 4.50 Temkin isotherm plot for the adsorption of rhodamine B from RB+MB system on PSD

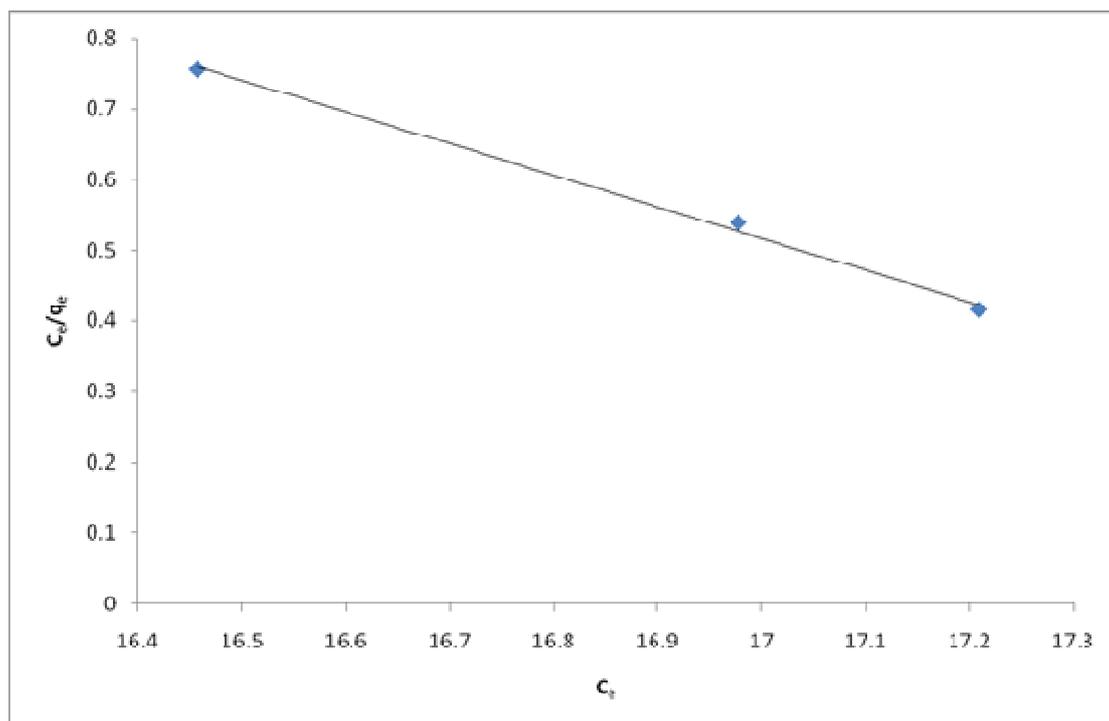


Fig. 4.51 Langmuir isotherm plot for the adsorption of rhodamine B from RB+AB system on PSD

