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Research Article

ADSORPTION OF MALACHITE GREEN BY ACTIVATED *EUPATORIUM ODORATUM* CARBON: KINETIC AND THERMODYNAMIC STUDIES

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ABSTRACT

Kinetics and thermodynamic studies were carried out on the adsorption of aqueous Malachite Green dye solution by activated carbon prepared from the leaves of *Eupatorium Odoratum*plant. In the optimum pH range of 5 to 6, the adsorption reached equilibrium after 60 minutes. Adsorption rate constants were determined by pseudo first order, pseudo second order kinetic studies and intra particle diffusion studies. Thermodynamic parameters such as ΔG,ΔH and ΔS were calculated. The studies indicate that the activated carbon prepared from *Eupatorium Odoratum* is a suitable adsorbent for the adsorption of dyes like malachite green from aqueous solutions.

Keywords: Eupatorium Odoratum, Kinetics, Thermodynamics.

1. INTRODUCTION

Malachite green is a basic and cationic dye. It has been widely used for dyeing leather, silk, wool etc. and as in distilleries. It is also used as fungicide and as antiseptic to control fish parasites It is also toxic to microorganisms. But it has been found showing carcinogenic, genotoxic, mutagenic and teratogenic properties due to the presence of nitrogen. It also retards photosynthetic activity, inhibits the growth of aquatic biota by reducing the sunlight penetration, decreases gas solubility and consumes DO[1,2]. Due to its inert properties, it is difficult to biodegrade or to remove malachite green from aqueous solutions[3].

Adsorption technique is one of the most effective processes of advanced waste water treatment and it could be expected to be promising for a wide range of compounds, than any of the other processes[2].

In the present work, the leaves of Eupatorium Odoratum (common name: Christmas bush), which is abundant and cheap plant was used to prepare of activated carbon. The plant belongs to Asteraceae family and it is a shrub plant and it grows mostly in every part of Tamilnadu, India.

2. EXPERIMENTAL

2.1. MATERIALS AND METHODS

2.1.1. Preparation of the activated carbon

In the present study, Eupatorium odoratum leaves were washed thoroughly bydouble distilled water to remove the dust and other impurities, dried in shade, then in hot air oven at 60^0C, made into fine powder and used as precursor. The activated carbon was prepared by chemical activation method using conc. H_2SO_4. In this process, the dried leaves were impregnated with conc. H_2SO_4 (1:1) for 24 hours, filtered, washed repeatedly with deionized water and then heated at 500^0C for 5 hours. After activation, the carbon was sieved for uniform particle size and used for adsorption[4].

2.1.2. Preparation of the dye solution

The characteristics of Malachite Green dye is given in the Table – 1. The dye used for the present study was purchased from Ranbaxy, Mumbai and used as such. The stock solution of 1000 ppm was prepared by dissolving 1000 mg of dye in 1L of deionized water. Other concentrations (100 ppm to 200 ppm) were prepared from the stock solution by appropriate dilution with double distilled water. The pH of the solutions was adjusted to desired values with 0.1M HCl or 0.1M NaOH[5].

Table 1: Characteristics of Malachite Green

Colour Index name	Basic Green 4 (BG 4)
Colour Index number	42000
Molecular Formula	$C_{23}H_{25}N_2Cl$
Molecular weight	365
Dye content, (%)	90
λ max, (nm)	618

2.1.3 Batch adsorption studies

Adsorption studies were done for 60 minutes (time to reach equilibrium stage),theq_t was determined for every 10 minutes. In these experiments, the adsorbent dosage taken was140 mg and dye concentration was 120 ppm. The dye concentration in supernatant solution was determined at characteristic wavelength of MG (λ_{max} = 617 nm) by double beam UV–visible spectrophotometer (Systronics, 2202). For kinetic and thermodynamic studies, dye solutions of different concentrations (100 ppm to 200 ppm) were shaken with the known amount of adsorbent (0.14 g) at 303,313, 323 and 333K till the equilibrium was reached. Then the residual MG concentration was determined[12].

