Adsorption of Acid Red 14 from Aqueous Solution by Parthenium L (Carrot Grass): Equilibrium, Kinetic and Thermodynamic Studies.

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Abstract

In present work, adsorption experiments were carried out for the removal of Acid red 14 from aqueous solution using Parthenium L. The results have shown that, the amount of dye adsorption increases with increasing the initial concentration of the dye and temperature. The adsorption kinetic data were analysed by using various kinetic models. It was found that the pseudo-second order kinetic model was the most appropriate model, describing the adsorption kinetics. Adsorption isotherms of Acid Red onto the Parthenium L were determined at 303, 308, 313 and 318 K. Equilibrium data were fitted to the Langmuir, Freundlich and Temkin isotherm models. Thermodynamic parameters such as ΔG, ΔH and ΔS were calculated. The negative values of ΔG indicate that the adsorption is spontaneous in nature and the positive value of ΔH shows the endothermic nature of the process.

Key words: Parthenium L, Acid red 14, adsorption, kinetic, thermodynamics.

Introduction

Synthetic dyes are one of the main pollutant groups of water and wastewater. Dye contamination in wastewater causes problems in several ways: the presence of dyes in water, even in very low quantities, is highly visible and undesirable; color interferes with penetration of sunlight into waters; retards photosynthesis; inhibits the growth of aquatic biota and interferes with gas solubility in water bodies[1-5]. The dyes cannot be decomposed easily[6-7]. Direct discharge of dyes containing effluents into environment may cause the formation of toxic carcinogenic breakdown products. The highest rates of toxicity were found amongst basic and diazo direct dyes[8-9]. Therefore, it is highly necessary to reduce dye concentration in the wastewater. The conventional methods for treating dye containing wastewaters are electrochemical treatment [10], coagulation and flocculation[11], chemical oxidation[12], liquid–liquid extraction[13] and adsorption[14-17]. Adsorption has been shown to be an effective way for removing organic matter from aqueous solutions in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances. A large number of plant based products like rice husk, teakwood bark, cotton waste[18], neem leaf powder[19], banana pith[20] and vilyati tulsi[21] are used as adsorbent.

The main objective of present work was to evaluate the adsorption aptitude of Parthenium L for the removal of Acid Red 14 as a model compound for basic dyes. Acid red 14 is a synthetic red food dye from the azo dye group. It is used for the purposes where the food is heat-treated after fermentation. Azo dyes generally have been known to be carcinogenic over 60 years and are linked particularly, to bladder cancer[22]. Acid red 14 can cause allergic or intolerance reaction, particularly amongst those with an aspirin intolerance. Other reactions can include a rash similar to nettle rash and skin swelling. Asthmatics

sometimes react badly to it. Adsorption behavior acid red 14 in aqueous solution on surface soils was investigated[23].

Adsorbents prepared from P. Hysterophorus L are tested to remove heavy metals and dyes [24-26]. The effects of contact time, initial dye concentration and temperature on adsorption capacity were investigated. Moreover, kinetic and equilibrium models were used to fit experimental data and the adsorption thermodynamic parameters were determined.

Materials and Methods

Preparation of sorbent
Naturally dried plant leaves of Parthenium L (PL) are cut into tiny pieces and treated with 0.0025 M sulphuric acid. It stirred for half an hour vigorously using mechanical stirrer at room temperature. It then filtered and washed with distilled water repeatedly to remove free acid till the pH of residual solution is in the range of 4.5 to 5.0. It is then dried in air and finally dried in oven at 363-373 K for 8-10 hours and powdered homogeneously using electric grinder. The homogeneous powder was passed through mesh for desired particle size 800-1,000 μm.

Preparation of sorbet
A cationic dye, acid red 14 (AR 14) was chosen as sorbet with 120 g L^{-1} water solubility. The dye stock solution was prepared by dissolving accurately weighed AR 14 in double distilled water to the concentration of 1×10^{-3} Molar. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to required initial concentrations.