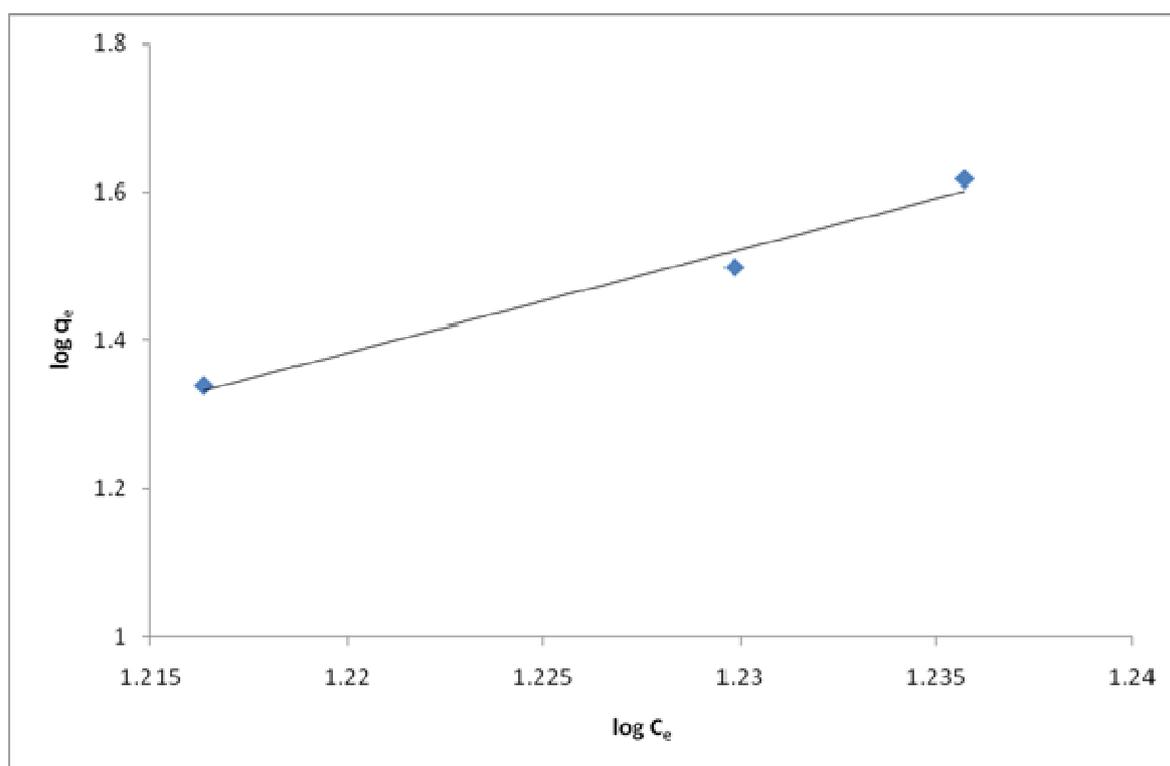


Fig. 4.52 Freundlich isotherm plot for the adsorption of acid blue from rhodamine B system on PSD

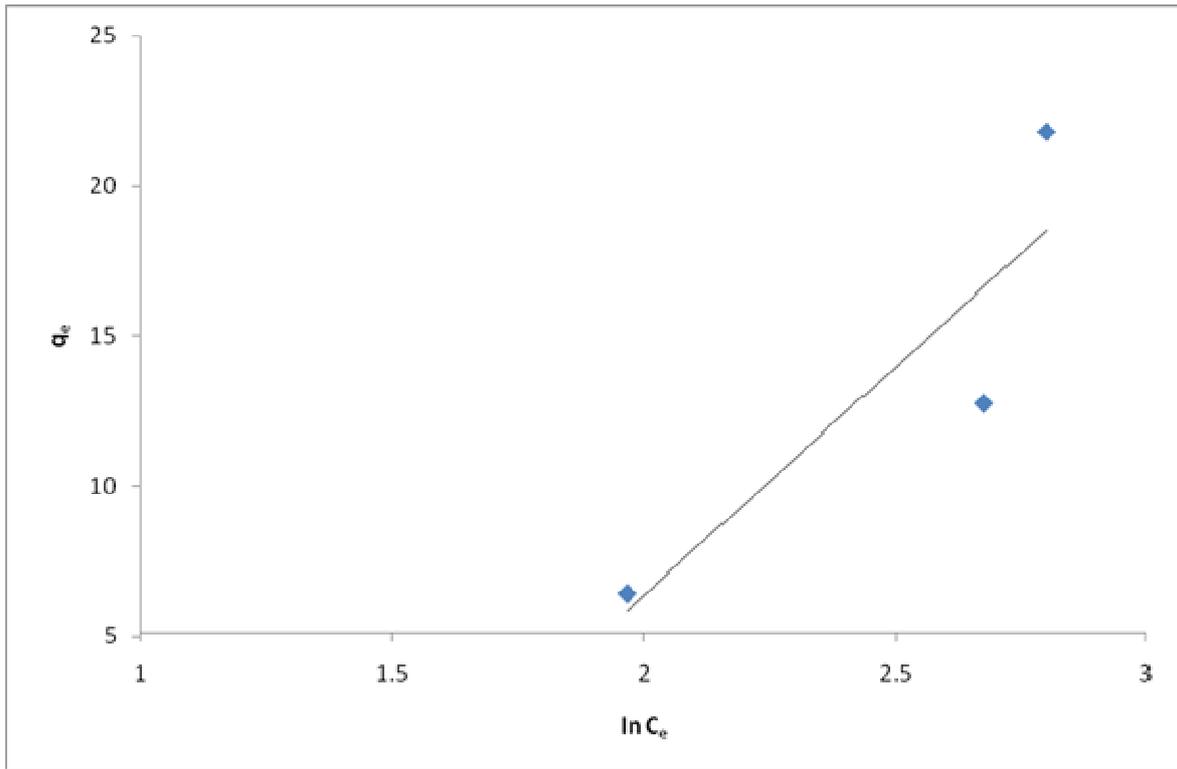


Fig. 4.53 Temkin isotherm plot for the adsorption of rhodamine B from RB+AB system on PSD