3. Results and Discussion

3.1. Adsorption Kinetic Studies

The adsorption kinetics is one of the important factors to define the efficiency of the adsorption[10]. In order to understand the process of adsorption, three kineticmodels (i)Lagergren's pseudo-first order,(ii) Ho's pseudo-second order model and (iii) Weberand Morris intraparticle diffusion model were appliedto analyse the experimental data.

3.1.1. Pseudo First order kinetic model

The first order rate expression of Lagergren based on solid capacity is generally expressed as

$$dq_t/d_t \quad = \quad k_1(q_e - q_t)$$

whereq_t is the quantity of dye adsorbed at time t(mg/g); qe is the adsorption capacity at equilibrium (mg/g); k_1 is the pseudo first order rate constant (min^{-1}); and t is the contact time (min).
The above equation on integration with the initial conditions qt = 0 as t → 0 gives

$$\log (qe - qt) = \log qe - k_1t / 2.303$$

The values of k_1 and regression coefficient R^2 were determined from the plot of log (qe – qt) against t (Fig.1) and given in the Table 2.

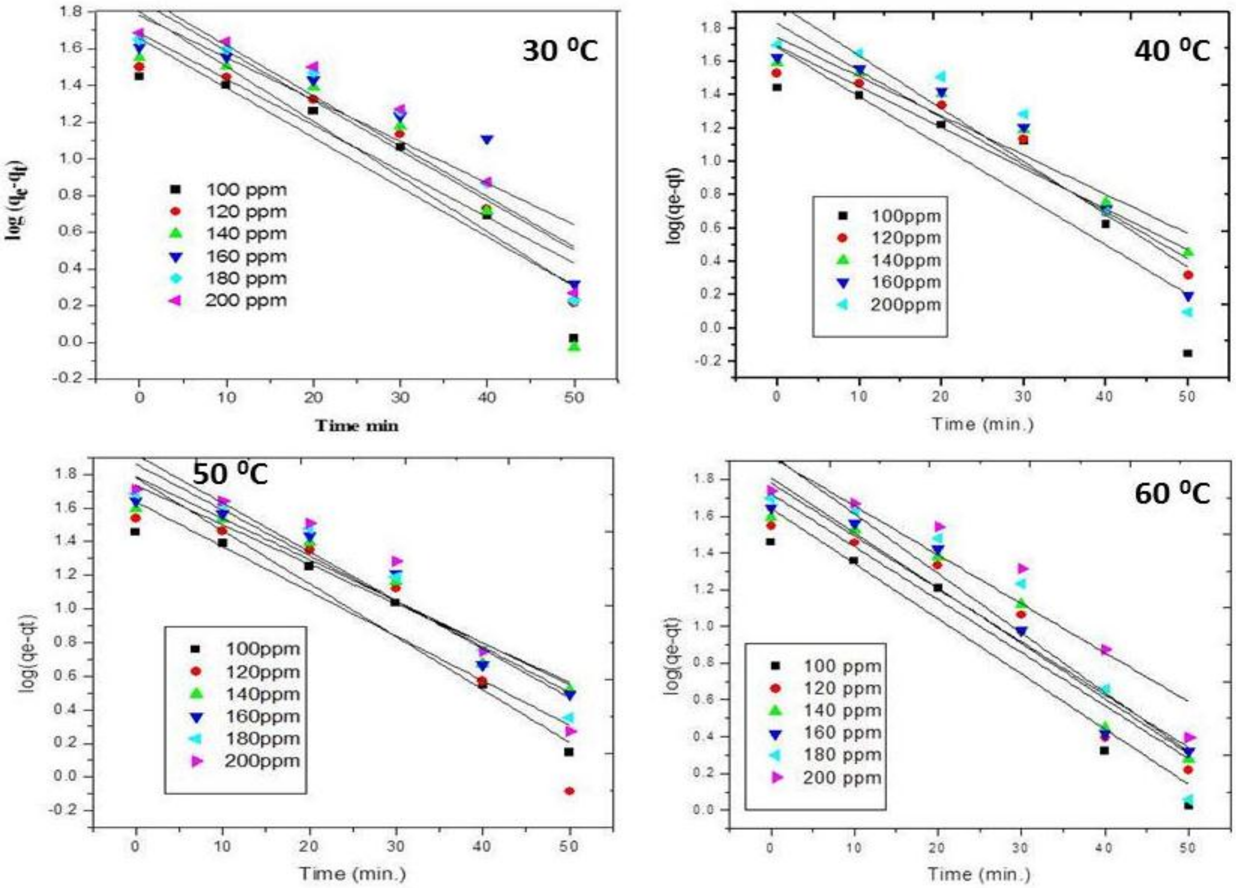

Fig. 1: Pseudo – first order plots for the adsorption of MG dye onto EOC at various temperatures

Table 2: Rate constants of pseudo – first order kinetic at different temperatures and different concentrations

Temp.(^{0}C)	C_0 (ppm)	q_e(exp)(mg/g)	q_e(calc.)(mg/g)	K_1(min^{-1})	R^2
