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Removal of Rhodamine-B dye from aqueous solution onto Pigeon Dropping: Adsorption, Kinetic, Equilibrium and Thermodynamic studies

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Abstract
A series of studies have been carried out for the removal of Rhodamine-B dye from waste water using Pigeon Dropping as adsorbent. The effects of contact time, concentration of the adsorbate, adsorbent dosage, pH and temperature have been studied. The adsorption process was well described by Langmuir and Freundlich adsorption isotherms. The adsorption followed pseudo-second-order rate equation and the intra particle diffusion equation. The thermodynamic studies showed that the process is exothermic and spontaneous. This study investigates the potential use of Pigeon Dropping for the removal of dye.

Keywords: Rhodamine-B, Pigeon Dropping, Adsorption Isotherm, Kinetics, Wastewater treatment.

Introduction
Water pollution is the burning issue of the current era with rapidly growing industrialization and urbanization. The effluents from industries like textile, paper, paints, plastics, cosmetics, leathers and foodstuffs contain dyes, which polluted the natural resources of water and thereby, causing serious environmental and biological problems [1-2]. Even at very low concentration, the presence of these dyes in water is highly visible, which effect the aquatic life [3-4]. The release of coloured water into the environment is a source of aesthetic pollution [5]. Rhodamine-B is widely used for analytical and biological staining purposes, in dyeing of various industrial products like in colouring paper, textile dyestuffs, ink manufacturing, plastic (P.V.C), spirit based coating, boards, krafts, mosquito coils and as a lab reagent [6-7]. Rhodamine-B dye has been known to cause an allergic reaction and its decomposition results in carcinogenic. It may cause irritation, redness and pain in eyes and skin [7]. When inhaled, Rhodamine-B causes irritation in respiratory tract with symptoms of sore of throat, coughing and chest pain. If swallowed, it causes irritation to the gastrointestinal tract. So, it is necessary that proper treatment of the dye effluent for the removal of colour is carried out before its discharge.
The removal of dyes from effluent is one of the indispensable processes in waste water treatment. A number of techniques have been employed for the removal of different types of dyes from waste water [8-13]. The conventional methods are not very effective methods and are expensive also. The adsorption method is one of the effective method for the removal of coloured matter from effluent. It was therefore, considered worth-whole to explore the use of adsorption method for the removal of basic dye Rhodamine-B. Ancient Mesopotamian, Egyptian, Indian, Talmudic, Greek, and Roman physicians agreed that animal excreta have valuable medical uses. The hugely influential Greek physician Galen reported the use of Pigeon Dropping in wound dressings [14]. Similarly, in India Pigeon Dropping has been used in the treatment of Haematemesis [15]. The present work is thus devoted to the removal of Rhodamine-B dye from aqueous solution by adsorption onto Pigeon Dropping as potential adsorbent and to study various factors, which affect the adsorption. The efforts have been done to throw some light on kinetics and thermodynamics of the process.

2. Materials and methods
2.1. Preparation of stock solution of Rhodamine-B
Rhodamine-B, [9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride is azo dye was purchased from S.D. Fine Chemicals, Mumbai, India. All other reagents were of analytical reagent grade. The studies were carried out by preparing the stock solution (i.e., 50 mg/L) in distilled water. The resulting stock solutions were stored in the air tight glass flasks. The stock solution was then properly wrapped with black paper and stored in a

dark place to prevent direct contact to sunlight. The other solutions (i.e., C_0 = 10, 20, 30, 40 and 50 mg/L) were prepared by successive dilutions of the stock solution. Absorbance measurements were carried out by using Shimadzu - 1800, UV-Visible Spectrophotometer. Absorbance maxima of Rhodamine-B (λ_{max}= 553.75 nm) was used as the monitoring wavelength for the estimation of dye in solution.

2.2. Adsorbent

Adsorbent, i.e., Pigeon Dropping was collected from local Pigeon store market. It was first dried and then was subjected to thorough washing with the water in order to remove coloured soluble impurities. The washed dropping was dried in oven and ground to a fine powder and was sieved through micron sized mesh. The dried powder form adsorbent obtained was then stored in desiccator for the subsequent use.

