Research Article

Theme- *New horizons in chemical sciences.*
Guest Editor- *R.P. Pawar*

Kinetic and Isotherm models for the Adsorption of Acid Red 1 from aqueous solution by *Parthenium hysterophorus L.*

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ABSTRACT
The adsorption behaviour of Acid red 1 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 modelled by using Langmuir, Freundlich and Temkin adsorption isotherms. The data were well represented by Langmuir isotherm equation and the calculated thermodynamic parameters indicated a spontaneous and exothermic nature of the adsorption process.

1. INTRODUCTION

Dyes have been widely used in the textile, leather, paper, rubber, plastics, cosmetics, pharmaceuticals and food industries. The presence of dyes in water, even at very low concentrations, will result in a considerable adverse aesthetic effect since they are visible pollutants. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic[1]. Many dyes are difficult to degrade, as they are generally stable to light, oxidizing agent and are resistant to aerobic digestion[2]. Hence, extensive use of dyes poses not only a severe public health concern, but also many serious environmental problems because of their persistence in nature and non-biodegradable characteristics. The conventional methods of dye removal from industrial effluents include ion exchange, membrane technology, coagulation, oxidation or ozonation, flocculation and adsorption[3-5]. 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. Amongst all, activated carbon is the most effective and commonly used adsorbent for the treatment of dye wastewaters. However, its relatively high price, high operating costs and problems with regeneration of the spent carbon hamper its large-scale application. This subsequently led to search for low cost, renewable, locally available materials as adsorbent for the removal of dye colours. A number of investigations have shown that some raw agricultural by-products have the potential of being used as alternative adsorbent for the removal of dyes from wastewater, which include rice hull[6], bagasse pith[7], barley husk[8], peanut hull[9], vilayati Tulsi[10], carrot grass[11-13] and other agricultural wastes.

1. MATERIALS AND METHODS

2.1. Preparation of adsorbent

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 800-1000 μm.

2.2. Preparation of adsorbent

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

2.3. Adsorption studies

The effect of initial concentration of AR 1 was studied using concentration range 5-25 mgL^{-1}. A typical experimental procedure was conducted by measuring accurately 100 ml of the AR 1 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 analysed for residual AR 1 using a UV-visible spectrophotometer at λmax of 506 nm. The amount of AR 1 uptake by PL in each flask was calculated using the following equation,

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

Where q_e is the equilibrium adsorption capacity of AR 1 adsorbed on unit mass of the PL; C_0 and Ce are the initial and equilibrium AR 1 concentrations respectively; V is the volume of the AR 1 solution; and W is the weight of the PL.
The dye percent removal was calculated by using the following equation,

$$\textbf{Removal percentage} = \frac{C_0 - C_e}{C_e} \times 100 \quad \text{---Equation 2}$$

Where C^0 and Ce are the initial and equilibrium concentrations (mgL^{-1}) respectively.
Adsorption kinetics and isotherm experiments were undertaken in a batch equilibrium system. The data on the adsorbed dye at various time intervals were fitted to various kinetic models and isotherm models.

2. RESULTS AND DISCUSSION
3.1. Effects of initial dye concentration
The effect of initial dye concentration and contact time on the adsorption rate of AR 1 is shown in Fig. 2. It is observed that percentage adsorption decreases with the increase in initial dye concentration (Fig. 3), but the actual amount of dye adsorbed per unit mass of PL increased with increase in dye concentration. 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[14,15]. It was found that the equilibrium time is independent of initial concentrations. Figure 2 and 3 reveals that the curves are smooth, and continuous, leading to saturation.
3.2. Dynamic adsorption studies
To investigate details of the adsorption processes of AR1 onto the PL, we analysed the adsorption kinetics using several models like pseudo-first order Lagergren equation[3], pseudo-second order equation[4] and Elovich model[5].

Pseudo first order model

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

Pseudo second order model

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

Elovich model

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \qquad --- \text{ Equation 5}$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t respectively, K_1 is the rate constant (L/min) of the pseudo-first-order model, K_2 is the rate constant (g/mg/min) of the pseudo-second-order model, α is the initial adsorption rate (mg/g/min) and β is the desorption constant (g/mg).