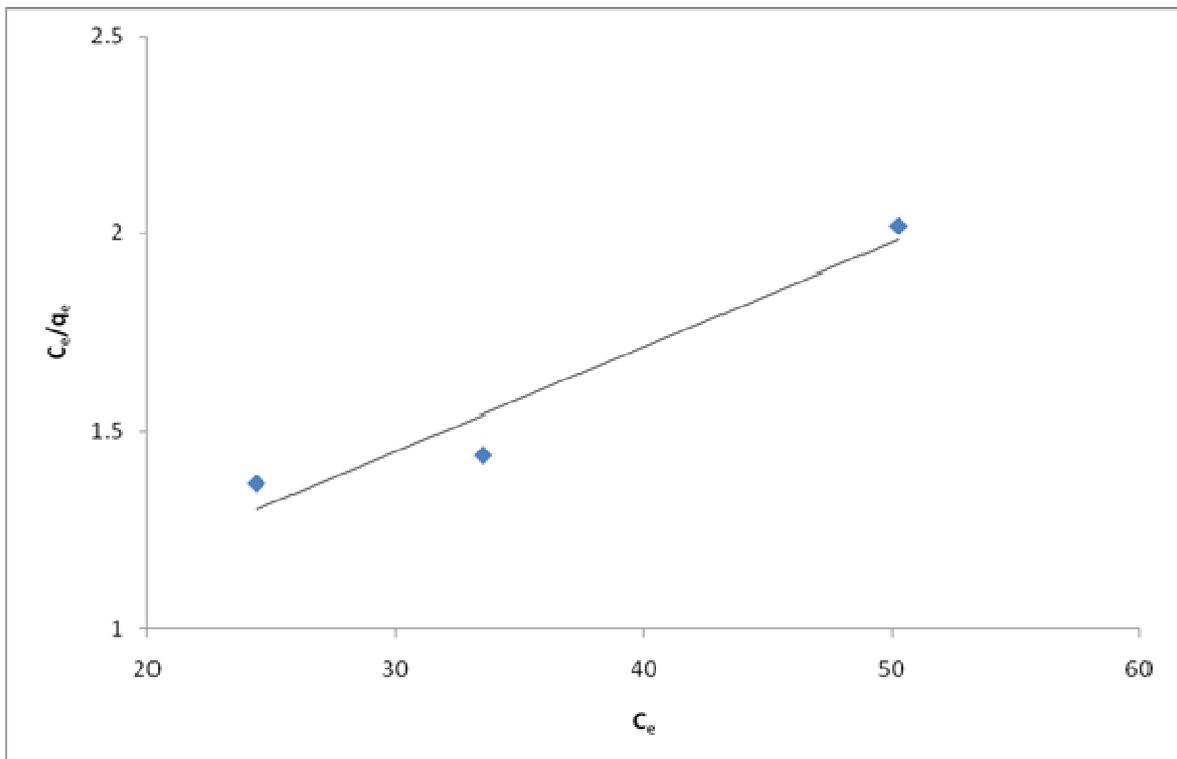


Fig. 4.54 Langmuir isotherm plot for the adsorption of rhodamine B from RB+MB+AB system on PSD