2.3. Experimental methods

The batch adsorption studies were conducted to study the effect of different parameters such as contact time, adsorbent dose, adsorbate concentration, pH and temperature. The amount of adsorbent (1.0, 2.0, 3.0, 4.0 or 5.0 g) is added to 100 mL solution of dye with initial concentration (10, 20, 30, 40 or 50 mg/L) and agitated on mechanical shaker. The solution was withdrawn at preset intervals of time and was filtered with the help of Whatman filter paper. The concentration of filterate was measured with the help of Shimadzu- 1800, UV-Visible Spectrophotometer at the wavelength 553.75 nm. The effect of different parameters like; contact time, dosage of adsorbent, initial concentration of adsorbate, pH and temperature were studied and reported in the result and discussion part.

3. Results and discussion

3.1. Effect of the amount of adsorbent

The adsorption of Rhodamine-B on Pigeon Dropping was studied by taking 100 mL dye solution for 30 mg/L of dye concentration and varying the adsorbent dose (1.0, 2.0, 3.0, 4.0 and 5.0 g). The data indicate that by increasing the amount of adsorbent, the adsorption capacity, i.e., amount adsorbed per unit mass decreases as shown in Figure 1(a), but the percentage removal of dye increases (Figure 1(b)). The percentage increase of dye removal is due to the reason that the number of available adsorption sites increases by increasing the amount of adsorbent, which results in the increase of adsorption percentage of dye adsorbed. The decrease in adsorption capacity with increase in the adsorbent dose is due to reason that concentration of solute in solution is less as compared to concentration of solute on the surface, which leads to desorption of solute [16].

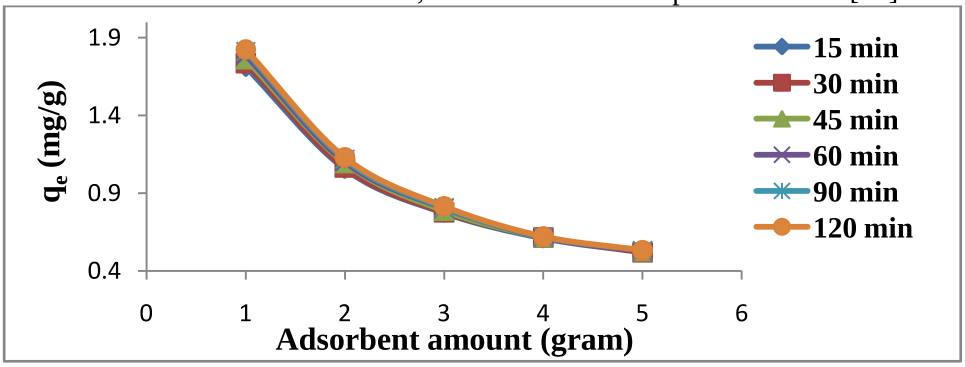

Figure 1(a): Effect of amount of adsorbent on the adsorption capacity of Rhodamine-B

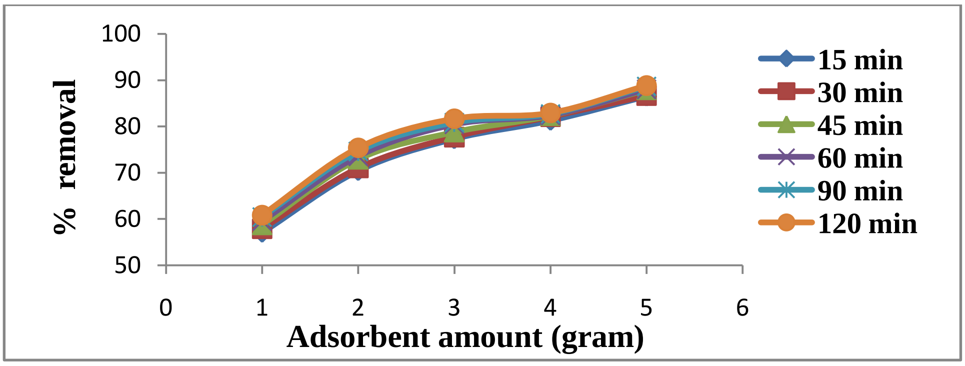

Figure 1(b): Effect of amount of adsorbent on the Percent removal of Rhodamine-B

3.2. Effect of the contact time on adsorption

The time - dependent behavior of adsorption of dye on Pigeon Dropping has been studied by stirring the 100 mL of dye solution of desired concentration along with 2.0 g of adsorbent at 450 rpm and at room temperature. The data indicate that the adsorption capacity and percentage removal of dye goes on increasing with increase of agitation time. Figure 2(a) show that the rate of adsorption of Rhodamine-B is fast initially and then become slower and dye adsorption equilibrium has been attained. As initially whole of the surface is free for adsorption. But with increase of contact time, more and more dye particles get adsorbed over the surface and free surface for adsorption decreases and hence the rate of adsorption also decreases. The percentage removal of dye with time is given in Figure 2(b) also followed the same pattern. The mechanism for the removal of dye by adsorption may be assumed to involve [17]:

- Migration of dye from bulk of the solution to the surface of the adsorbent.
- Diffusion of dye through the boundary layer to the surface of the adsorbent.
- Intra-particle diffusion of dye into the interior pores of the adsorbent particle.