The linear plots for pseudo first order, Pseudo second order and Elovich model are given in Fig. 3, Fig. 4 and Fig. 5 respectively. For evaluating the adsorption kinetics of AR 1, the pseudo-first-order, the pseudo-second–order, and Elovich model were used to fit the experimental data by using linear regression analysis method. The parameters of these models are summarized in Table. 1. The high correlation coefficient values indicate the fitness of the model. From the kinetic data, the pseudo-first-order and pseudo-second-order correlation coefficient value were almost same. The q_e values calculated from the pseudo second order model are greater than that of the experimental value. But the q_e values calculated from the pseudo- first order model are nearly equal to the experimental value. So that the adsorption of AR 1 on PL follows the pseudo–first -order kinetic model, which is also confirmed by statistical parameter (Table 4).

3.3. Adsorption isotherms

The isotherm results were analysed using the Langmuir, Freundlich and Temkin isotherms.

3.3.1. Langmuir isotherm

It is the most commonly used isotherm. The linear form of Langmuir isotherm[19] can be represented as,

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \qquad --- \text{ Equation 6}$$

where $q_e (mg/g)$ and $C_e (mg/L)$ are the amount adsorbed dye per unit mass of the adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively. Ce is the equilibrium concentration of the adsorbate, and Q_0 and b are Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively.

The linear plot of C_e/q_e against the equilibrium concentration (C_e) (Fig, 6) shows that the adsorption obeys the Langmuir model. The Langmuir constants were determined from the slope and intercept of the plot and are presented in Table 2. Since the adsorption process is exothermic, the adsorption capacity decreases with increasing temperature.

According to Hall et. al.[20], 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:

$$R_L = \frac{1}{1 + bC_0} \qquad --- \text{ Equation 7}$$

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The parameter R_L indicates the nature of the adsorption isotherm. $R_L > 1$ unfavourable adsorption $0 < R_L < 1$ favorable adsorption $R_L = 0$ irreversible adsorption $R_L = 1$ linear adsorption. The R_L value between 0 and 1 indicate favourable adsorption (Table 3).

3.3.2. Freundlich isotherm
The linear form of the Freundlich isotherm[21] can be represented as

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad --- \text{ Equation 8}$$

where K_f and n are the Freundlich constants with K_f the adsorption capacity and n giving an indication of how favourable the adsorption process. The slope, *1/n* ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. The values of K_f and n are calculated from the intercept and slope of the plot (Fig. 7) and are presented in Table 2.

3.3.3. Temkin model
The linear form of Temkin model[22] can be presented as follows,

$$q_e = BlnA + BlnC_e \qquad --- \text{ Equation 9}$$

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. 8) also shows linearity. The values of A and B are calculated from intercept and slope and are presented in Table 2.

The correlation coefficient indicates the better fitting of Langmuir isotherm and Freundlich isotherm than Temkin model.

3.4. Thermodynamic studies
The thermodynamic parameters calculated using the following equations,

$$\Delta G = -RTlnK_0 \qquad --- \text{ Equation 10}$$

$$K_0 = \frac{C_{solid}}{C_{liquid}} \qquad --- \text{ Equation 11}$$

$$\Delta G = \Delta H - T\Delta S \qquad --- \text{ Equation 12}$$

$$lnK_0 = -\frac{\Delta G}{RT} \qquad --- \text{ Equation 13}$$

$$lnK_0 = \frac{\Delta G}{R} - \frac{\Delta H}{RT} \qquad --- \text{ Equation 14}$$

The values of ΔH and ΔS were calculated from the slope and intercept of plot of lnK_0 against 1/T (Fig. 9) and are presented in Table 5. The adsorption data indicates that ΔG values were negative at all temperatures. The negative values of ΔG confirm that the adsorption process is spontaneous and favourable. In addition, the free energy decrease upon

increasing the temperature suggests that the process is favoured at high temperatures. The magnitude of ΔG suggest that the adsorption is physical adsorption process. The negative values of ΔH suggest the exothermic nature of adsorption process and positive values of ΔS shows the increased randomness at the solid solution interface during the adsorption of AR 1 onto PL.

