



Adsorption modelling studies for the removal of Rose Bengal dye from aqueous solutions using a natural adsorbent perlite

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Modelling studies for the adsorptive eradication of a dye Rose Bengal dye in aqueous solutions using an adsorbent perlite have been exploited. A batch mode adsorption technique was performed to find the influence of contact time, strength of the Rose bengal dye, dosage of the perlite, pH and temperature. The equilibrium of the adsorption has been achieved only after the contact time of 40 min. The kinetic behaviour of the adsorption has been evaluated using the pseudo first-order as well as the second-order types. The achieved kinetic equation statistics of pseudo second-order kinetic equation has a close proximity with unity. Equilibrium adsorption values are obtained from the Freundlich and Langmuir isotherm. From the correlation data, Freundlich isotherm remains suited to describe the adsorption behaviour of Rose bengal dye on the perlite. From the experimental data, the thermodynamic parameters like ΔH° , ΔS° , and ΔG° are assessed. The calculated result was shown that the adsorption behaviour is exothermic as well as immediate in description. The dimensionless separation factor has been shown that perlite is the substitute to other adsorbents for the elimination of rose Bengal dye from the aqueous solution.

Keywords: Adsorption, Isotherm, Perlite, Rose Bengal, Thermodynamics

The effluence of the atmosphere of the environment is predominantly affected by the abnormal progress of human population, urbanization and industrialization. The bleaches are generally employed in the dyeing, textile, paper, printing, leather, photography, food, cosmetics as well as the petroleum productions. The dyeing and textile industries are consuming larger quantity of water and also they produce largest wastewaters to the environment. About 40 % of dyes remain in the effluents to the surroundings and it affects the environment critically¹. The lower concentrations of dyes in water can reduce the water transparency, dissolved oxygen content and could affect photosynthetic process significantly. This decreased dissemination of the light may reduce the life span of the aquatic organisms²⁻⁴. Meanwhile, the complex organic configurations of the synthetic dye which of chemical, optical as well as thermal steadiness⁵. The dyes are non-biodegradable in nature and not affected by chemicals, oxidizing agents and heat⁶. The developed conservative procedures namely chemical reduction, ion-exchange, reverse osmosis, electro-dialysis, precipitation as well as the coagulation are employed for the elimination of the dyes from the textile effluents. However, these

technical processes possess some difficulties like the partial elimination of the dye, expensive equipment, larger quantity of reagent and discarding difficulties⁷. Among all, the adsorption process is frequently considered as an effective method of elimination of dyes from the industrial wastes. Since, this one has simple design, well versed operation and low cost technique over other conventional processes.

Various adsorbent materials were successfully used in the aqueous solution as well as the waste water to eliminate the dye. Numerous materials were tested with various researchers and the activated carbon as adsorbent substance, it predicts proven results over others in the waste water to eliminate various dyes⁸⁻¹¹. But the price of activated carbons is quite high which mainly restricts their utilization¹². This has led to necessarily discover a cheap adsorbent which exhibits superior adsorbent ability. There are varieties of naturally occurring clay constituents which progressively attaining great consideration, due to its cost effective and structure with high surface area^{13,14}. Numerous of the researchers have been used the various clay materials¹⁵⁻¹⁷ for the dye removal process. These minerals also own excellent application in the adsorption¹⁸.

Results and Discussion

Adsorbent dosage effect

The influence of the adsorbent dose involved in the rose bengal dye elimination. This investigation were analyzed by varying the adsorbent dose from 0.04 g to 1 g while keeping other parameters like pH is 7, speed of stirring at 150 rpm and temperature of $25^{\circ}C$. The influence of adsorbent dose upon the rose bengal adsorption using the perlite was shown in Fig. 2. The Fig. 2 reveals that the equilibrium of the dye uptake capacity is reduced as the adsorbent dosage rises due to the spitting influence of the flux which is amongst the adsorbate and the adsorbent. By enhance the dose of perlite; the quantity of dye adsorbed per unit mass of the adsorbent was reduced significantly. The reducing pattern of adsorption is due to the adsorption locations continues to be unsaturated throughout the adsorption technique. Similarly, there is the formation of equilibrium amid the dye particles that are attached to the adsorbent and others that were left over in the solution. For the maximum dye uptake occurred at 0.05g of adsorbent dose in 50 mL. Hence the adsorbent dosage of 0.1 g in 100 mL is appropriately the most favourable reading which is used for all the conforming investigates.