The boundary layer resistance will be affected by the rate of adsorption and increase in contact time, which will reduce the resistance and increase the mobility of dye during adsorption.

The equilibrium time required by the adsorbent used in this present study is less as compared to other adsorbents reported in literature [18-19**].** This is significant as equilibrium time is one of the important considerations for economical wastewater treatments. This instantaneous adsorption phenomenon is advantageous since the shorter contact time effectively allows for a smaller size of the contact equipment, which in turn directly affects both the capacity and operational cost of the process.

3.3. Effect of initial adsorbate concentration

The experimental results for adsorption at various initial dye concentrations (10, 20, 30, 40 and 50 mg/L) with 2.0 g adsorbent at different time interval are shown in Figures 2(a) and 2(b). The data indicate that the percentage adsorption decrease with increase of initial dye concentration but adsorption capacity increase with increase of initial dye concentration. It is due to reason that at lower concentration the ratio of initial number of dye molecules to available surface is low and at higher concentration the ratio of number of dye molecules to available surface become high [7].

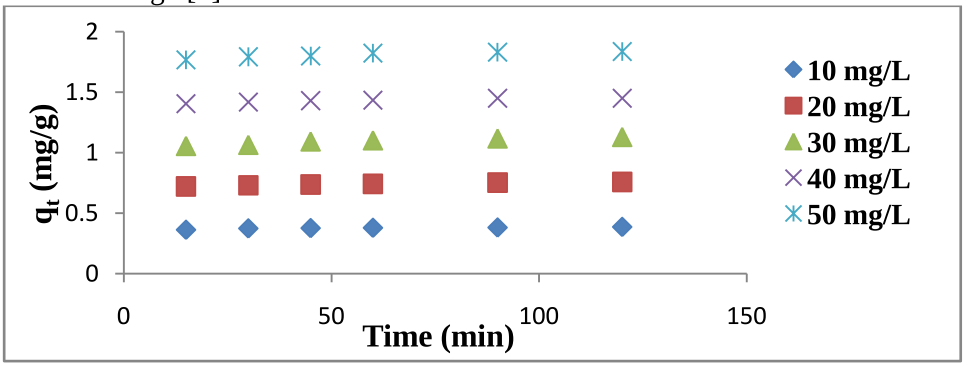

Figure 2(a): Effect of initial dye concentration and time on adsorption capacity of Rhodamine-B

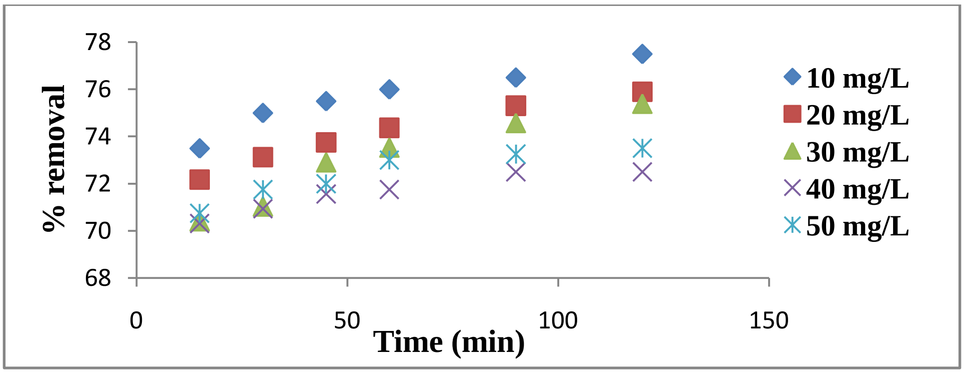

Figure 2(b): Effect of initial dye concentration and time on percent removal of Rhodamine-B

3.4. Effect of pH

The effect of pH on the adsorption capacity of Pigeon Dropping was studied at different pH (2.0, 4.0, 6.0 and 8.0) by agitating 100 mL of 30 mg/L of dye solution with 2.0 g of adsorbent at room temperature. It has been observed that the cationic Rhodamine-B dye uptake by Pigeon Dropping was higher at lower pH, i.e., at pH 2.0 (Figure 3). It may be due to reason that in acidic medium polarization of adsorbent takes place, which leads to aggregation of dye on adsorbent surface.