3.5. Test for validity of kinetic Models

The following tests were used for the validity of models.

1. 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,

$$RMSE = \sqrt{\frac{1}{N-2}\sum_{i=1}^{N}\left(q_{e(exp)} - q_{e(cal)}\right)^2} \qquad ---\text{ Equation 15}$$

2. The average relative error (ARE)

$$ARE = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{\left|\left(q_{e(exp)} - q_{e(cal)}\right)\right|}{q_{e(exp)}}\right] \qquad ---\text{ Equation 16}$$

3. The sum of error squares (SSE%)

$$\%SSE = \frac{\sqrt{\Sigma\left(q_{e(exp)} - q_{e(cal)}\right)^2}}{N} \qquad ---\text{ Equation 17}$$

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

4. CONCLUSION

The adsorption of AR 1 from aqueous solutions was investigated under different experimental conditions. The conditions of maximum adsorption of dyes were optimized. The kinetic parameter with high correlation coefficient and theoretical and calculated q_e values shows that adsorption follows pseudo first-order kinetics. The adsorption data fit the Langmuir and Freundlich isotherms, showing that adsorption was monolayer in nature. The thermodynamic parameters were found to be thermodynamically favourable physical adsorption process. Since the adsorbent material is freely available in large quantities, the treatment method seems to be economical.

5. REFERENCES

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

Dye Conc.	First order				Second order				Elovich model		
(mg L^{-1})	K_1 (min^{-1})	q_e(exp) (mg g^{-1})	q_e(cal) (mg g^{-1})	R^2	K_2 (min^{-1})	q_e(exp) (mg g^{-1})	q_e(cal) (mg g^{-1})	R^2	β (mg g^{-1})	α (mg g^{-1} min^{-1})	R^2
5	0.0413	0.3866	0.4118	0.9912	0.0552	0.3866	0.5457	0.9992	8.4133	0.0367	0.9917
10	0.0428	0.7528	0.7855	0.9961	0.0295	0.7528	1.0600	0.9977	4.2875	0.0734	0.9973
15	0.0437	1.0573	1.0869	0.9957	0.0237	1.0573	1.4502	0.9975	3.0942	0.1085	0.9957
20	0.0461	1.2945	1.3276	0.9979	0.0216	1.2945	1.7417	0.9970	2.5484	0.1404	0.9930
25	0.0473	1.5062	1.5088	0.9999	0.0211	1.5062	1.9803	0.9965	2.2227	0.1739	0.9889

Table 2. Langmuir, Freundlich and Temkin isotherm parameters for adsorption of AR 1 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	0.0980	2.7681	0.9930	1.4435	0.2836	0.9885	1.1258	0.5562	0.9884
308	0.1118	2.7395	0.9914	1.4981	0.3181	0.9972	1.2671	0.5562	0.9792
313	0.1329	2.6426	0.9921	1.5557	0.3544	0.9980	1.4404	0.5519	0.9812
318	0.1672	2.4744	0.9921	1.6444	0.3988	0.9952	1.7059	0.5354	0.9866

Table 3. Dimensionless separation factor R_L.

Dye Conc.	Temperature (K)			
(mg L^{-1})	303 K	308 K	313 K	318 K
5	0.6711	0.6415	0.6009	0.5447
10	0.5050	0.4722	0.4295	0.3743
15	0.4048	0.3736	0.3341	0.2851
20	0.3378	0.3090	0.2734	0.2302
25	0.2898	0.2635	0.2314	0.1931

Table 4. Statistical parameters of kinetic models 3.

Kinetic models	% SSE	RMSE	ARE
Pseudo I order	0.0121	0.0350	3.2758
Pseudo II order	0.1672	0.4826	37.0286
Elovich	0.2753	0.7946	165.0238

Table 5. Thermodynamic parameters for adsorption of AR 1 on PL.