Batch Adsorption Studies
The effect of initial concentration of AR 14 was studied using concentration range 5-25 mgL^{-1}. A typical experimental procedure was conducted by measuring accurately 100 ml of the AR solution of known concentration; 0.9 g of PL was added and agitated up to 80 min, based on the results obtained from the equilibrium time studies, carried out as a preliminary study. Samples were withdrawn, at fixed time intervals, centrifuged, and the supernatant was analyzed for residual AR 14 using a UV-visible spectrophotometer at λ*max* of 510 nm. The amount of AR 14 uptake by PL in each flask was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)}{W} \times V \qquad (1)$$

Where q_e is the equilibrium adsorption capacity of AR 14 adsorbed on unit mass of the PL (mg g^{-1}); C_0 and C_e are the initial and equilibrium AR 14 concentration (mg L^{-1}) respectively; V is the volume of the AR solution (L); and W is the weight of the PL (g).

The dye percent removal was calculated using the following equation:

$$Removal(\%) = \frac{(C_0 - C_e)}{W} \times 100 \qquad (2)$$

Where; C_0 and C_e are the initial and equilibrium dye concentrations (mg L^{-1}) respectively.

Adsorption Kinetic Models
The data on the adsorbed dye a various time interval were fitted in to following kinetic models

First Order Kinetic Model

The kinetics of AR 14 adsorption on the PL was analyzed using First-order kinetic model. The simple form of Lagergren[27] can be written as

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \qquad (3)$$

where K_1 (min^{-1}) is the adsorption rate constant and t is contact time.

The adsorption rate constant, K_1, can be experimentally determined by the slope of linear plot $\log(q_e - q_t)$ versus t.

Second Order Kinetic Model

The integrated form pseudo second order equation developed by Ho[17] can be written as

$$\frac{1}{(q_e - q_{t)}} = \frac{1}{q_e} + K_2 t \qquad (4)$$

The above equation can be rearranged as

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad (5)$$

Where $h (=K_2 q_e^2)$ is the initial adsorption rate mg·g^{-1} min^{-1}

The plot of t/q_t and t of Eq. (5) should give a linear relationship. The initial adsorption rate (h), the equilibrium adsorption capacity q_e and pseudo second order rate constant K_2 can be determined experimentally from the slope and intercept of the plot of equation (5).

The Elovich model

The simplified Elovich equation[28-29] is written as

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \qquad (6)$$

where α and β are the constants.

If Acid red dye adsorption fits the Elovich model, a plot of q_t vs. *ln* (*t*) should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln (\alpha\beta)$.

Adsorption models

Following adsorption models were used

Langmuir model

The simplified for of Langmuir isotherm[30-31] can be represented as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_a} \qquad (7)$$

where q_m is Langmuir constant related to adsorption capacity and K_a Langmuir sorption equilibrium constant. According to Hall et al.[32], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter RL, which is defined by the following relationship:

$$R_l = \frac{1}{1 + K_a C_0} \qquad (8)$$

The parameter RL indicates the nature of the adsorption isotherm.

RL > 1 unfavorable adsorption

0 < RL < 1 favorable adsorption

RL = 0 irreversible adsorption

RL = 1 linear adsorption

Freundlich model

In simple form the Freundlich isotherm[33] equation is

$$q_e = K_f C_e^{1/n} \qquad (9)$$

where K_f is the measure of adsorption capacity, *n* is adsorption intensity.

The intensity of adsorption is an indicative of the bond energies between dye ion and adsorbent. The values of 'n' and *f K* were calculated from slope and intercept of plot log q_e versus log C_e.

Temkin model

The linear form of Temkin model[30] can be presented as follows

$$q_e = B \ln(A) + B \ln C_e \qquad (10)$$

where A is Temkin isotherm equilibrium binding constant and B is constant related to heat of adsorption. By plotting q_e versus ln C_e one can calculate B and A from slope and intercept of this curve respectively.