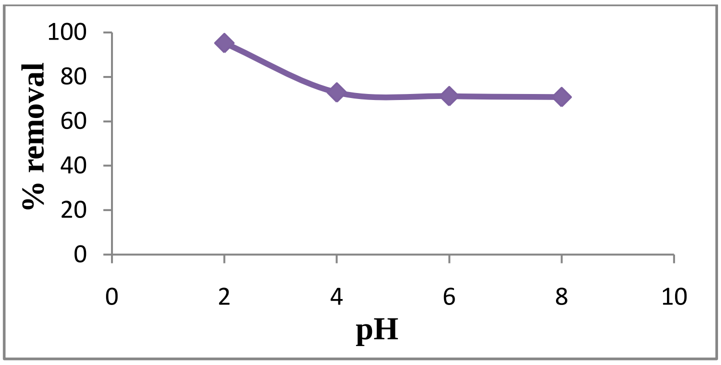

Figure 3: Effect of pH on percent removal of Rhodamine-B dye

3.5. Adsorption Isotherms

The equilibrium adsorption isotherm is of fundamental importance in the design of adsorbate-adsorbent interaction. There are several isotherm reported in literature. But the Langmuir and Freundlich adsorption isotherms are the most frequently used among the several isotherms available in the literature to describe experimental data on adsorption.

3.5.1. Langmuir adsorption isotherm

The linear form of the Langmuir adsorption isotherm equation [20] can be expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \cdot b_L}$$

where, q_e is the amount of dye adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), q_m is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity (mg/g) and b_L is Langmuir adsorption equilibrium constant (L/mg) that is related to the apparent energy of adsorption.

The data fit well to Langmuir isotherm for the adsorption of Rhodamine-B on Pigeon Dropping (shown in Figure 4). Langmuir constants q_m and b_L have been evaluated from the slope ($1/q_m$= 0.1169) and intercepts ($1/q_m.b_L$= 6.3886) of the plot, along with the correlation coefficient. It is evident from the Figure 4, the value of q_m = 8.5499 mg/g and b_L = 0.0183 L/mg at temperature 305 K. The higher value of q_m (>>1) indicates a strong adsorbate-adsorbent interaction.

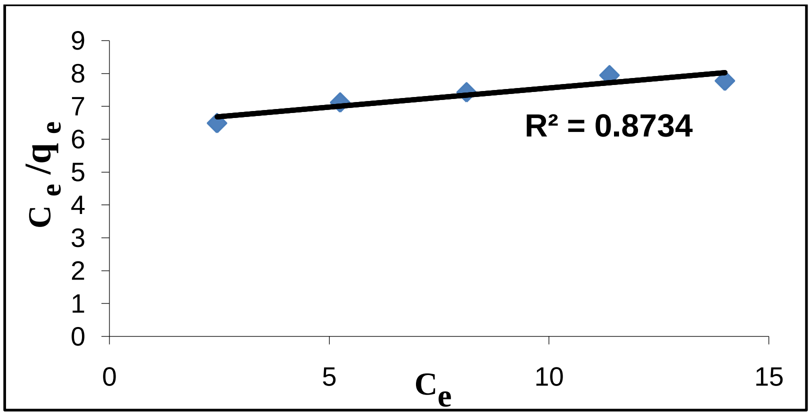

Figure 4: Langmuir adsorption isotherm for Rhodamine-B on Pigeon Dropping

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined as:

$$R_L = \frac{1}{(1 + b_L . C_0)}$$

The parameter R_L, as reported from literature [21] indicates the type of adsorption. The value of R_L<1.0 indicate favorable adsorption for the adsorbate-adsorbent system.

A comparison of adsorbent capacity of Pigeon Dropping with other adsorbents (Table 1) shows that Pigeon Dropping has a greater adsorption capacity than others.

Table 1: Adsorption capacities of Rhodamine-B on various adsorbents

Adsorbent	q_m (mg/g)	References
Coal	1.24	Khan et al. [22]
Fly ash	2.33	Khan et al. [23]
Coir pith	2.56	Namasivayam et al. [24]
Mango leaf powder	3.31	Khan et al. [7]
Tamarind fruit shells activated carbon	3.94	Vasu [25]
Pigeon Dropping	8.55	Present study

3.5.2. Freundlich adsorption Isotherm

The Freundlich equation in its logarithmic form [26] is given below:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where, q_e is the amount adsorbed at equilibrium (mg/g), K_f is the Freundlich constant, 1/ n is the heterogeneity factor which is related to the capacity and intensity of the adsorption and C_e is the equilibrium concentration (mg/L).

