Adsorption Studies of Acid Red 73 on Parthenium hysterophorus L.

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Abstract

The adsorption behavior of Acid red 73 onto Parthenium hysterophorus L from aqueous solution was investigated. Adsorption kinetics, equilibrium, and thermodynamics were investigated as a function of initial concentration and temperature. Three kinetic models – the pseudo first-order, second order and Elovich were used to investigate the adsorption mechanism. Evaluation of kinetic models showed that the pseudo first order kinetic model was found to correlate the experimental data. The adsorption data were modeled by using Langmuir, Freundlich and Temkin adsorption isotherms. The data were well represented by Freundlich isotherm equation and the calculated thermodynamic parameters indicated a spontaneous and exothermic nature of the adsorption process.

Key words: Parthenium L., Acid Red 73, Adsorption kinetics, Thermodynamics.

Introduction

In this work, the ability of PL to remove Acid Red 73 from aqueous solution by adsorption was investigated. Many industries like textile, leather, paper, cosmetic, plastic, painting, food and pharmaceuticals use the various dyes[1]. Most of the used solutions containing such dyes are discharged as effluents. Some of the dyes or their metabolites are known to be toxic, carcinogenic and mutagenic[2]. Many dyes are stable to light and the oxidizing agent, hence difficult to degrade. The dyes even at lower concentration impart color to water bodies; prevent photosynthesis and poses danger to aquatic life[3,4,5]. The removal of dyes from waste water is very important from the environmental point of view[6].

There are many processes used for removal of colored dye from industrial effluent which are like coagulation, flocculation, chemical oxidation, ion exchange, biodegradation, electrolysis, photo catalysis, and adsorption. Adsorption is one of the most effective processes used for the dye removal if the adsorbent is effective, eco-friendly and readily available. Literature survey shows that activated carbon is the most effective adsorbent for the adsorption of dyes but it is expensive and hence there is an increasing need for equally effective and cheaper adsorbent.

Many investigations have been done on the feasibility of low-cost material as the adsorbent coir pith[7,8], peanut hull[9], rice husk[10], baggaspith[11], Parthenium hysterophorus L[13,14], Vilaytitulsi[15] and agricultural wastes.

Materials and Method

Preparation of Sorbet

In the present study, an anionic dye Crocein scarlet or Acid Red 73 (C. I. = 27290, chemical formula $C_{22}H_{14}N_4Na_2O_7S_2$, formula weight = 556.490, λmax = 508 nm) supplied by Aldrich Chemicals was used as the adsorbate. The chemical structure of it is shown in Fig. 1. Acid Red 73 (AR 73) was used without further purification. The dye stock solution was prepared by dissolving accurately weighed dye content. The experimental solutions were prepared by proper dilution.
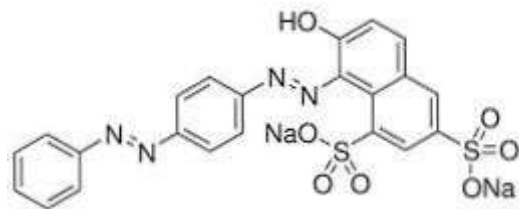
Fig.1: Structure of Acid Red 73

Preparation of Adsorbent

Naturally dried plant leaves of Parthenium hysterophorus L (PL) were cut into tiny pieces and treated with 0.0025 M sulphuric acid. It stirred for half an hour vigorously using mechanical stirrer at temperature 303K. It then filtered and washed with distilled water repeatedly to remove free acid till the pH of the residual solution is in the range of 4.5 to 5.0. It is then dried in air and finally dried in the oven at 363-373 K for 8-10 hours and powdered homogeneously using the electric grinder in order to increase its surface area. The homogeneous powder was passed through mesh for the desired particle size of 800-1,000 μm.