ZeroPoint Charge Measurements

The pH drift technique was employed for the zero point charge (pH_{zpc}) value of perlite²². In this technique a jacketed vessel was taken and filled with the 0.01 M NaCl with perlite. Then by the accumulation of the HCl or NaOH into the solution has altered the readings of the pH from 2 till 12. The stabilization of initial pH was attained only when the nitrogen gas was effervesced into the solution at the temperature of $25^{\circ}C$ in order to eliminate the dissolved carbon dioxide. Later the perlite of 0.15 g is mixed into 50 mL solution, where the final pH reading was verified. Figure 3 reveals the graph of plot between the final pH against the initial pH . It was inferred that the initial pH and final pH readings were equally noted as pH_{zpc} . From the test it was concluded the pH_{zpc} of the perlite is recorded as 8.2.

pH effect

Solution pH remains as the most vital factor to be considered in the adsorption process that has been changing the absorbent and adsorption capacity²³. The level of the pH is altered between the values 3 and 14. Figure 4 displays the Influence of pH upon the adsorption of rose Bengal dye on top of perlite. The dye solution whose pH reading is found to be increased

from the value 3 to 7, the adsorption capacity of perlite was significantly decreased from 346.4 to 272.8 mg/g and then slowly decreases by increasing the pH from 7 to 13. This performance is best described using the adsorbent zero point charge reading. If the $pH > pH_{zpc}$, the cations in the solution was readily adsorbed by the adsorbent. Whereas the $pH < pH_{zpc}$, the adsorption of anions in the solution is favoured²⁴. Therefore the pH_{zpc} of the perlite achieved was 8.2. It proves that the top of the perlite is additionally positively charged as the pH of the dye solution reaches the reading lesser than 8.2 and it is negatively charged on the condition when the pH has achieved the reading more than 8.2. The dye rose Bengal is an anionic dye, therefore the positive charged surface