The plot between log q_e versus log C_e is a straight line plot (Figure 5) with good regression coefficients indicating that the adsorption of Rhodamine-B on adsorbent follow the Freundlich isotherm. The value of K_f and n are 0.1701 and 1.1282 respectively.

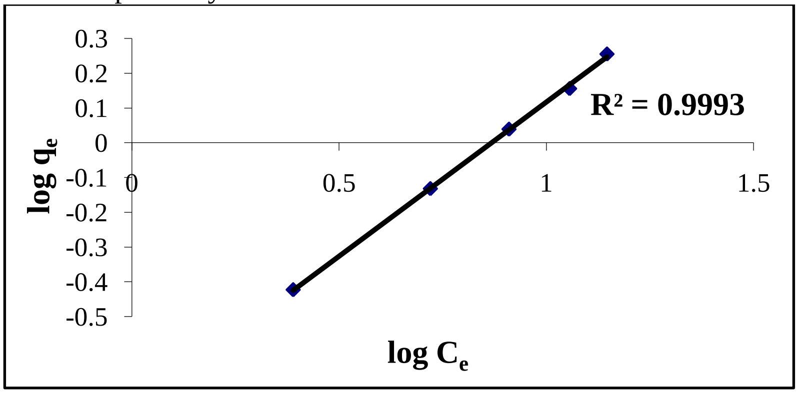

Figure 5: Freundlich adsorption isotherm for Rhodamine-B on Pigeon Dropping

The value of intensity of adsorption is an indication of bond energies between dye and adsorbent and the lower value of n indicate that physisorption is more favourable [27-28].

3.6. Kinetic studies

Many kinetic models have been applied to study the controlling mechanism of dye adsorption from aqueous solution. In order to investigate the mechanism of adsorption of Rhodamine-B dye onto Pigeon Dropping, the following kinetic models were considered.

3.6.1. Pseudo first order kinetic model

The integrated linear form of Lagergren's first order rate equation [29] is as follows:

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

where, q_e is the amount of dye adsorbed at equilibrium (mg/g), q_t is the amount of dye adsorbed at any time t (mg/g), and K_1 is the first order rate constant (min^{-1}). But the data do not follow pseudo first order equation.

3.6.2. Pseudo second order kinetic model

The adsorption equation for pseudo second order model is given by following equation [30]:

$$\frac{t}{q_t} = \frac{1}{K_2 . q_e^2} + \frac{1}{q_e} t$$

where, K_2 is the pseudo second order rate constant ($g.mg^{-1}.min^{-1}$), q_e is the amount of dye adsorbed on the adsorbent at equilibrium (mg/g) and q_t is the amount of dye adsorbed on the adsorbent at any time t (mg/g). It is evident from Figure 6 that the adsorption process follows the pseudo second order kinetics. The value of rate constant and q_e are listed in Table 2.

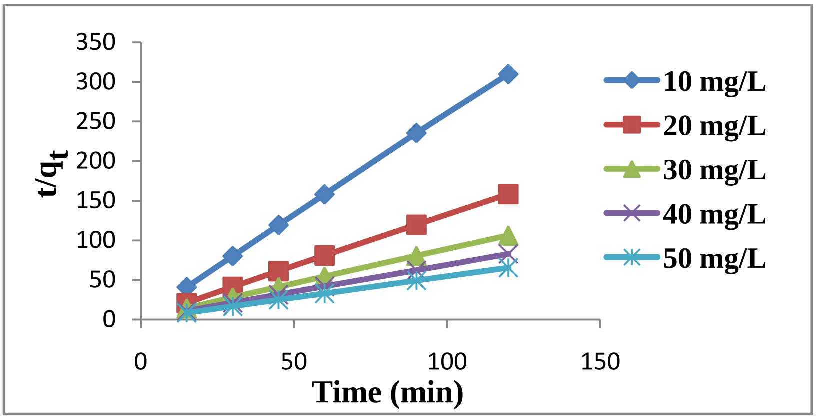

Figure 6: Pseudo second order kinetic plot for Rhodamine-B adsorption on Pigeon Dropping