30	100	45.33	29.41	6.227 x 10^{-2}	0.82684
	120	48.42	32.55	5.7759 x 10^{-2}	0.85691
	140	51.41	36.79	6.9021 x 10^{-2}	0.80303
	160	63.61	42.08	6.8690 x 10^{-2}	0.86662
	180	72.39	46.65	6.2530 x 10^{-2}	0.83611
	200	78.04	50.31	6.3217 x 10^{-2}	0.85184
40	100	48.75	29.76	6.9067 x 10^{-2}	0.79904
	120	49.36	35.03	5.6562 x 10^{-2}	0.8911
	140	55.46	40.57	5.4305 x 10^{-2}	0.9044
	160	66.97	44.16	6.5059 x 10^{-2}	0.86595
	180	80.85	48.36	7.2038 x 10^{-2}	0.8367
	200	89.17	52.80	7.3120 x 10^{-2}	0.8432
50	100	43.24	30.81	6.1260 x 10^{-2}	0.89025
	120	60.14	36.26	7.2544 x 10^{-2}	0.83435
	140	54.10	41.51	5.3959 x 10^{-2}	0.9128
	160	61.07	46.23	5.6930 x 10^{-2}	0.90523
	180	72.36	50.63	6.2573 x 10^{-2}	0.9089
	200	82.59	54.66	6.6579 x 10^{-2}	0.87169
60	100	43.81	31.16	6.9228 x 10^{-2}	0.89523
	120	52.62	36.67	6.6465 x 10^{-2}	0.88783
	140	60.17	41.98	6.6372 x 10^{-2}	0.88822
	160	64.27	47.27	6.9228 x 10^{-2}	0.91267
	180	86.16	52.34	7.4663 x 10^{-2}	0.85946
	200	87.26	58.39	6.1352 x 10^{-2}	0.88093

3.1.2. Pseudo Second order kinetic model

The pseudo second order rate equation is given by (10)

$$\mathbf{t/q_t = 1/k_2\, q_e^2 + t/q_e}$$

where k_2 is the rate constant of pseudo second-orderadsorption (g (mg min)$^{-1}$). The q_e and k_2 values werecalculated from slope and intercept of the t/q_t*vs*. t plots (Fig.5), respectively and shown in the Table – 3.