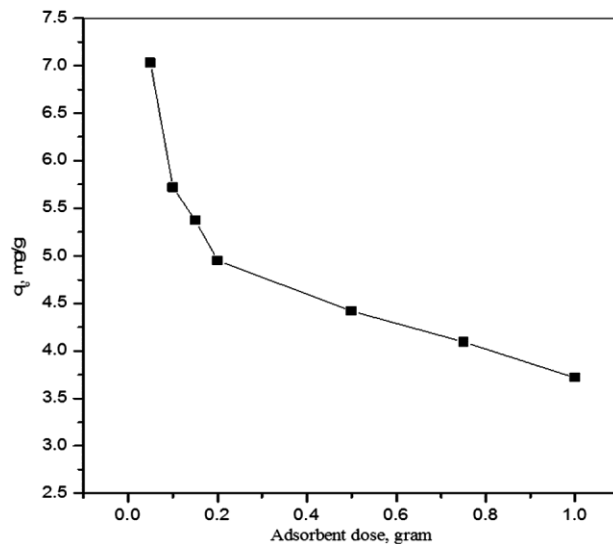


Fig. 2 — Influence of adsorbent dose on the elimination of Rose bengal

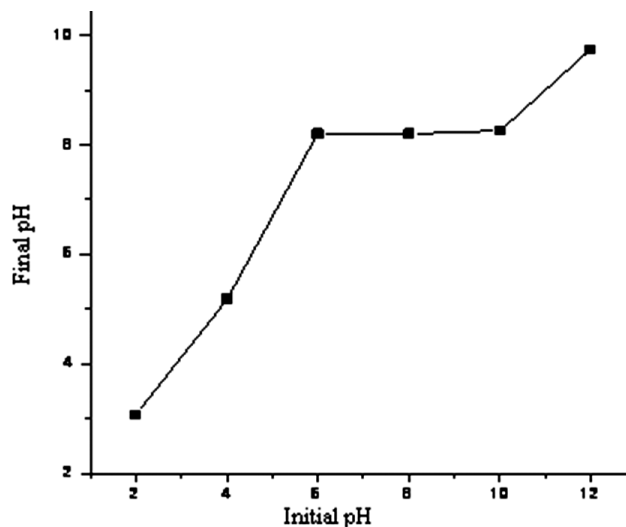


Fig. 3 — Zero point charge (pH_{zpc}) of the Rose bengal onto perlite

containing perlite adsorbing readily at the lower pH or below its zero point charge.

Temperature effect

The temperature plays an important role in terms of the adsorption capacity of perlite which is possible as the

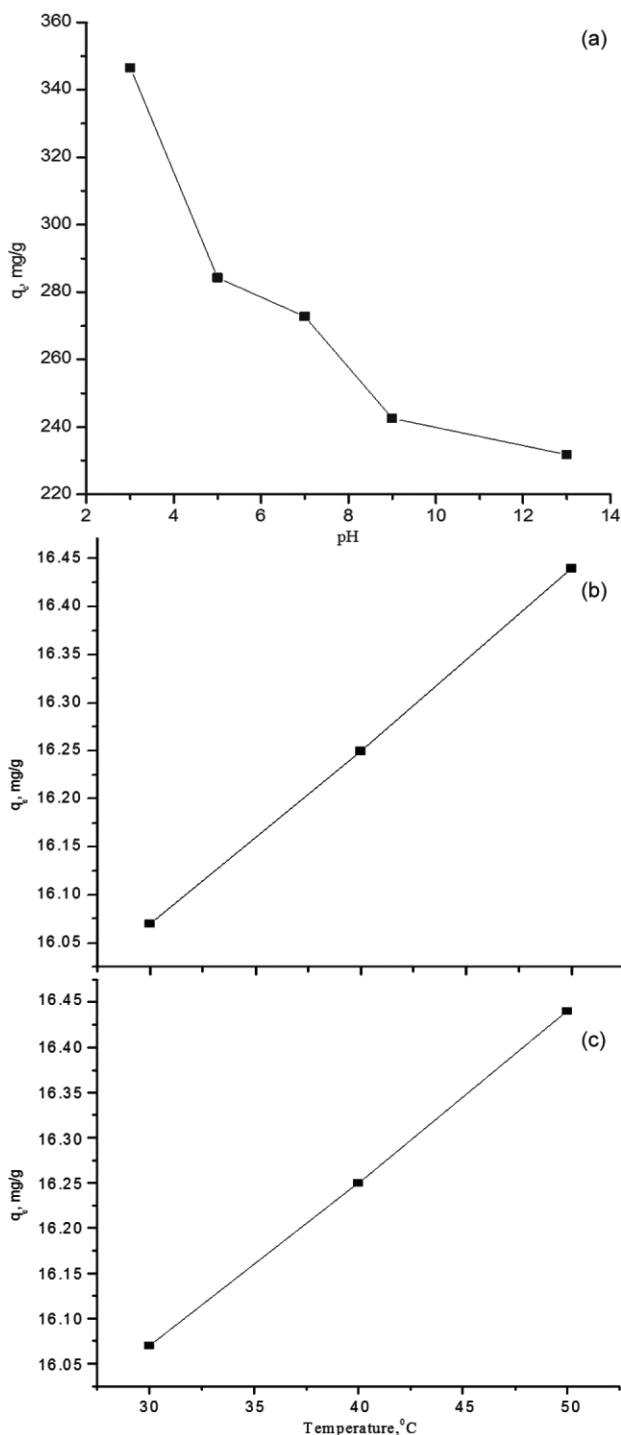


Fig. 4 — (a) Effect of pH for the adsorption of Rose Bengal onto perlite; (b) – Effect of temperature on adsorption capacity of perlite for Rose Bengal and (c) – Effect of dye concentration and time