Adsorption thermodynamics

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Gibb's free energy change, ΔG, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG is a negative. The thermodynamic parameters ΔG, ΔH, and, ΔS for the adsorption processes are calculated using the following equations:

$$\Delta G = -RT \ln K_0 \qquad (11)$$

$$K_0 = \frac{C_{solid}}{C_{liquid}} \qquad (12)$$

$$\Delta G = \Delta H - T\Delta S \qquad (13)$$

$$\ln K_0 = -\frac{\Delta G}{RT} \qquad (14)$$

$$\ln K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (15)$$

Where K is equilibrium constant C_{solid} is solid phase concentration at equilibrium (mg L^{-1}), C_{liquid} is liquid phase concentration at equilibrium (mgL^{-1}), T is absolute temperature and R is gas constant. The values of *H* and *S* can be calculated from slope and intercept of the plot of *ln K* versus 1/T

Test for validity of kinetic Models

To evaluate the fitness of kinetic experimental data, the residual root mean square residual error (RMSE) was used to measure the kinetic and isotherm constants. The RMSE can be defined as

$$RMSE = \sqrt{\frac{1}{N-2}\sum_{i=1}^{N}\left(q_{e(exp)} - q_{e(cal)}\right)^2} \qquad (16)$$

The validity of models was also determined by calculating

The average relative error (ARE) using

$$ARE = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{\left|\left(q_{e(exp)} - q_{e(cal)}\right)\right|}{q_{e(exp)}}\right] \qquad (17)$$

The sum of error squares (SSE%)

$$\% \, SSE = \frac{\sqrt{\Sigma\left(q_{e(exp)} - q_{e(the)}\right)^2}}{N} \qquad (18)$$

Where the subscripts '*the*' and '*exp*' refer to the theoretical (calculated) and experimental data and N is the number of data points.

Result and Discussion

Effect of initial dye concentration and contact time

The initial concentrations of AR 14 solution was varied from 5 to 25 mg L^{-1} and batch adsorption experiments were carried out with 0.9 g of the adsorbent at 303 K. The effect of initial dye concentration and contact time on the adsorption rate of AR 14 is shown in Fig.1.