Table 2: Pseudo-second-order and Intra-particle diffusion values for adsorption of Rhodamine-B on Pigeon Dropping

C_o (mgL^{-1})	Pseudo second order Calculated			Intra-particle Calculated		
	K_2 ($g.mg^{-1}.min^{-1}$)	q_e (mg/g)	R^2	K_{ipd} ($mgg^{-1}min^{-1}$)	C (mg/g)	R^2
10	0.6834	0.4032	0.9999	0.0025	0.3610	0.9285
20	0.8269	0.7776	0.9999	0.0062	0.7015	0.9539
30	0.7303	1.1701	0.9999	0.0093	1.0200	0.9684
40	0.1344	1.4501	1.0000	0.0050	1.3910	0.9971
50	0.1450	1.8566	1.0000	0.0104	1.7260	0.9631

3.6.3. Intra-particle diffusion study

In the batch mode adsorption process, initial adsorption occurs on the surface of the adsorbent. In addition, there is a possibility of the adsorbate to diffuse into the interior pores of the adsorbent. Weber and Morris suggested [31] the following kinetic model to investigate whether the adsorption is intra-particle diffusion or not. The relationship is given as:

$$q_t = K_{ipd} . t^{1/2} + C$$

where, q_t is the amount of dye adsorbed at time t (mg/g), C is the constant (mg/g), which gives the thickness of the boundary layer and K_{ipd} is the intra-particle diffusion rate constant ($mg.g^{-1}.min^{-1}$). The calculated values of C from the intercept of the plot, shows that the larger the C, greater is the contribution of surface adsorption in the rate limiting step [7]. The linear portion in Figure 7 represents the intra particles diffusion effect. The correlation coefficients for intra-particles diffusion are also close to unity, thereby indicating that adsorption of Rhodamine-B onto Pigeon Dropping follow the intra-particle diffusion model. The value of K_{ipd} and C are listed in Table 2.

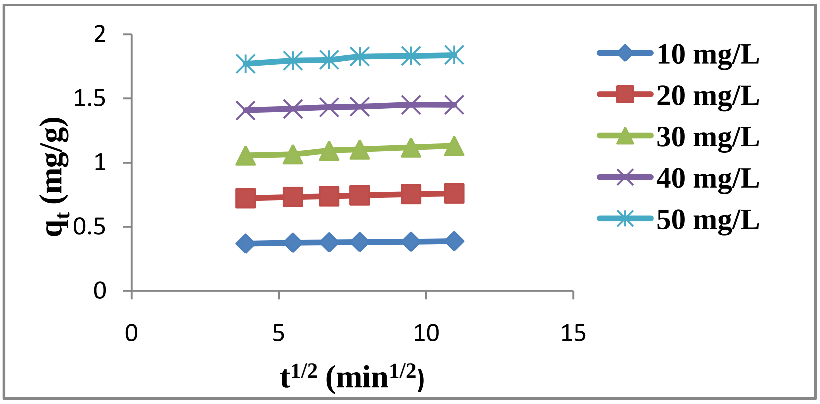

Figure 7: Intra-particle diffusion study plot for Rhodamine-B adsorption on Pigeon Dropping

3.7. Thermodynamic parameters

In order to observe the feasibility and the nature of adsorption process, adsorption studies of Rhodamine-B onto Pigeon Dropping have been conducted at three different temperature: 305, 315 and 325 K. Thermodynamic parameters such as the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS), were calculated from the variation of the thermodynamic equilibrium constant [23], K_o using equations given below and the values of ΔG, ΔH and ΔS for initial concentrations of 10, 20, 30, 40 and 50 mg/L are listed in Table 3.

$$\Delta G = -RT_1 \ln K_1$$

$$\Delta H = R\,\frac{T_3 . T_2}{T_3 - T_2} \ln\frac{K_3}{K_2}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_1}$$

The contents of Table 3 indicate that the adsorption of Rhodamine-B on Pigeon Dropping is exothermic and spontaneous process. The low values of ΔH indicate that the interaction between adsorbate-adsorbent are weak. On this basis we may conclude that adsorption of Rhodamine-B on Pigeon Dropping is a physisorption process.