temperature ranges from 30°C to 50°C. The result values reveals the evidence as the temperature rises from 30°C to 50°C, the ability of adsorption also rises more considerably from 16.07 mg/g to 16.44 mg/g. That is displayed in the Fig.4B, the uppermost temperature enabled the dye adsorption upon the perlite. The rising temperature has initiated the enlargement influence upon the interior configuration of the adsorbent material²⁵. There are thermodynamic parameters namely the free energy change (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) involved in the adsorption technique were estimated and the results were tabulated in the Table 1. The readings were calculated using the conveyed approaches²⁶. The free energy change (ΔG°) whose negative reading has proven that the adsorption of rose bengal dye onto perlite is spontaneous one. A smaller amount negative reading of the variation in enthalpy (-10.88 kJ/mol) indicates the adsorption process to be exothermic and it is physical in nature which comprises of weak forces of attraction that therefore confirms the process to be energetically stable one. The positive entropy change (ΔS°) values (48.04 J/mol K) implies the degree of disorderness of the adsorbed types upon the interface of solid and liquid.

Effect of Contact time and Initial dye concentration

This study reveals the levels of the strength which varies from 20 to 100 mg/L was employed to explore the influence of the initial dye concentration experiment upon the adsorption of rose Bengal to perlite. The outcomes which were achieved at 30°C are displayed in the Fig 4C. It has also revealed that there is a rapid adsorption process was found at the contact time of 40 min. This predicts the adsorption process to be saturated at the mentioned time. Once the equilibrium time has reached the quantity of dye adsorbed doesn't considerably disturbs the adsorption process.

The equilibrium adsorption and equilibrium capability of perlite (q_e), was increased by increasing an initial dye concentrations. The adsorption capacity of dye onto perlite has rising from 8.0 mg/g to 36.86 mg/g as the concentration of the dye rises from 40 mg/L to

Table 1—Thermodynamic parameter values for the adsorption of Rose Bengal onto perlite

Dye(mg /L)	K_0 (kJ/mol)			ΔG^0 (KJ/mol)			ΔH^0 (kJ/mol)	ΔS^0 (J/mol.K)
	30°C	40°C	50°C	30°C	40°C	50°C		
20	4.319	4.865	5.645	-3.685	-4.117	-4.647	-10.886	48.041
40	4.089	4.333	4.618	-3.547	-3.815	-4.108	-4.959	28.059
60	3.598	3.732	4.618	-3.225	-3.426	-3.462	-3.09	20.835
80	3.171	3.249	3.343	-2.907	-3.066	-3.241	-2.153	16.692
100	2.805	2.858	2.915	-2.598	-2.732	-2.873	-1.587	13.802

100 mg/L. The above result has also proven that the initial concentration performs vital role in the adsorption capacity. The Rose Bengal ions around the surface of the adsorbent sites surges as initial Rose Bengal concentration rises. Hence, the adsorption method was carried out more significant resulting in the increase of the equilibrium adsorption capacity.

Adsorption Isotherm

There are numerous categories of the isotherm equations that exist for investigating experimental adsorption equilibrium factors. The isotherms are Langmuir and Freundlich. Langmuir adsorption isotherm was employed to elucidate the equilibrium data involved in the adsorption processes. The simple hypothesis concerned will be the creation of the adsorbate monolayer on the adsorbent exterior layer and in addition there is no likelihood for the adsorption²⁷.

A well-known Langmuir linear form of equation was conveyed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot b} + \frac{C_e}{Q_0} \quad \dots (4)$$

where, C_e will be the equilibrium strength of the rose bengal (mg/L), q_e will be the quantity of rose Bengal adsorbed (mg/g) in addition the Langmuir constants associated to the adsorption energy (L/mg), maximum adsorption ability (mg/g) are b & Q_0 respectively.