It is observed that percentage adsorption decreases from 87 to 67 % with increase in initial dye concentration (Fig. 2), but the actual amount of dye adsorbed per unit mass of PL increases from 4.6 to 18.5 mg. It means that the adsorption is dependent on initial concentration of dye. At lower concentration, the ratio of the initial number of dye molecules to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration[34-35]. Equilibrium have established at 80 minutes for all concentrations. Figure 1 and 2 reveals that the curves are smooth, and continuous, leading to saturation.
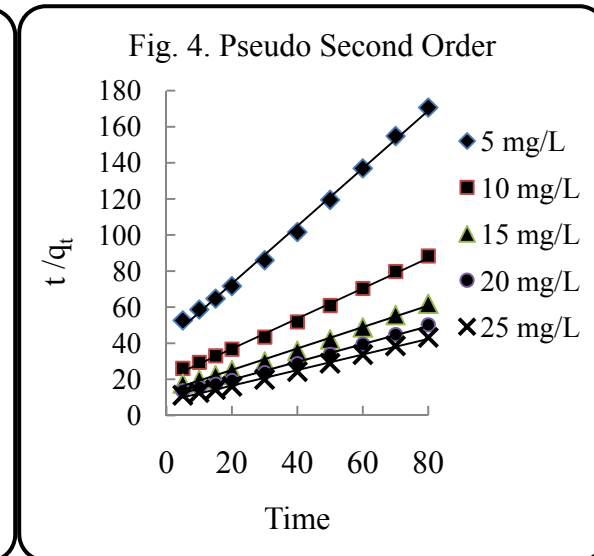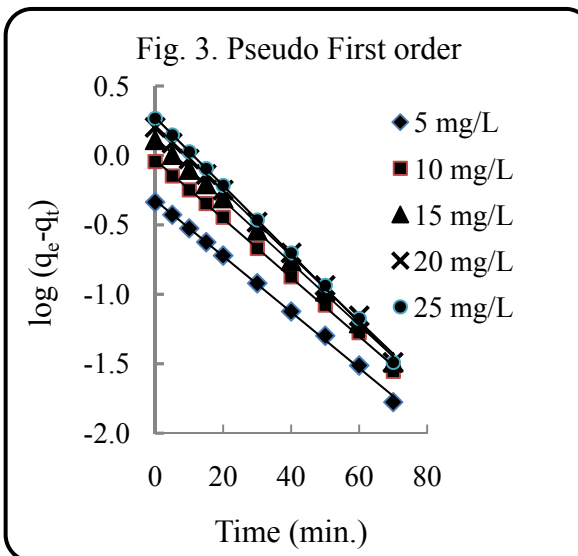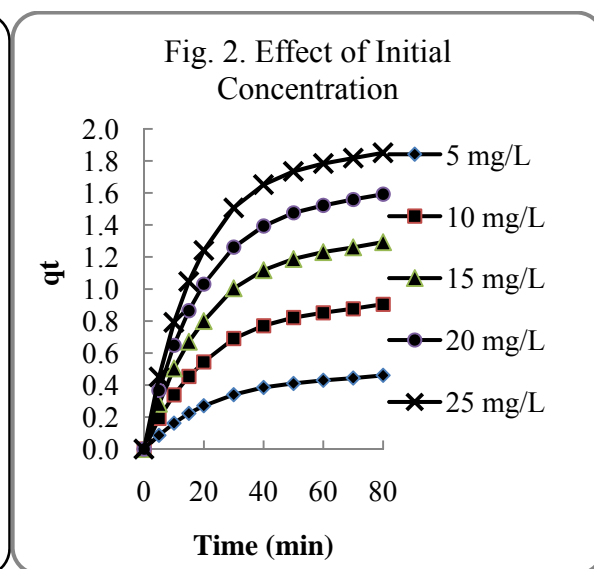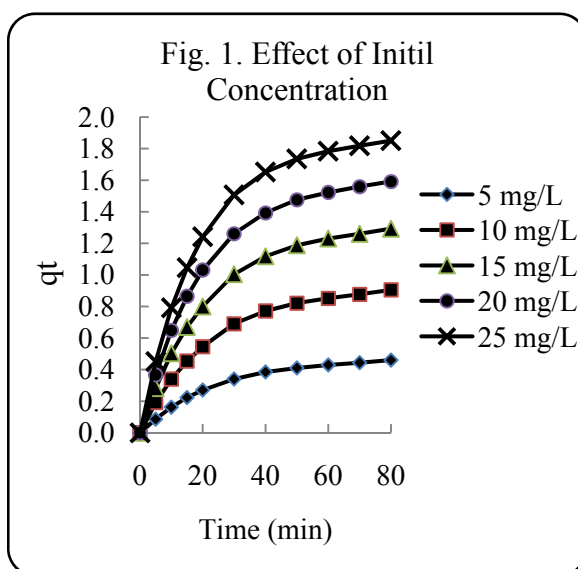
Adsorption dynamics