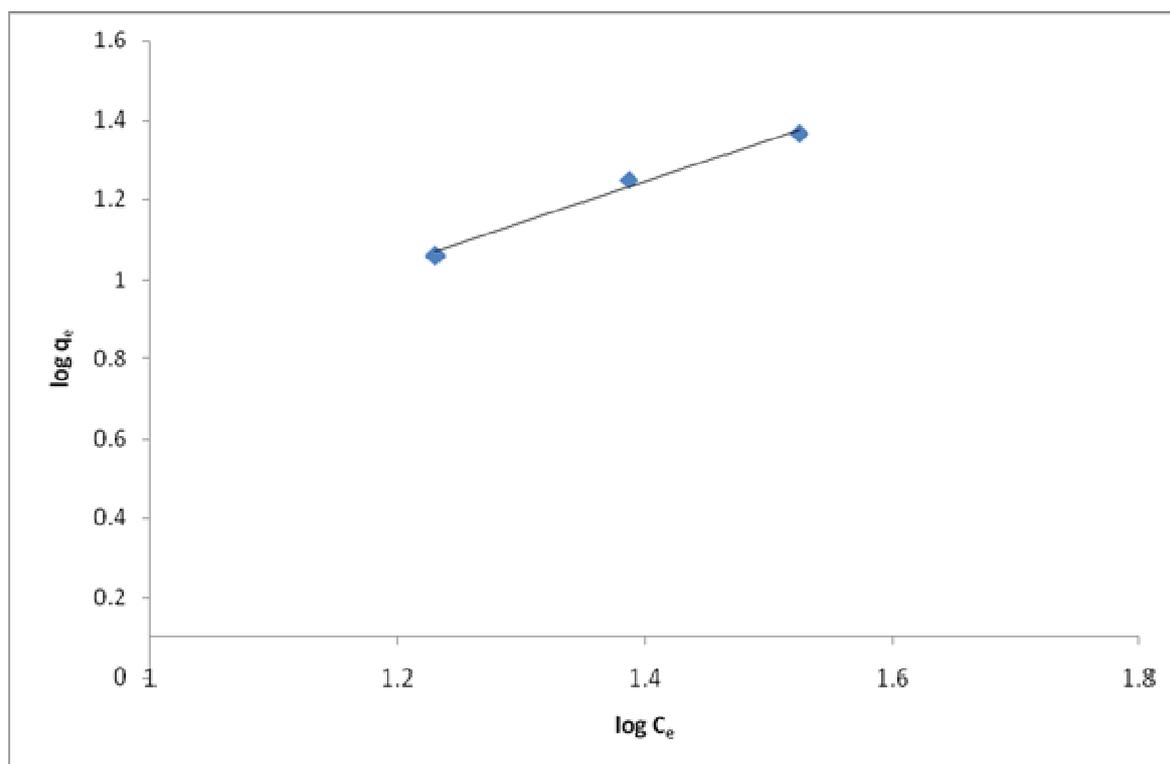


Fig. 4.55 Freundlich isotherm plot for the adsorption of rhodamine B from RB+MB+AB system on PSD