From the equation 4, a graph is drawn between the readings of C_e/q_e against C_e . A straight line whose slope is $1/Q_0$ as well as the intercept value is $1/Q_0 \cdot b$ was obtained only possible if the adsorption comply with the Langmuir calculation²⁸. The essential practice involved in the Langmuir isotherm is to calculate a dimensionless factor, R_L whose formula is shown below:

$$R_L = \frac{1}{(1 + b_L \cdot C_0)} \quad \dots (5)$$

where, the factors such as the b_L and C_0 readings are taken from the formula of Langmuir isotherm. The readings of R_L specifies the kind of the isomerism when it is not favourable it holds ($R_L > 1$) or when linear ($R_L = 1$) or when favourable ($0 < R_L < 1$) or when irreversible it holds ($R_L = 0$).

The Freundlich practical equation is utilized for the determination of the heterogeneous classifications which in turn is been described in terms of the heterogeneity parameter $1/n$, and also it defines the reversible adsorption which has not been a

constrained in regards to the monolayer realization.

The adsorption size is governed strength of the dyes at equilibrium. The distinguished logarithmic Freundlich formula²⁹ prototype is given below:

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

Where k_f will be the Freundlich constant, q_e will be the quantity of the dye adsorbed in (mg/g) at equilibrium, $1/n$ will be the measure of intensity of the adsorption and C_e is the strength of the dye at equilibrium (mg/L). Then a graph is drawn taking the readings of $\log q_e$ vs. $\log C_e$, then readings of the slope in addition to the intercept denotes the k_f and $1/n$. Adsorption isotherms outcomes were achieved via the equation (5) and (6) and were tabulated in Table 2. Fig. 5A and 5B displays the plots of both the isotherms of Langmuir and Freundlich.

The correlation coefficients (0.9964, 0.9974 and 0.9985 at 30, 40, and 50°C) of Freundlich isotherm were noted to be greater when compared to the correlation coefficients of Langmuir isotherm. It was inferred the Freundlich isotherm will be the best suited for all the investigational data of the existing system. There has been a beneficial understanding with the Freundlich isotherm which illustrates the surface of the perlite is extremely heterogeneous. The n value specifies the modification from the linearity of adsorption and the value of n achieved at equilibrium is beyond unity which signifies the positive adsorption. Further the dimensionless factor, R_L readings lies in between 0 and 1. It displays the positive adsorption which occurs amongst the perlite as well as the Rose bengal.

Kinetic Studies

The kinetic outcomes which were achieved from the batch tests were evaluated employing the prevailing prototypes such as the pseudo first order, pseudo second-order as well as the intra-particle diffusion. Lagergren's (1898) first order rate equation proto-type in the linear form is shown below as:

$$\ln(q_e - q_t) = \ln(q_e - k_1 t) \quad \dots (7)$$

where, q_t will be the amount of Rose bengal adsorbed by the adsorbent at specified time t (mg/g), q_e will be the quantity of Rose Bengal adsorbed on adsorbent at equilibrium (mg/g), and k_1 (min^{-1}) is pseudo first order rate constant of the adsorption which was noted from the linear plots slope of

$\ln(q_e - q_t)$ vs. t (slope = k_1 , $q_e = \text{exp. intercept}$).

The linearized pseudo second order prototype³⁰ is specified as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \dots (8)$$

where, q_e will be the quantity of rose bengal dye adsorbed on adsorbent at equilibrium (mg/g), k_2 (min^{-1}) will be the pseudo second order rate constant, and q_t will be the amount of Rose bengal dye adsorbed upon perlite at a definite time t (mg/g). Then the graph is drawn between the t/q_t vs. t , the readings of the slope and intercept give a value of k_2 (min^{-1}). From the Fig, it was implied that these straight tracks for the entire