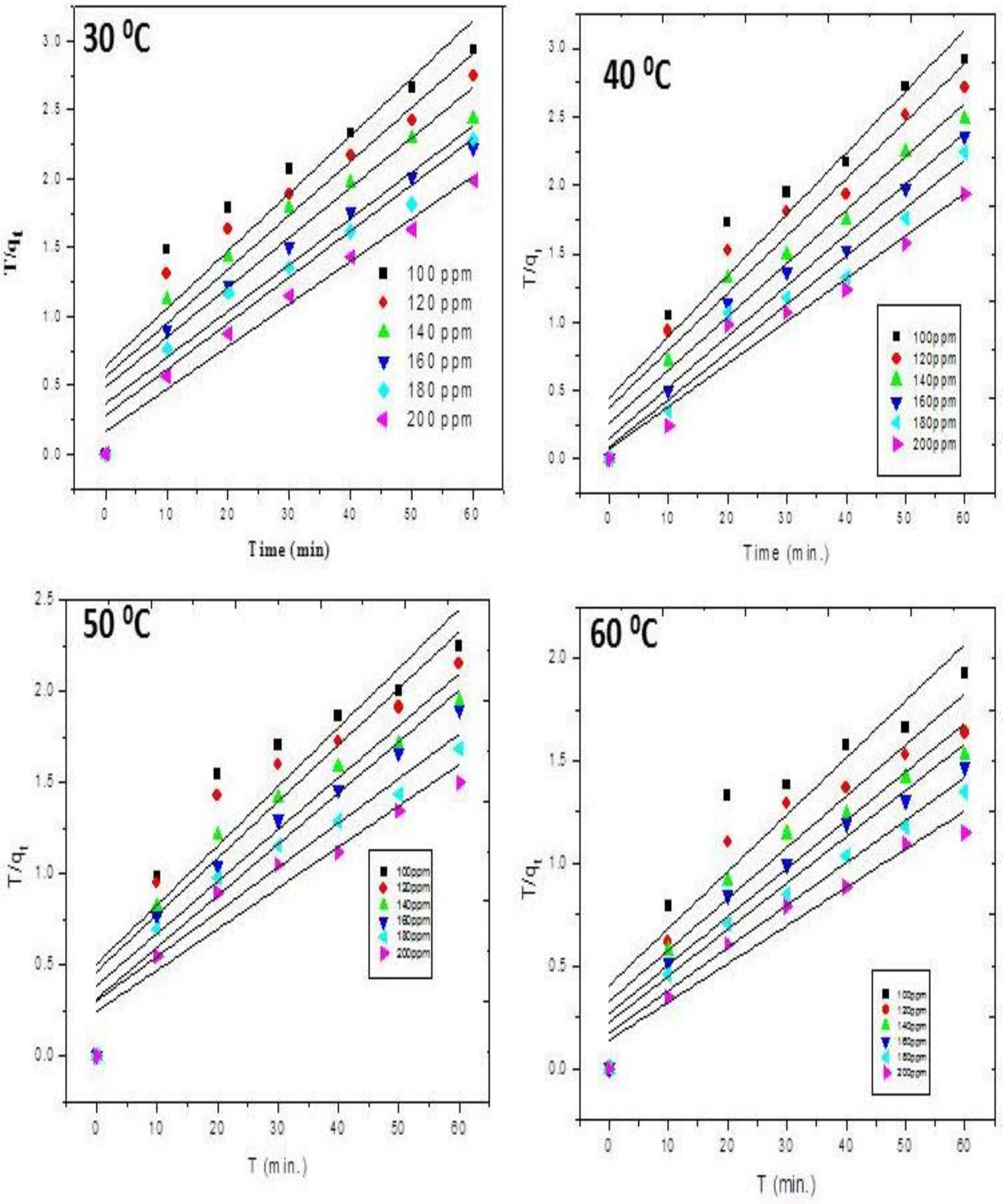

Fig. 2: Pseudo – second order plots for the adsorption of MG dye onto EOC at various temperatures

Table 3: Rate constants of pseudo – second order kinetic at different temperatures and different concentrations