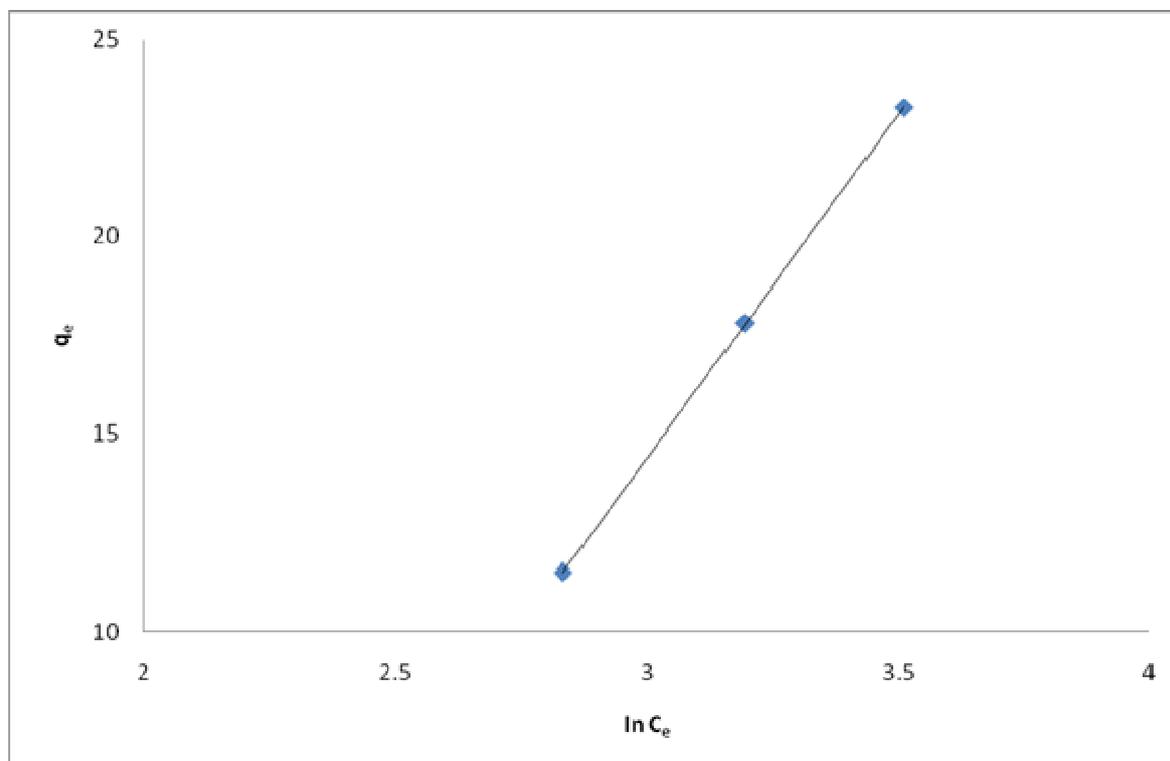


Fig. 4.56 Temkin isotherm plot for the adsorption of rhodamine B from RB+MB+AB system on PSD

Table 2: Isotherm Model Parameters for Adsorption of rhodamine B onto PSD

Adsorbate	LANGMUIR			FREUNDLICH			TEMKIM		
	R <sup>2</sup>	q <sub>o</sub>	b	R <sup>2</sup>	K <sub>f</sub>	1/n	R <sup>2</sup>	A <sub>T</sub>	b <sub>T</sub>
<b>RB</b>	0.643	43.48	0.003	0.999	2.56	0.659	0.966	1.00	485.48
<b>RB+MB</b>	0.997	34.48	0.038	0.995	1.51	0.782	0.987	1.70	454.39
<b>RB+AB</b>	0.996	36.62	0.055	0.981	4.36	0.631	0.779	4.85	166.61
<b>RB+MB+AB</b>	0.963	38.46	0.039	0.989	1.64	0.430	1	8.76	145.20

### 3.9 ADSORPTION THERMODYNAMICS

Thermodynamic parameters such as free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) change of adsorption can be evaluated from temperature parameters using Van t Hoff equation and is given as

$$\Delta G = -RT \ln K_0 \quad (8)$$

Where

$$K_0 = \frac{q_e}{C_e} \quad (9)$$

Also,

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

Therefore,

$$\Delta H - T\Delta S = -RT \ln K_0 \quad (11)$$

Linear form

$$\ln K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (12)$$

Where  $K_0$  is the sorption distribution coefficient,  $\Delta G$  ( $\text{KJmol}^{-1}$ ) is the free energy of adsorption,  $T$  (Kelvin) is the absolute temperature,  $R$  is the universal gas constant,  $\Delta H$  ( $\text{KJmol}^{-1}$ ) is the heat of adsorption,  $\Delta S$  ( $\text{KJmol}^{-1}\text{K}^{-1}$ ) is entropy change.

Negative values of  $\Delta G$  indicate spontaneous nature of the adsorption process, positive values of  $\Delta H$  indicate endothermic nature of the reaction while negative values of  $\Delta H$  indicate exothermic nature of the reaction [34].

Values for  $\Delta H$  and  $\Delta S$  were calculated from the slope and intercept of plot  $\ln K_0$  versus  $1/T$  (Fig. 27),  $\Delta G$  was calculated using Van t Hoff equation (equation 10 above) for adsorption of RB in single, binary, and ternary systems and shown in table 5.

$\Delta G$  has negative values. These negative values of  $\Delta G$  show that the adsorption process is feasible.  $\Delta H$  has positive values. These positive values of  $\Delta H$  confirm that the reaction is endothermic. Moreover,  $\Delta S$  has positive values. These positive values of  $\Delta S$  indicate the random movement of dye molecules at all the temperatures. Similar reports were given in the literature [15,35].