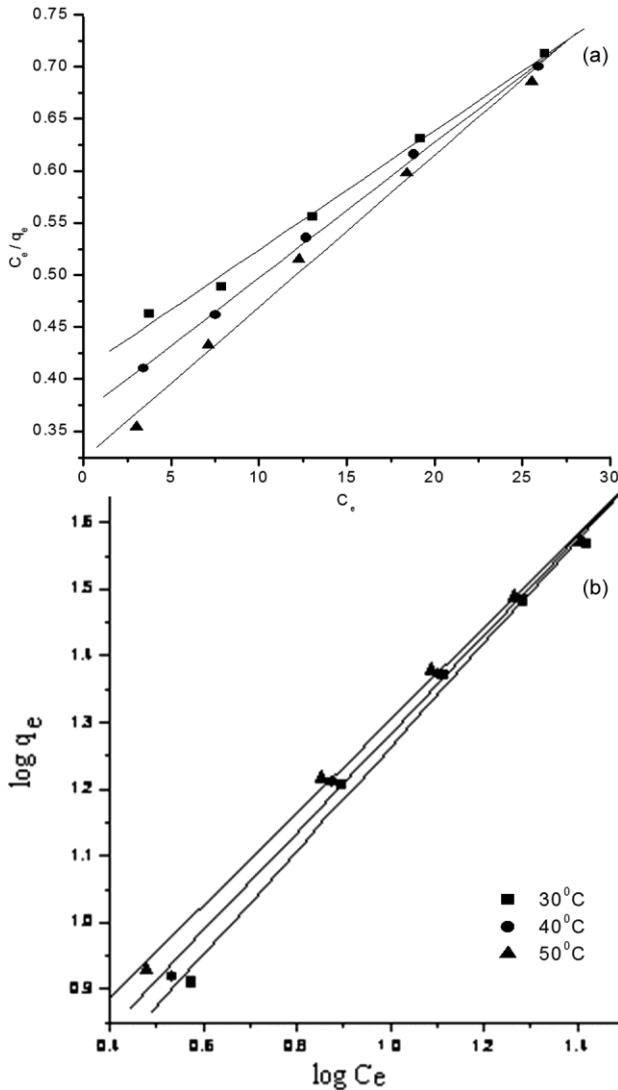


Fig. 5 — (a) Langmuir adsorption isotherms plot for the Rose Bengal on to perlite; (b) Freundlich isotherms for the adsorption of Rose Bengal on to perlite

preliminary concentrations (Fig 6a and 6b) having tremendously extraordinary correlation coefficients (<0.99) for the pseudo-second-order kinetic prototype than the pseudo-first-order prototype for the adsorption of Rose Bengal dye upon the perlite has intensely suggests that the entire adsorption classifications are the pseudo-second-order equation. The first-order kinetic equation was utilized to determine the q_e reading which was achieved too low than the investigational q_e readings. The pseudo-second order model has undergone a suitable contract between the calculated and investigational results. The