Temp.(^{0}C)	C_0 (ppm)	q_e(exp)(mg/g)	q_e(calc.)(mg/g)	k_2(g/mg min)	R^2
30	100	23.86	29.41	2.7474 x10^{-3}	0.83866
	120	25.51	32.55	2.7484 x10^{-3}	0.85640
	140	27.55	36.79	2.7191 x10^{-3}	0.86833
	160	29.77	42.08	3.0846 x10^{-3}	0.9107
	180	32.26	46.65	2.9826 x10^{-3}	0.9133
	200	33.45	50.31	3.1894 x10^{-3}	0.9694
40	100	22.33	29.76	4.5068 x10^{-3}	0.91079
	120	23.90	35.03	4.6804 x10-^{3}	0.92478
	140	25.67	40.57	5.8331 x10^{-3}	0.95161
	160	26.90	44.16	9.1607 x10^{-3}	0.9684
	180	28.61	48.36	1.4669 x10^{-2}	0.95665
	200	32.07	52.80	1.4082 x10^{-2}	0.9495
50	100	30.80	30.81	2.0909 x10^{-3}	0.87236
	120	32.22	36.26	2.0746 x10^{-3}	0.86999
	140	35.09	41.51	2.0995 x10^{-3}	0.85795
	160	35.46	46.23	2.5257 x10^{-3}	0.90573
	180	40.95	50.63	1.9791 x10^{-3}	0.88433
	200	44.35	54.66	2.0773 x10^{-3}	0.89756
60	100	36.06	31.16	1.8960 x10^{-3}	0.92242
	120	39.98	36.67	1.9133 x10^{-3}	0.83921
	140	42.48	41.98	2.0625 x10^{-3}	0.88668
	160	44.17	47.27	2.2854 x10^{-3}	0.91458
	180	48.15	52.34	2.5013 x10^{-3}	0.94408
	200	53.68	58.39	2.5323 x10^{-3}	0.94142

It can be said that based on R^2 values shown in the above two tables (Table -2 & Table -3) the pseudo second order plots shows a better fit than pseudo first order kinetic model. So the adsorption process can be more satisfactorily explained by pseudo second order. Also when the calculated q_e values are compared with the experimentalq$_e$ values, the calculated qe values for pseudo second order are much closer to the experimental values. These facts suggest that the pseudo-second order mechanism is predominant and that chemisorption might be the rate – limiting step that controls the adsorption process. Thus the rate of adsorption of MG on EOC depends on both availability of the adsorption sites and the concentration of adsorbate in the bulk solution[9].

3.1.3. Intra particle diffusion

Weber and Morris model is a widely used intra particle diffusion model to predict the rate determining step. The equation for the model is

$$q_t = k_{id}t^{1/2} + C_i$$

where q_t is the amount of adsorbed MG ion at the time t, $t^{1/2}$ is the square root of time, $C_i$is the intercept. The intercept value represents the thickness of the boundary layer[7,8]. The larger the intercept value, the greater the contribution of surface sorption in the rate controlling step. The plots of q_t against $t^{1/2}$at different C_0 of MG dye (Fig. 3) indicates that the adsorption process took place in two steps – step one is external surface adsorption or instantaneous adsorption (sharp rise) and the second step is the gradual adsorption stage, where intra particle diffusion is the rate determining. In the first step, the rate of dye removal is higher in the beginning due instantaneous availability of large surface areas and active adsorption sites. In this case, since the plot is not linear and does not pass through origin, the intra particle diffusion was not the only rate controlling step.