Experimental procedure

The equilibrium adsorption study of the AR 73 onto PL was carried out by contacting 0.9g of the substrate with 100 ml of different concentrations from 5 mg/L – 25mg/L in 250 ml conical flask intermittently shaking for 80 minutes on the orbital shaker. The resulting samples were centrifuged and the remaining AR 73 in the solution was measured by UV–vis-spectrometer at λmax = 508 nm. The amounts of AR 73 adsorbed at time t, q_t (mg/g), were calculated by the following mass–balance relationship:

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

Where C_0 and C_e are the initial and final AR 73 concentrations (mg/L) at time t, respectively, V is the total volume of the solution (l), and W is the mass of adsorbent used (g)

The dye percent removal was calculated by using the following equation

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

Where C_0 and C_e are the initial and equilibrium concentrations (mgL^{-1}) respectively.

Result and Discussion

Effect of initial dye concentration and contact time

The initial concentrations of AR 73 solution were varied from 5 to 25 mg L^{-1} and batch adsorption experiments were carried out with 0.9g of the adsorbent at 303 K. The effect of initial dye concentration and contact time on the adsorption rate of AR 73 is shown in Fig.2. It is observed that percentage adsorption decreases from 88 to 69 % with the increase in adsorption of dye with initial dye concentration (Fig.3), but the actual amount of dye adsorbed per unit mass of PL increases from 0.6 to 2.4 mg. It means that the adsorption is dependent on the 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 become fewer and hence the percentage removal of dye is dependent upon initial concentration[16,17]. Equilibrium has established at 80 minutes for all concentrations. Figure 2 and 3 reveals that the curves are smooth, and continuous, leading to saturation.

Adsorption Dynamics

To investigate the kinetics of adsorption dynamics of AR 73 onto PL, pseudo-first order, pseudo-second order and Elovich models were used to fit the experimental data by using linear regression analysis.

First - Order Kinetic Model: The kinetics of AR 73 adsorption on the PL was analyzed using first-order kinetic model. The simple form of Lagergren[18] can be written as

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

Where K_1 (min^{-1}) is the adsorption rate constant and t is contact time. The adsorption rate constant, K_1 is experimentally determined by the slope of plot log $(q_e - q_t)$ versus t. (Fig.4.)

Second Order Kinetic Model: The integrated form of pseudo-second order equation developed by Ho[19] 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

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

Where h($=K_2 q_e^2$) is the initial adsorption rate mg·g^{-1} min^{-1} The plot of t/qt and t of Eq. (5) give a linear relationship (Fig.5.). 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[20,21] 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. The plot of q_t versus *ln t* is shown in Fig. 6.

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The kinetic parameters K_1, K_2, q_e(exp) and q_e(the) were calculated from the plot and are summarized in Table 1. In above three models, the most of the correlation coefficient exceeds 0.99 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[22] (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 2) are lower for first order and Elovich model in comparison to second order that explains the better fitting of the kinetic model.

Adsorption studies

The adsorption isotherms of AR 73 were studied after adding 0.9g of an adsorbent into the aqueous solution containing a desired AR 73 concentration (5 – 20 mg L^{-1}) and shaking 80 minutes at 303^0K on the orbital shaker. For thermodynamic studies, these procedures were repeated at 305^0, 313^0 and 318^0K. The adsorbed dye data were fitted into following isotherm models.

Langmuir model- The simplified form of Langmuir isotherm[23] 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 adsorption equilibrium constant. According to Hall et. al.[24], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined by the following relationship:

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

The parameter R_L indicates the nature of the adsorption isotherm. $R_L > 1$ unfavorable adsorption $0 < R_L < 1$ favorable adsorption $R_L = 0$ irreversible adsorption $R_L = 1$ linear adsorption.

The linear plots of C_e/q_e versus C_e suggest the applicability of Langmuir isotherm (Fig. 7). The values of q_m and K_a were determined from the slope and intercept and are presented in Table 3. From the results, it is clear that the value of adsorption efficiency and adsorption energy of PL increases with increasing temperature. To confirm the favorability of adsorption process, the separation factor (dimensionless factor) (R_L) was calculated and presented in Table 4. The values of separation factor (R_L) were found to be between 0 and 1 and thus again confirmed that the Langmuir isotherm model was favorable for adsorption of AR 73 onto PL.