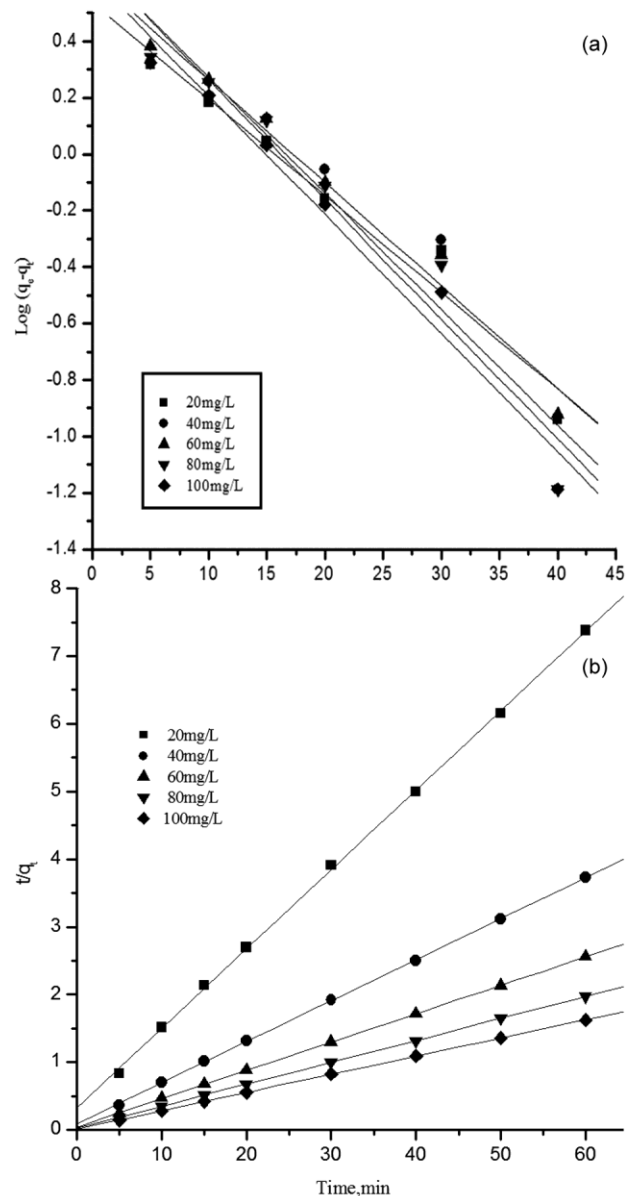


Fig. 6 — (a) Pseudo first order for the adsorption of Rose Bengal; (b) Pseudo second order for the adsorption of Rose Bengal

investigational data for the adsorption of Rose bengal with extraordinary correlation co-efficient ($r^2=0.999$) is realized by the pseudo-second order model. It was also determined that the investigational adsorption capacities (q_e) were calculated to be precisely nearer to the adsorption capacities that have been estimated by the pseudo-second order kinetic prototype.

Intra particle diffusion

Weber *et al.* (1963) proposed the subsequent kinetic prototype to explore whether it is the intra-particle diffusion in adsorption or not.

$$q_t = K_{ipd}t^{1/2} + C \quad \dots(9)$$

Where, q_t will be the amount of Rose bengal adsorbed onto perlite for different periods t (mg/g), intercept value will be C and K_{ipd} indicates the rate constant of intra particle diffusion (min^{-1}). Then the graph is drawn between the readings of q_t and $t_{1/2}$ depicted in the Fig. 4B. The results have predicted that the correlation coefficients of the intra-particle diffusion prototype as well as the traces whose linear part don't go across the origin. This has depicted the process for the elimination of Rose bengal by perlite will be the surface adsorption in addition to the intra-particle diffusion have given a way to the rate-determining stage.

Analytical studies

FTIR Studies

The identification of functional groups lies on the sorbent which influence the nature of the sorption process. Therefore, the finding of nature of the groups present on the perlite is essential to get peaceful process. The FTIR characterization of perlite was

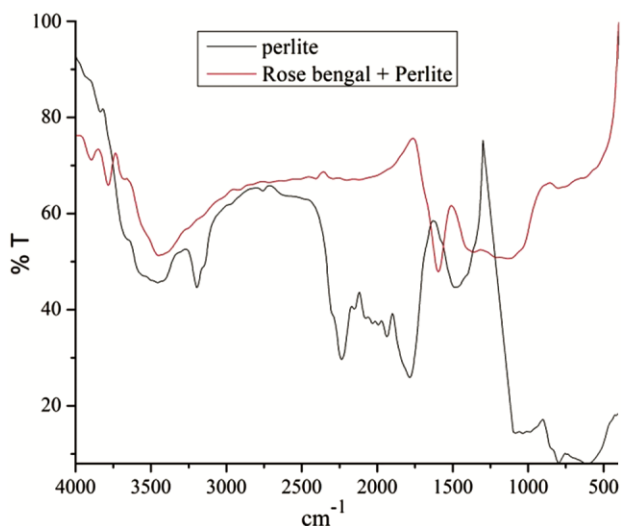


Fig. 7 — FTIR spectrum of Perlite and perlite+ rose bengal dye

presented in Fig. 7. The black line in the Fig shows different peaks in 3550, 3220, 2250, 1750, 1448, 1046 and 780 cm^{-1} . The strong and broad peak at 3550 cm^{-1} represents the presence of OH group. The medium resolution peak at 3220 and 2250 cm^{-1} depicts the CH and CH_2 group present in it. There is a presence of strong and weak band at 1750 and 1448 cm^{-1} due to the C=O stretching of carboxyl ate ion. The peaks at 1046 and 780 cm^{-1} show there is C-O, C-O-C stretching in perlite material. The Rose Bengal dye loaded spectrum (red line) as 3500, 1620 and 1180 cm^{-1} bands. This difference of peak positions reveals that a strong process of sorption and strong interaction between the Rose bengal and perlite.