Table 3: Equilibrium constant and thermodynamic parameters for the adsorption of Rhodamine-B onto Pigeon Dropping

C_o (mgL^{-1})	-ΔH ($KJmol^{-1}$)	ΔS ($KJmol^{-1}K^{-1}$)	K_o			-ΔG ($KJmol^{-1}$)		
			305 K	315 K	325 K	305 K	315 K	325 K
10	0.0425	0.0092	3.0816	1.4242	1.4236	2.8537	0.9260	0.9540
20	2.5789	0.0001	2.8095	2.4782	2.4042	2.6194	2.3766	2.3702
30	2.6642	-0.0005	2.6923	2.6641	2.5820	2.5111	2.5660	2.5628
40	6.1768	-0.0125	2.5164	2.5088	2.3333	2.3400	2.4089	2.2894
50	0.6383	0.0057	2.5710	2.5651	2.5460	2.3943	2.4667	2.5250

3.8. Fourier transform infrared spectroscopy (FT-IR) analysis

The FT-IR spectra of Pigeon Dropping and loaded Rhodamine-B were recorded in the region of 4000 - 450 cm^{-1}. The spectra shown in Figure 8 (a), (before adsorption) the peak at 3419, 1646, 1515, 797 and 694 cm^{-1} may be due to stretching and bending mode of amine. The FT-IR spectra in Figure 8 (b), (after adsorption) consist of 3419 and 694 cm^{-1} at slight shifted positions. The shift may be due to the weak interaction between carboxylic group of dye and amine group of adsorbent. This clearly indicate that the adsorption of dye on adsorbent by physical forces.

3.9. Scanning Electron Microscopic studies

The SEM image of Pigeon Dropping and loaded Rhodamine-B were recorded and are shown in Figure 9(a) and 9(b). The images show a view from external side of adsorbent used in this study before and after the adsorption of dye. In the SEM Micrograph 9 (a), the spots show the rough and porous surface of the adsorbent, which is one of the factor increasing adsorption efficiency of the adsorbent. The loaded SEM images show the adsorption of Rhodamine-B on the Pigeon Dropping. In Figure 9(b), the surface of particle after adsorption, the pores and surfaces of adsorbent were covered by dye. The SEM images show that how the adsorbate is adsorbed on the surface of adsorbent.