Freundlich model: In simple form the Freundlich isotherm[25] 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 K_f were calculated from slope and intercept of plot log q_e versus log C_e.

Freundlich adsorption plot for the adsorption for AR 73 onto PL is shown in Fig. 8 and the values of adsorption capacity (K_f) and intensity of adsorption (n) are given in Table 3. The values of 1/ n were between 0 and 1 indicating that the adsorption was favorable at the studied condition.

Temkin model: The linear form of Temkin model[26] can be presented as follows

$$q_e = BlnA + BlnC_e \qquad (10)$$

where A is Temkin isotherm equilibrium binding constant and B is constant related to the heat of adsorption.

In the Temkin plot, q_e against lnC_e (Fig. 9) also shows linearity. The values of A and B are calculated from intercept and slope and are presented in Table 3.

In all above three isotherm models, the values of the correlation coefficient of Freundlich isotherm are comparatively greater than Langmuir isotherm and Temkin isotherm. Freundlich isotherm model fits better for adsorption of AR 73 onto PL other than two models[27].

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:

$$\Delta G = -RTlnK_0 \qquad (11)$$
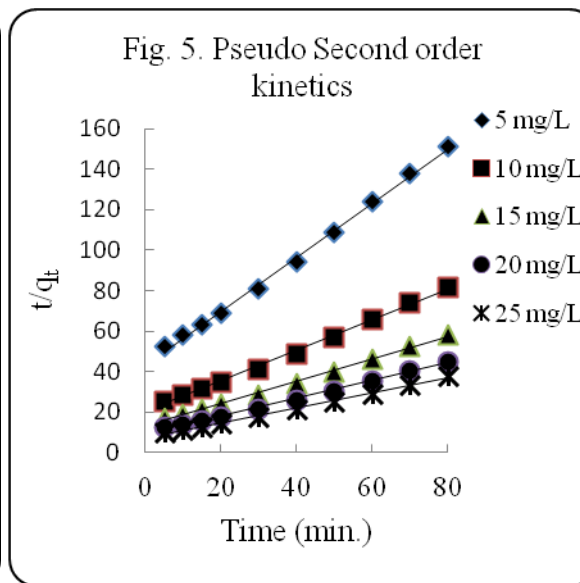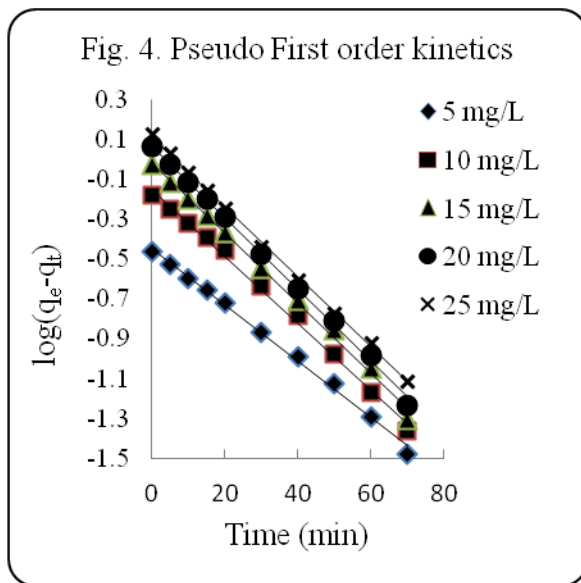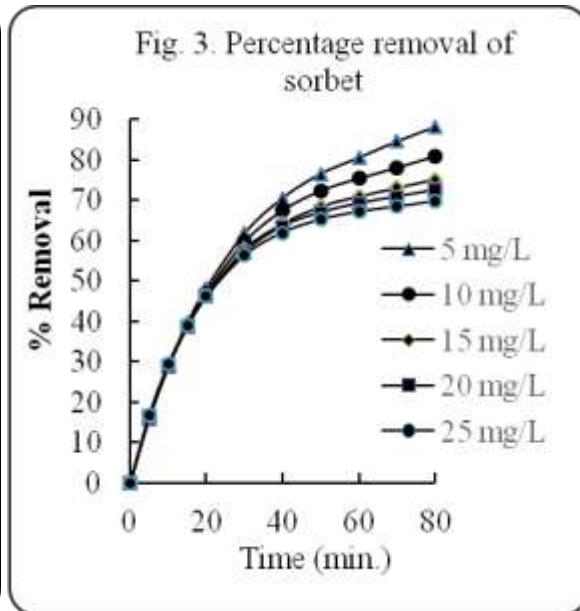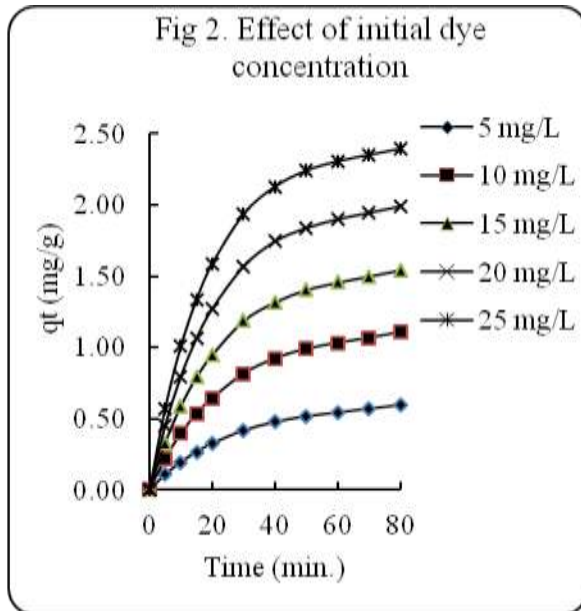
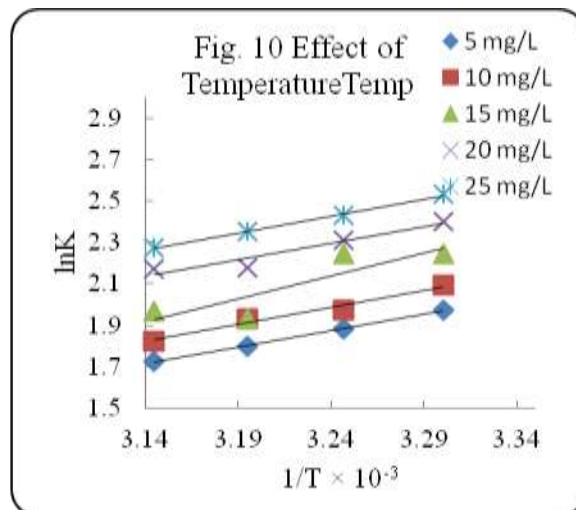$$K_0 = \frac{C_{solid}}{C_{liquid}} \qquad (12)$$
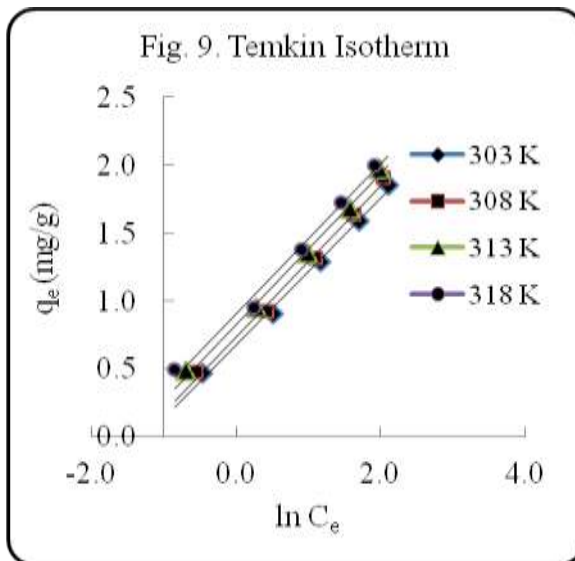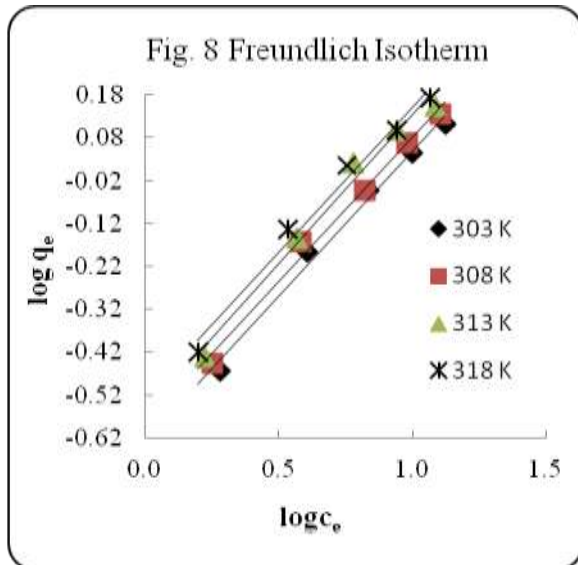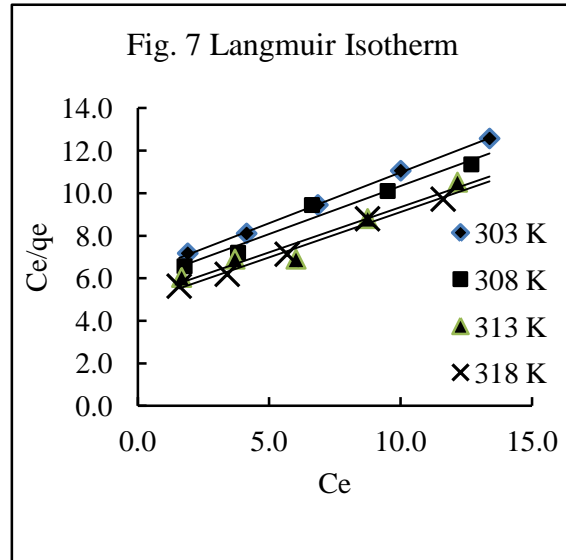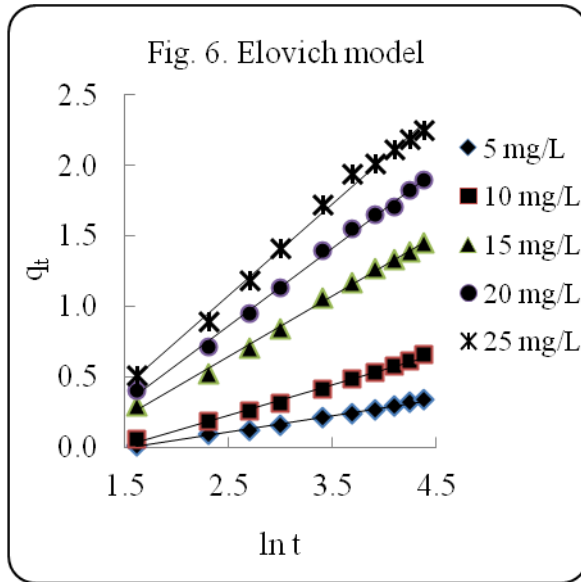
$$\Delta G = \Delta H - T\Delta S \qquad (13)$$