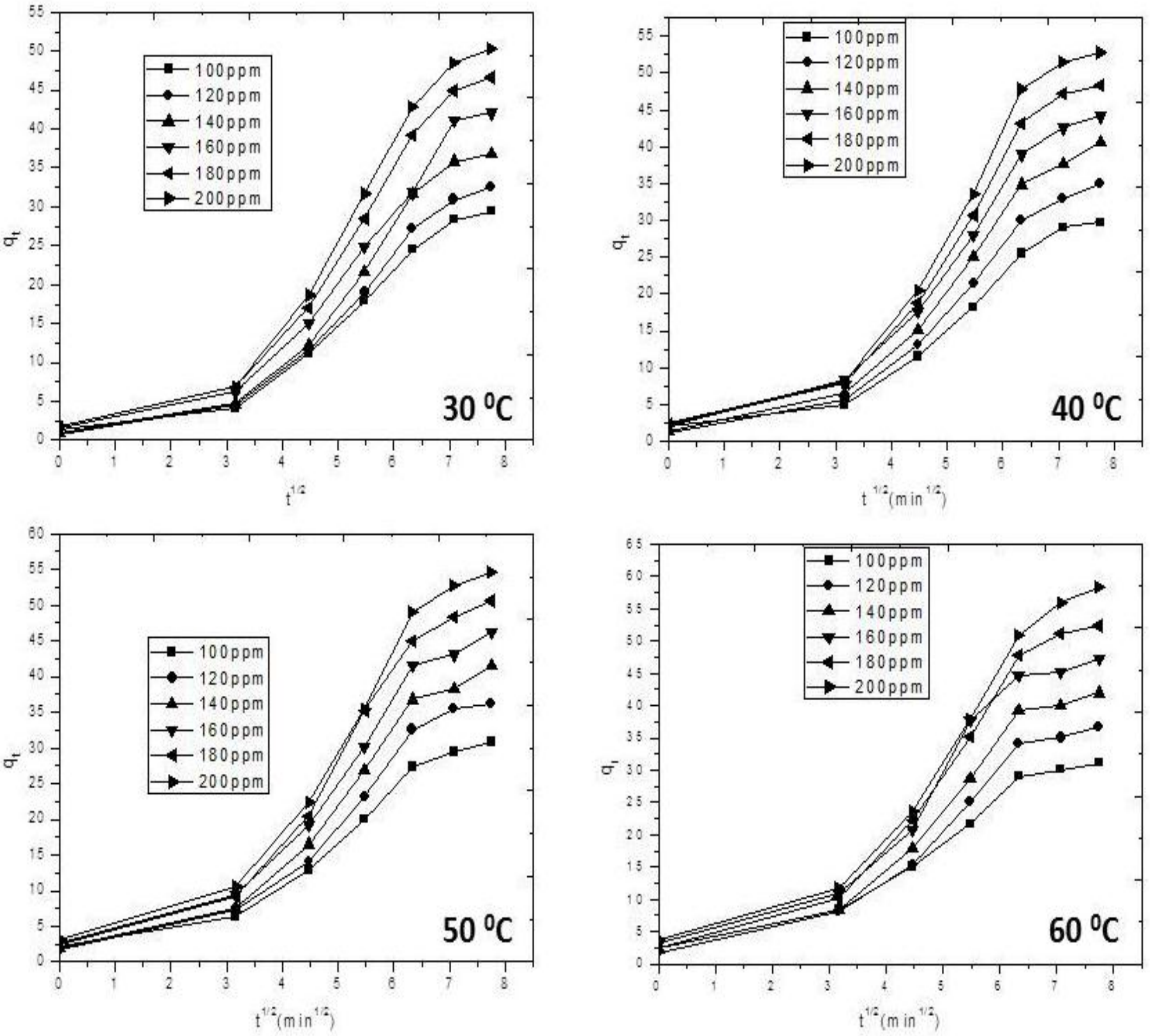

Fig. 3: Intra particle diffusion plots for the adsorption of MG dye on EOC at various temperatures

3.2. Thermodynamic parameters

Thermodynamic parameters like ΔG^0, ΔH^0 andΔS^0 are determined for the adsorption process using the following equations[10]

$$\Delta G^0 = - RT \ln K_d$$

$$\ln K_d = (\Delta S^0 / R) - (\Delta H^0 / RT) \text{ (vant'Hoff equation)}$$

whereK_d = qe/Ce, R is the ideal gas constant (8.314 KJ mol^{-1} K^{-1}) and T is the temperature in Kelvin scale. The enthalpy change (ΔH [-(ΔH= R x slope x 2.033] and the entropy change (ΔS) [ΔS = R x intercept x 2.303] are calculated from the graph of $\ln K_d$against 1/T. (Fig.4). The calculated values of ΔG^0, ΔH^0 andΔS^0 are showed in the Table. 4. The negative values for ΔG shows that the adsorption process is spontaneous and the degree of spontaneity increases with temperature, the adsorption is more favourable at higher temperatures. The complete adsorption process is endothermic. (ΔH is positive) .This result also suggests that adsorption capacity of EOC for the dye increases with increasing temperature.
The ΔS^0values were also positive. This is due to the increase in randomness of adsorbate molecules at the solid surface than in bulk solution[9].