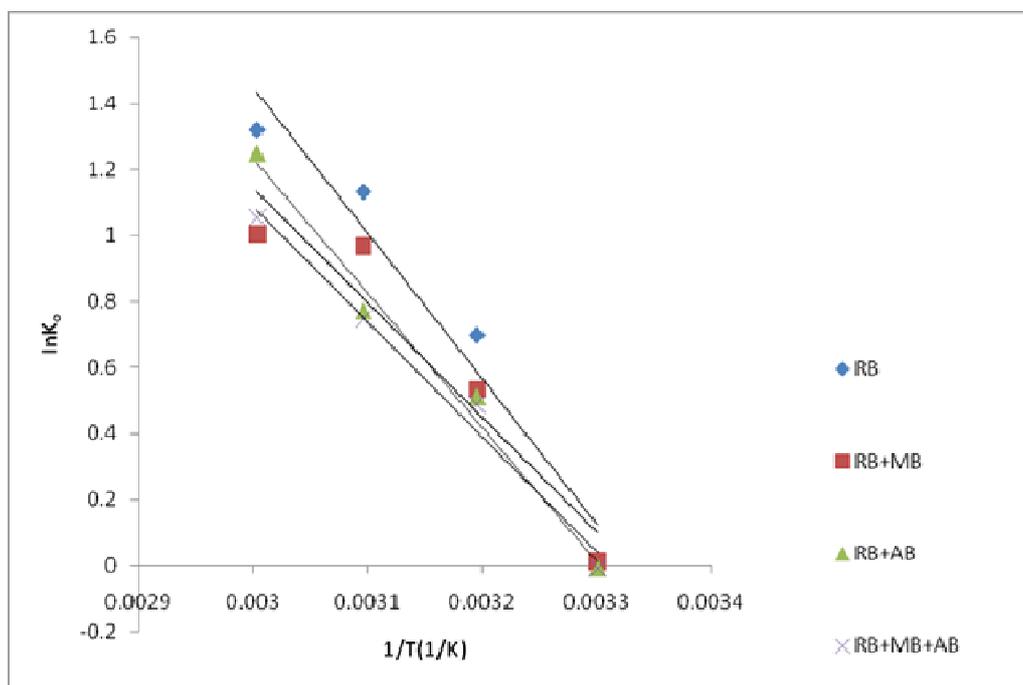


Fig. 4.65 A plot of  $\ln K_o$  against  $1/T$  for the adsorption of rhodamine B in single, binary and ternary mixture on PSD

Table 3: Thermodynamic Parameters for Adsorption of Rhodamine B onto PSD

Temp	Single system			Binary system (RB+MB)			Binary system (RB+AB)			Ternary system (RB+MB+AB)		
	$\Delta G$	$\Delta H$ (KJ)	$\Delta S$ (J/Kmol)	$\Delta G$	$\Delta H$ (KJ)	$\Delta S$ (J/Kmol)	$\Delta G$	$\Delta H$ (KJ)	$\Delta S$ (J/Kmol)	$\Delta G$	$\Delta H$ (KJ)	$\Delta S$ (J/Kmol)
303	-46.4492			-25.3798			-24.4240			-19.197		
313	-1816.95	36639.8	121.9664	-1382.4	28882.84	96.10984	-1324.49	33837.98	111.7402	-1272.29	28965.98	95.94356
323	-3041.9			-2596.27			-2067.94			-2003.34		
333	-3655.19			-2778.05			-3454.48			-2919.9		

## CONCLUSION

Adsorption of rhodamine B (RB) onto PSD is optimum at a pH of 3.1. Adsorption increased with time and equilibrium was established within 45 hrs. Adsorption capacity,  $q_e$ , decreased with increasing adsorbent dose but increased with increase in initial dye concentration and temperature. Adsorption isotherm follows Freundlich isotherm for rhodamine B in single system, adsorption of RB in binary system Langmuir Isotherm, while adsorption of RB in ternary system follows Temkin Isotherm. Adsorption kinetics for adsorption of RB in single, binary and ternary system followed pseudo second order kinetics.

$\Delta G$  for all the adsorption processes is negative showing the feasibility of the adsorption processes,  $\Delta H$  is positive indicating that the adsorption processes are endothermic while the values of  $\Delta S$  are high showing there is randomness in the adsorption systems. Therefore, sawdust of *Parkia biglobosa* is a potential and viable adsorbent for the removal of rhodamine B.

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