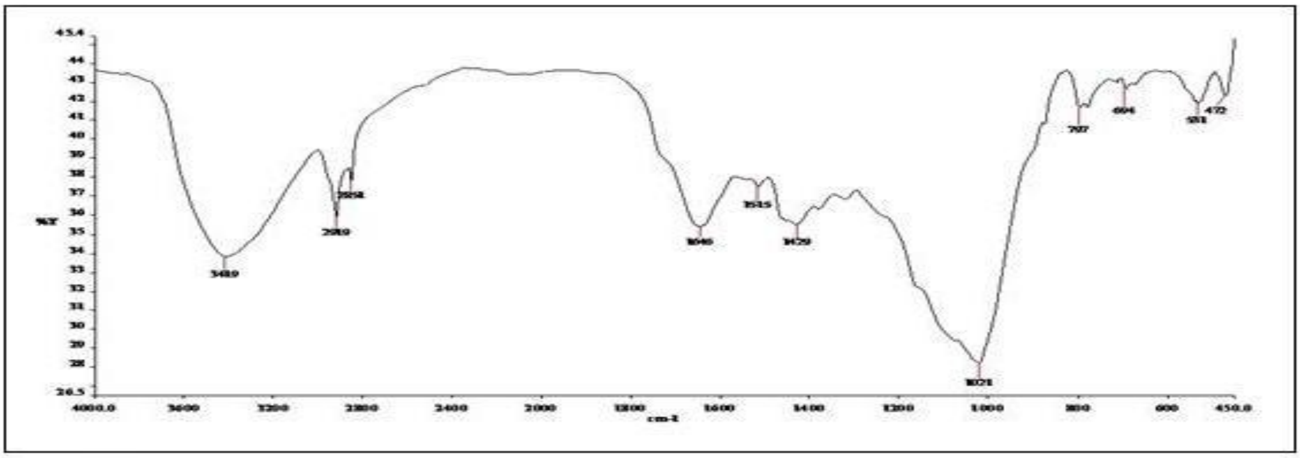

Figure 8(a) FT-IR spectra of Pigeon Dropping before adsorption

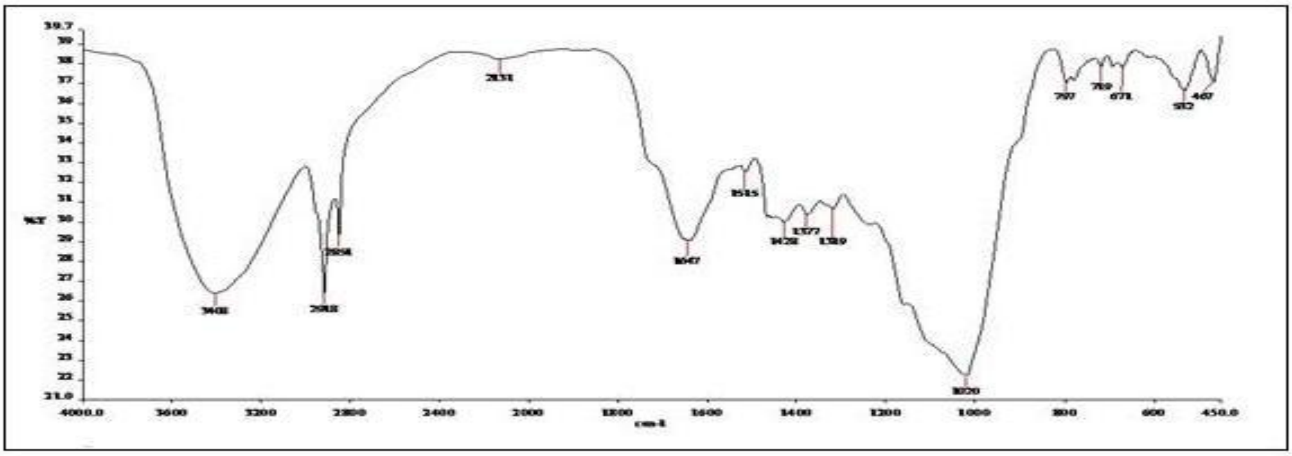

Figure 8(b) FT-IR spectra of Pigeon Dropping and loaded Rhodamine-B after adsorption

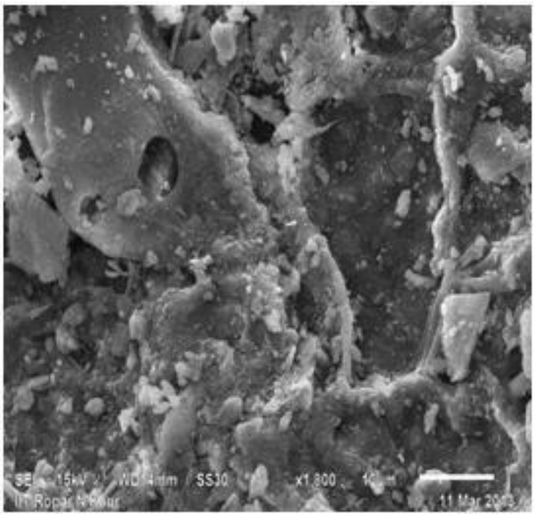

Figure 9(a): SEM image of the Pigeon Dropping before the adsorption

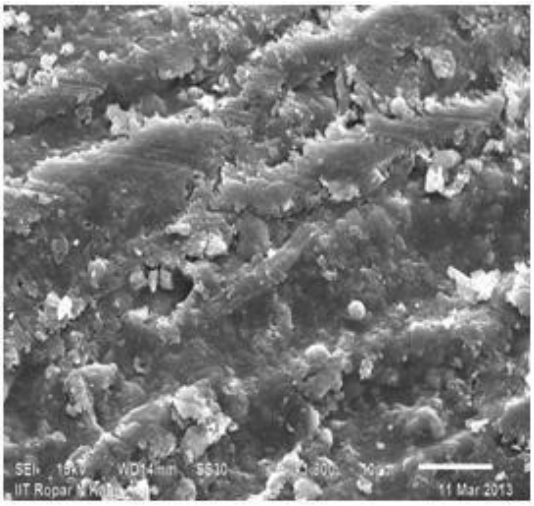

Figure 9(b): SEM image of the Pigeon Dropping after the adsorption of dye

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Conclusion

The present work is an effort to explore the use of adsorption technique for the removal of toxic Rhodamine-B dye from aqueous solution using waste material- Pigeon Dropping (without giving any pretreatment). The experimental data associate practically well with Langmuir and Freundlich adsorption isotherm. The value of the separation factor (R_L) and n showed that the Pigeon Dropping can be effectively used for the removal of Rhodamine-B dye from aqueous solution. The adsorption process follows the pseudo-second order rate equation. The values of ΔH, ΔG and low equilibrium value also indicate that adsorption has good potential to remove Rhodamine-B dye from aqueous solution by using Pigeon Dropping as an effective adsorbent. This instantaneous adsorption phenomenon is advantageous, which in turn directly affects both the adsorption capacity and operation cost of the process.

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