Table 4: Thermodynamic parameters at various concentrations

Conc. (ppm)	T K	Δ G (KJ/mol)	Δ S (KJ mol^{-1} K^{-1})	Δ H (KJ/mol)
100	303	- 1279.7241	64.4619	18.8420
	313	- 1509. 7258		
	323	- 2170.5087		
	333	- 2473.9980		
120	303	- 303.8676	59.6114	17.6223
	313	- 1219.9637		
	323	- 1812.9525		
	333	- 2078.2892		
140	303	- 12.9675	59.1504	17.7238
	313	- 116.1385		
	323	- 1497.1498		
	333	- 1732.8504		
160	303	- 40.0039	50.5045	15.3027
	313	- 505.7539		
	323	- 1112.4743		
	333	- 1485.6432		
180	303	- 78.1876	46.2108	14.1962
	313	- 210.6265		
	323	- 754.3988		
	333	- 1239.4689		
200	303	-5.3219	43.2395	13.5252
	313	- 31.2367		
	323	- 407.7437		
	333	- 929.1701		

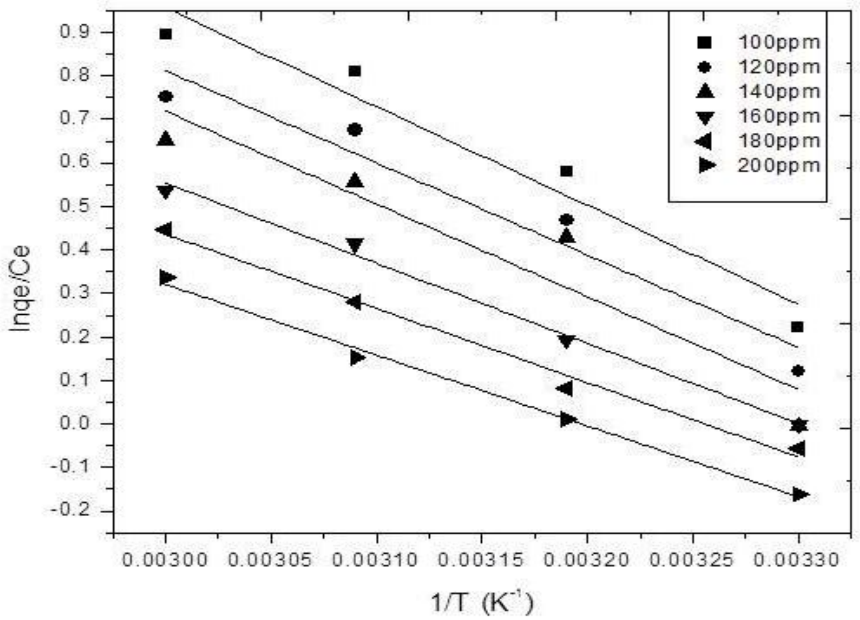

Fig. 4: Van't Hoff plot for the adsorption of MG dye on EOC at various concentrations

CONCLUSION

From the present study it may be concluded that the adsorption of Malachite green dye on Eupatorium odoratum carbon follows the pseudo-second order kinetic model, such that the rate limiting step was governed by chemisorption; the thermodynamic parameters of change inenthalpy (ΔH) is positive, showsthat the adsorptionprocess was endothermic. The negative valueof the Gibbs free energy change (ΔG) indicates that at various temperaturesthe adsorption process was spontaneous and the positive value of ΔSshows the increasing randomnessbetween the solid–solution interface during adsorption.

From these evidences it could concluded that the leaves of Eupatorium Odoratum can be used as precursor for preparing activated carbon for the effective adsorption of dyes such as Malachite Green from waste water.

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