SEM Studies

Figure 8 shows the Scanning Electron Microscopic image of perlite (Fig. 8a) rose Bengal loaded perlite

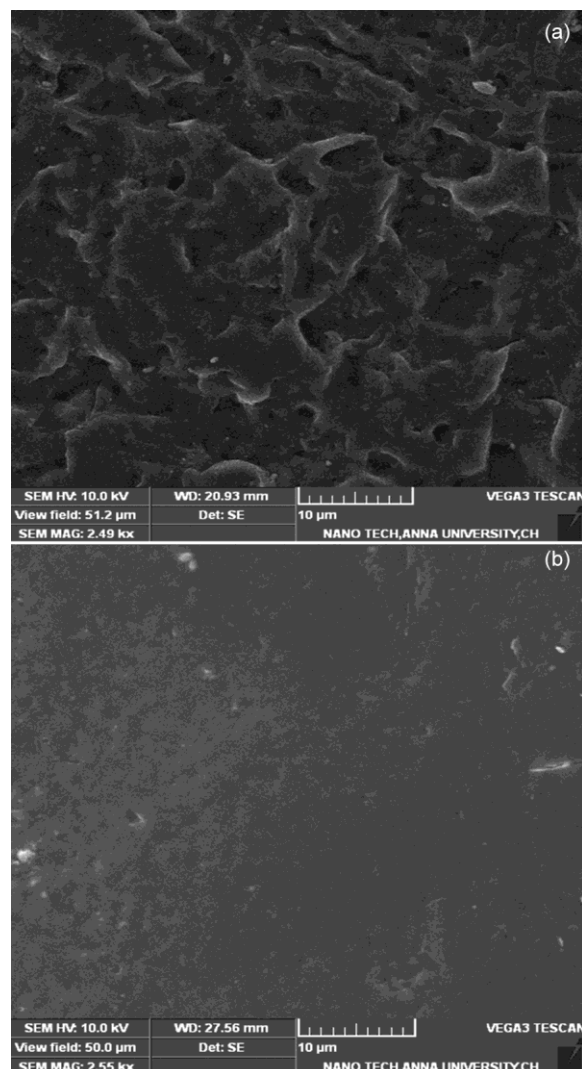


Fig. 8 — SEM image of a) Perlite and b) perlite + rose bengal dye

(Fig 8b). Figure 8a shows a pores and void surface. But the rose bengal loaded perlite in Fig. 8b, does not show porous layered structure but it shows totally covered surface of the adsorbent. This trend confirms that the rose bengal dye strongly adsorbed on the surface of the perlite.

Conclusions

The research findings have elucidated that the adsorbent perlite is efficiently utilized for instance an adsorbent for the quantitative elimination of Rose bengal dye from the aqueous solutions. The quantity of dye adsorbed is established with adsorbent dose, initial dye concentration, pH as well as the temperature. The equilibrium adsorption has been accomplished at the contact time of 40 min. The Freundlich and Langmuir adsorption prototypes are related with the equilibrium statistics. The situation is detected such that the adsorption data has incorporated the best to the Freundlich prototype than the latter. Enthalpy (ΔH°) free energy (ΔG°) and entropy (ΔS°) changes are also estimated by means of equilibrium constants as the temperature varies. The negative readings of the enthalpy and free energy changes have proven that the adsorption is spontaneous as well as exothermic in nature. Positive value of ΔS° indicates the adsorbed dye particles residues is on top of the perlite layer which is found to be in arbitrary manner. The pseudo-first order in addition to the pseudo-second-order prototypes was certified to explore the adsorption procedure. The pseudo second-order prototypes the exact fit for the dynamical adsorption performance of Rose bengal dye.

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