Dye conc.	ΔG (J mole-1)				Δ H	Δ S
(mg L^{-1})	303 K	308 K	313 K	318 K	(J/mole)	(J/K mole)
5	- 3693.91	- 3321.19	- 3030.14	- 2688.62	- 23.73	66.18
10	- 3947.94	- 3859.19	- 3653.89	- 3486.66	- 14.97	34.57
15	- 4450.56	- 4361.99	- 4231.83	- 3912.85	- 13.57	31.68
20	- 4902.02	- 4747.28	- 4581.08	- 4554.05	- 12.26	24.37
25	- 5167.68	- 5047.25	- 5007.77	- 4999.13	- 8.49	11.05
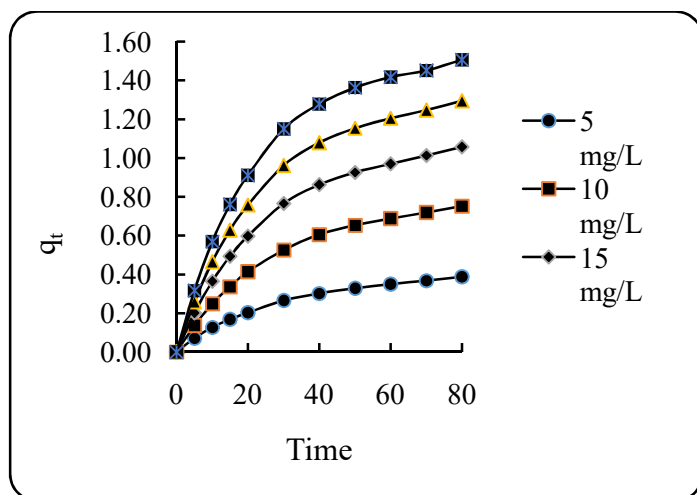
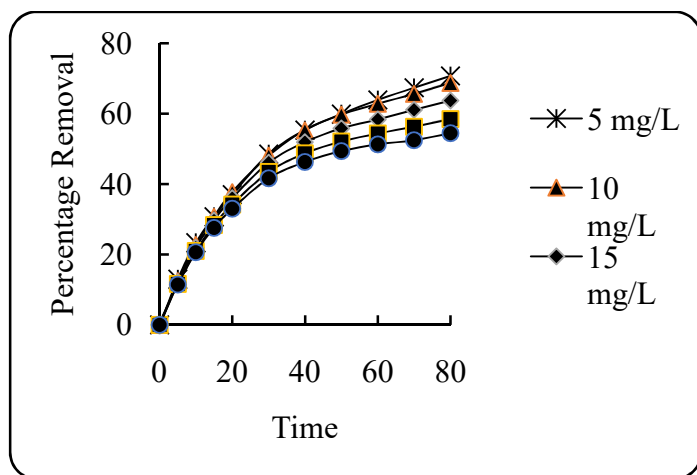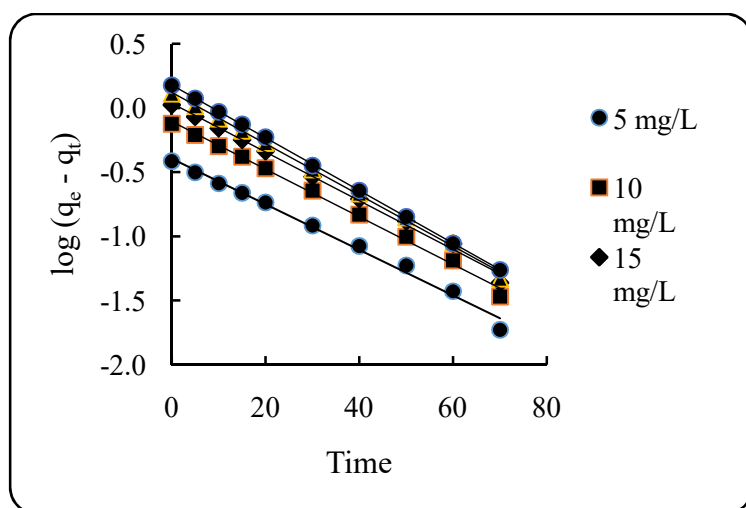**Fig.1.** Effect of Initial Concentration.