To investigate the kinetics of adsorption of AR 14 onto PL, pseudo-first order, pseudo-second order and Elovich models were used to fit the experimental data by using linear regression analysis. The straight lines of plot of log (q$_e$-q$_t$) versus t for pseudo-first order reaction (Fig. 3), t/q$_t$ versus t for pseudo-second order reaction (Fig. 4), and q$_t$ versus l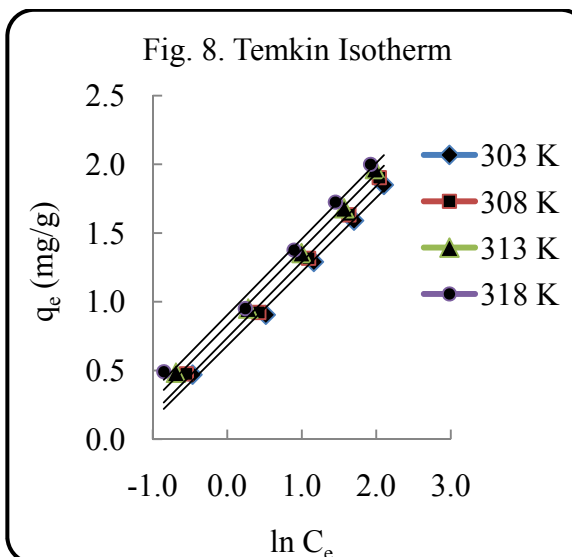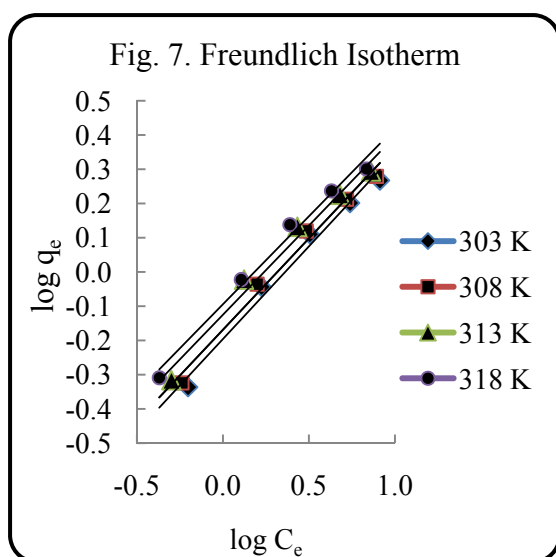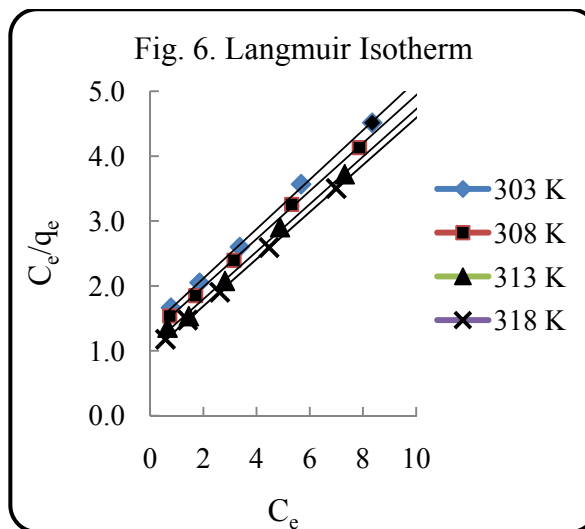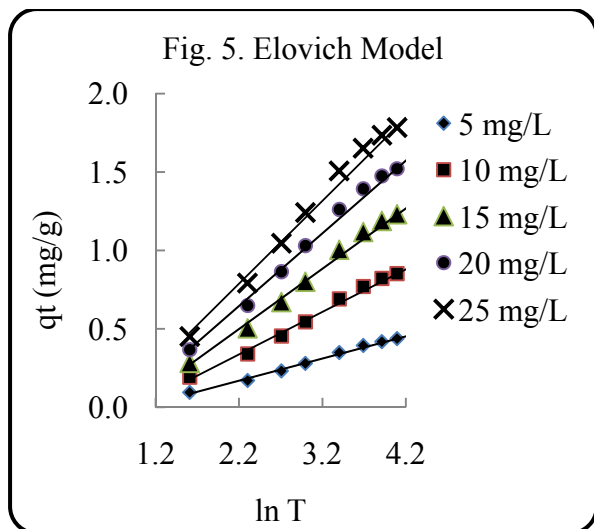n (t) for the Elovich equation (Fig. 5) for adsorption of AR 14 on PL has also been tested to obtain the rate parameters. The kinetic parameters K1, K2, q$_e$(exp) and q$_e$(the) were calculated from these plots and are summarized in Table 1. In above three models the most of the correlation coefficient exceeds 0.9 suggesting that all models are closely fitted the experimental results. While comparing the experimental and theoretical values of equilibrium adsorption capacity for all kinetic models it is observed that the values of q$_e$(exp) are closer to the q$_e$(the) for first order kinetic model (Table 1). This shows that the first order kinetic model fits better as compared to other kinetic