$$lnK_0 = -\frac{\Delta G}{RT} \qquad (14)$$

$$lnK_0 = \frac{\Delta G}{R} - \frac{\Delta H}{RT} \qquad (15)$$

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 ΔH and ΔS can be calculated from slope and intercept of the plot of ln K versus 1/T

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 the plot of *ln K* versus 1/T (Fig. 10) and results are summarized in Table 5. The negative values of ΔG indicate that the adsorption of AR 73 on to PL is spontaneous and thermodynamically favorable. The magnitude of ΔG suggests that the adsorption is a physical process. The ΔH and ΔS values are all negative. The negative values ΔH confirms the exothermic nature of AR 73 – PL adsorption process. The very low ΔH value depicts the adsorption of AR 73 on PL is physical adsorption[28]. Also the negative values for both ΔH and ΔS suggest that the adsorption is physical in nature with weak forces of attraction and decrease in randomness at AR 73 – PL interface during the adsorption process.

Fig 2. Effect of initial dye concentration

Fig. 3. Percentage removal of sorbet

Fig. 4. Pseudo First order kinetics

Fig. 5. Pseudo Second order kinetics

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Fig. 6. Elovich model

Fig. 7 Langmuir Isotherm

Fig. 8 Freundlich Isotherm

Fig. 9. Temkin Isotherm

Fig. 10 Effect of TemperatureTemp

Table 1: Rate constants for First-order, Second-order and Elovich mode.l

Dye Conc.	First order				Second order				Elovich model		
(mg L^{-1})	K$_1$	q$_{e(exp)}$	q$_{e(cal)}$	R^2	K$_2$	q$_{e(exp)}$	q$_{e(cal)}$	R^2	β	α	R^2
	(min^{-1})	(mg g^{-1})	(mg g^{-1})		(min^{-1})	(mg g^{-1})	(mg g^{-1})		(mg g^{-1})	(mg g^{-1} min^{-1})	
5	0.0440	0.5299	0.5733	0.9925	0.0412	0.5299	0.7498	0.9978	8.6359	0.0425	0.9947
10	0.0466	0.9837	1.0187	0.9977	0.0281	0.9837	1.3289	0.9971	4.5639	0.0803	0.9940
15	0.0496	1.3720	1.4047	0.9982	0.0240	1.3720	1.7956	0.9968	2.3170	0.1583	0.9968
20	0.0530	1.7721	1.8182	0.9987	0.0210	1.7721	2.2770	0.9962	1.8112	0.2025	0.9967
25	0.0564	2.1270	2.1836	0.9991	0.0199	2.1270	2.6788	0.9961	1.5337	0.2391	0.9942

Table 2: Statistical parameters of kinetic models

Kinetic models	% SSE	RMSE	ARE
Pseudo first order	0.0195	0.0563	3.8803
Pseudo second order	0.1904	0.5497	32.3795
Elovich model	0.0125	0.0362	0.7428

Table 3: Langmuir, Freundlich and Temkin Isotherm parameters for adsorption of AR 73 on PL

Temp (K)	Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm		
	Ka	Q$_0$	R^2	n	K$_f$	R^2	A	B	R^2
	(L mg^{-1})	(mg g^{-1})			(mg g^{-1})		(L mg^{-1})	(J mole^{-1})	
303	0.0655	2.5057	0.9987	1.4231	0.1914	0.9910	0.7532	0.5007	0.9940
308	0.0663	2.6552	0.9726	1.4304	0.2063	0.9905	0.8388	0.5450	0.9950
313	0.0700	2.8520	0.9551	1.3817	0.2198	0.9754	0.8133	0.5688	0.9960
318	0.0737	2.8658	0.9897	1.4144	0.2357	0.9870	0.8558	0.5706	0.9900

Table 4: Dimensionless Separation factor R$_L$

Dye conc.	Temperature (K)			
(mg L^{-1})	303	308	313	318
5	0.7330	0.7306	0.7195	0.7092
10	0.5785	0.5755	0.5619	0.5494
15	0.4778	0.4747	0.4609	0.4484
20	0.4070	0.4040	0.3907	0.3788
25	0.3544	0.3516	0.3391	0.3278

Table 5: Thermodynamic parameters for adsorption of AR 73 on PL

Dye conc.	ΔG (J / mole)				ΔH	ΔS
(mg L^{-1})	303 K	308 K	313 K	318 K	(kJ/mole)	(J K^{-1}mole^{-1})
5	-4963.29	-4817.38	-4680.07	-4568.43	-12.9799	-26.4818
10	-5271.64	-5055.26	-5026.26	-4818.74	-13.6654	-27.7694
15	-5657.28	-5748.98	-5026.26	-5193.40	-18.5618	-42.3683
20	-6052.91	-5921.84	-5661.17	-5748.61	-13.2200	-23.7484
25	-6376.61	-6221.19	-6123.00	-6012.44	-13.5957	-23.8724

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