Fig. 2. Percentage removal of sorbet.
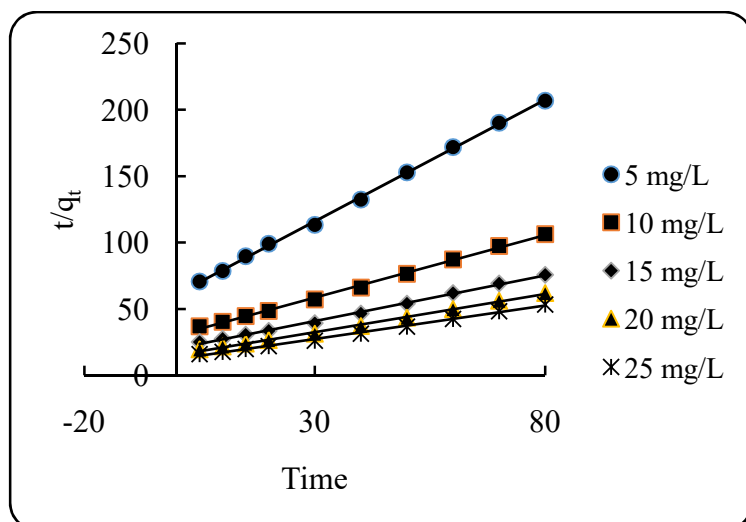

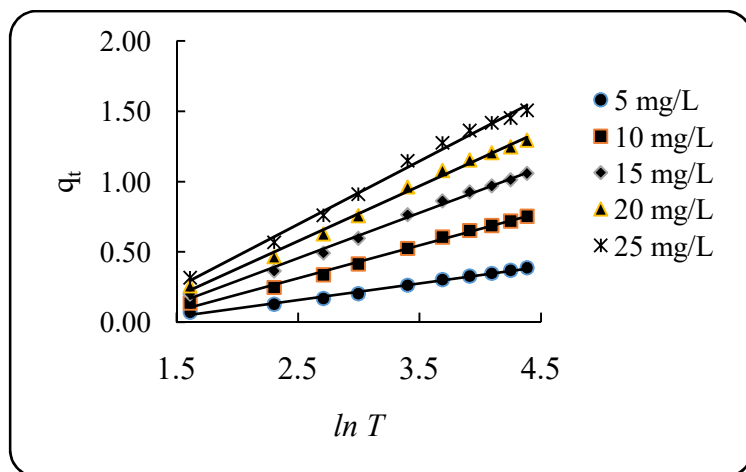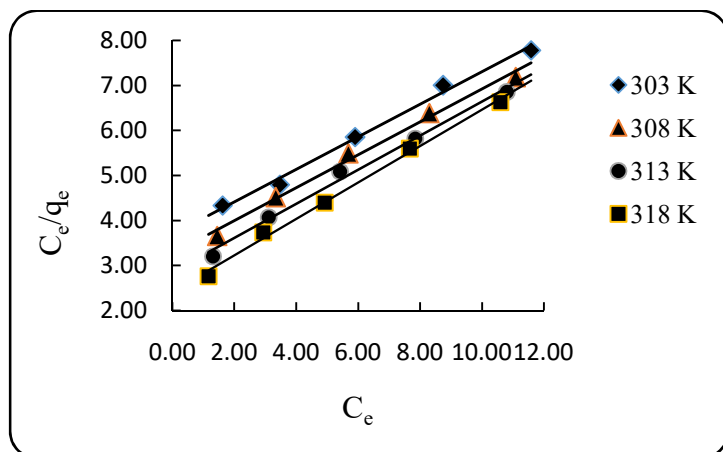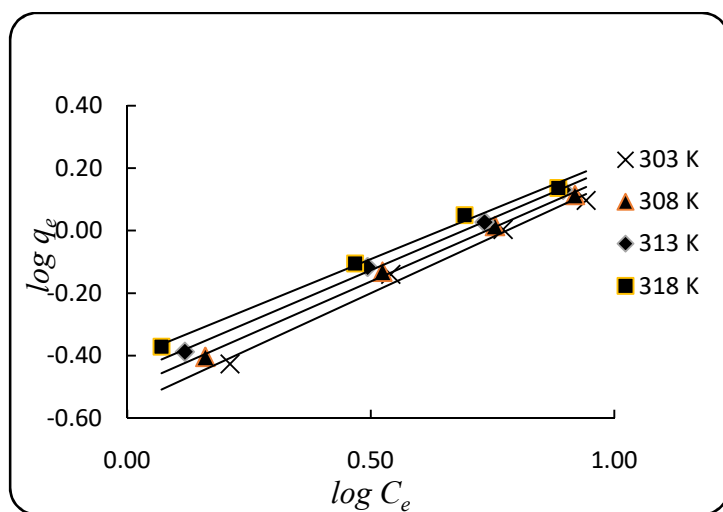**Fig. 3.** Pseudo First Order kinetics.