models. The values of % SSE, RMSE and ARE (Table 4) are lower for first order in comparison to second order and Elovich model that explains the better fitting of first order model.

Table 1 Rate constants for First-order, Second-order and Elovich model

Dye Conc.	First order				Second order				Elovich model		
	K_1	$q_{e(exp)}$	$q_{e(cal)}$	R^2	K_2	$q_{e(exp)}$	$q_{e(cal)}$	R^2	B	A	R^2
5	0.0467	0.461	0.48	0.998	0.062	0.4689	0.63	0.997	7.0711	0.0519	0.994
10	0.0488	0.905	0.93	0.998	0.035	0.9050	1.19	0.996	3.6848	0.0995	0.992
15	0.0518	1.292	1.34	0.998	0.026	1.2924	1.69	0.996	2.6005	0.1410	0.991
20	0.0540	1.592	1.64	0.997	0.024	1.5916	2.03	0.996	2.1568	0.1700	0.990
25	0.0567	1.850	1.88	0.999	0.024	1.8501	2.31	0.996	1.8918	0.1938	0.985

Fig. 1. Effect of Initil Concentration

Fig. 2. Effect of Initial Concentration

Fig. 3. Pseudo First order

Fig. 4. Pseudo Second Order

Fig. 5. Elovich Model

Fig. 6. Langmuir Isotherm

Fig. 7. Freundlich Isotherm

Fig. 8. Temkin Isotherm

Fig. 9. Effect of Temperature
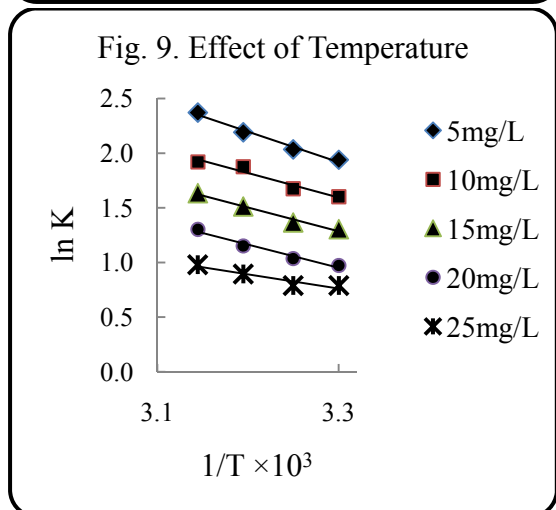
Adsorption Isotherm

The analysis of isotherm data by fitting them to different isotherm model is an important step to find the suitable model that can be used for design purpose. The experimental analysed according to linear form of Langmuir isotherm, Freundlich isotherm and Temkin isotherm.

Langmuir Isotherm

The linear plots of C_e/q_e versus C_e suggest the applicability of Langmuir isotherm (Fig. 6). The values of q_m & K_a were determined from slope and intercept and are presented in Table 2. From the results it is clear that the value of adsorption efficiency and adsorption energy of PL increases on increasing temperature. To confirm the favorability of adsorption process, the separation factor (dimensionless factor) (RL) was calculated and presented in Table 3. The values of separation factor (RL) were found to be between 0 and 1 and thus again confirmed that the Langmuir isotherm model was favorable for adsorption of AR 14 onto PL.

Table 2. Langmuir, Freundlich and Temkin isotherm parameters for adsorption of AR 14 on PL

Temp (K)	Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm		
	Ka (L mg^{-1})	Q$_0$ (mg g^{-1})	R^2	N	K$_f$ (mg g^{-1})	R^2	A (L mg^{-1})	B (J mole^{-1})	R^2
303	0.276	2.645	0.984	1.8474	0.644	0.999	3.524	0.539	0.994
308	0.296	2.710	0.986	1.8725	0.678	0.999	3.792	0.553	0.995
313	0.344	2.733	0.980	1.9190	0.750	0.997	4.482	0.553	0.996
318	0.376	2.759	0.991	1.9440	0.800	1.000	5.114	0.553	0.990

Table 3. Dimensionless separation factor R$_L$

Dye conc. (mg L^{-1})	Temperature (K)			
	303	308	313	318
5	0.420	0.404	0.368	0.347
10	0.266	0.253	0.225	0.209
15	0.194	0.184	0.163	0.151
20	0.153	0.144	0.127	0.117
25	0.123	0.119	0.104	0.096

Table 4. Statistical parameters of kinetic models

Kinetic models	% SSE	RMSE	ARE
Pseudo first order	0.016	0.047	3.014
Pseudo second order	0.164	0.473	29.704
Elovich model	0.025	0.073	3.643

Freundlich Isotherm

Freundlich adsorption plot for the adsorption for AR 14 onto PL is shown in Fig. 7 and the values of adsorption capacity (K_f) and intensity of adsorption (n) are given in Table 2. The values of 1/ n were between 0 and 1 indicating that the adsorption was favorable at studied condition.

Temkin Isotherm

In the Temkin plot q_e against ln C_e (Fig. 8) also shows linearity. The values of A and B are calculated from intercept and slope and are presented in Table 2. In all above three isotherm models the values of correlation coefficient of Freundlich isotherm are comparatively greater than Langmuir isotherm and Temkin isotherm. Freundlich isotherm model fits better for adsorption of AR 14 onto PL other than two models.

Table 5. Thermodynamic parameters for adsorption of AR on PL

Dye conc. $(mg\ L^{-1})$	ΔG (k J mole^{-1})				ΔH (kJ mole^{-1})	ΔS (J K^{-1}mole^{-1})
	303 K	308 K	313 K	318 K		
5	- 4.888	- 5.704	- 5.704	- 6.270	23.195	92.47
10	- 4.034	- 4.287	- 4.884	- 5.080	18.642	74.76
15	- 3.287	- 3.500	- 3.937	- 4.320	18.140	70.53
20	- 2.454	- 2.655	- 3.000	- 3.444	17.608	66.01
25	- 1.986	- 2.019	-2.327	- 2.588	10.793	41.94

Adsorption thermodynamics

The thermodynamic parameters like free energy, enthalpy and entropy have an important role to determine spontaneity and heat changes for adsorption process. The values of ΔH and ΔS are calculated from slope and intercept of plot of *ln K* versus 1/T (Fig. 9) and results are summarized in Table 5. The adsorption data indicates that ΔG is negative at 303, 308, 313 and 318 K. The negative ΔG confirms the spontaneous nature of adsorption process. The magnitude of ΔG suggests that the adsorption is physical process. The decrease in ΔG with the increase of temperature indicates more efficient adsorption at higher temperature. The positive ΔH value confirms that the adsorption process is endothermic for AR 14 which is an indication of the existence of strong interaction between PL and AR 14. Thus the positive value of ΔH indicates that the adsorption increases with increasing temperature. The positive value of ΔS shows increased randomness at the solid-solution interface during the adsorption. In this condition the adsorbed water molecules which are displaced by the sorbet species, gains more translational entropy than is lost by sorbet molecule, thus allowing the prevalence of randomness in the system. However the values of ΔG was found to be decreased as the initial concentration increases, resulting in the decrease of randomness of AR 14.

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