Fig. 4. Pseudo Second Order kinetics.

Fig. 5. Elovich Model.

Fig. 6. Langmuir Isotherm.

Fig. 7. Freundlich Isotherm.

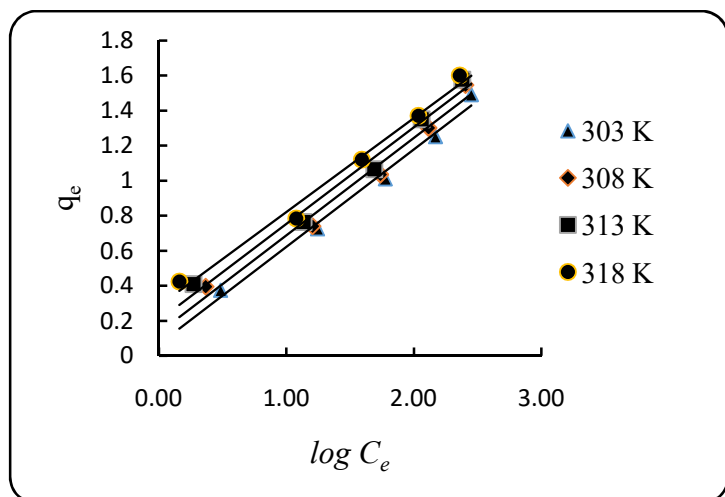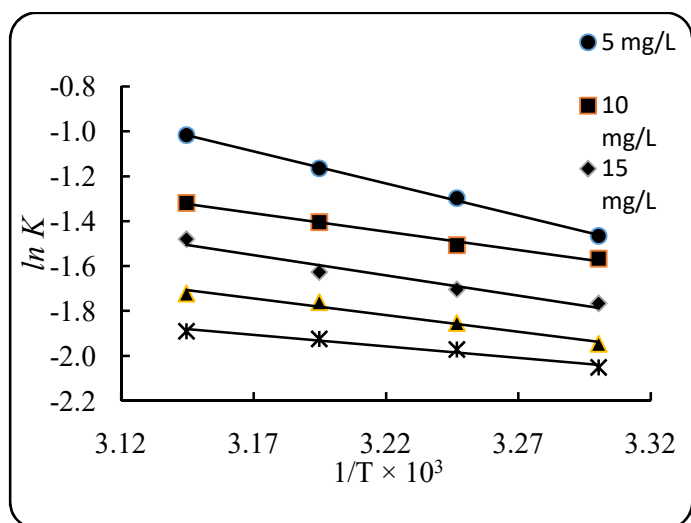**Fig. 8.** Temkin Isotherm.

Fig. 9. Effect of Temperature.