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LOW-COST NON-CONVENTIONAL ACTIVATED CARBON FOR THE REMOVAL OF REACTIVE RED 4: KINETIC AND ISOTHERM STUDIES

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ABSTRACT

Activated carbon with high surface area was prepared from ***Euphorboa antiquorum L*** *wood through chemical impregnation with* H_3PO_4 *solution followed by thermal activation. This carbon is analysed for its ability for the removal of Reactive Red 4 (anionic – reactive dye) from its aqueous solution. At 25 mg/L of initial dye concentration, a maximum of 94.29 % of removal was observed. Various kinetic models were employed for the analysis of kinetics of adsorption. The pseudo second-order model explains the adsorption well with high correlation coefficient. Langmuir monolayer adsorption capacity increases from 222.22 to 227.27 mg/g while increasing the temperature from 30 to 50°C. Thermodynamic parameters were also calculated. The standard enthalpy change of adsorption indicates that the adsorption is endothermic in nature. Desorption increases while increasing the pH from 2 to 8 and no change in desorption there after.*

Key words : *Euphorboa antiquorum L, adsorption, reactive red 4, Kinetics, Isotherms.*

INTRODUCTION

Developments in industrial and agriculture sector have resulted in generation of large amount of waste water containing toxic pollutants. Organic dyes are one of the larger group of pollutants which are released from textile industrial waste water. Some of the effects of dye bearing waste water are aesthetic pollution of environment and also carcinogenicity due to their degradation products. Many techniques like electrochemical coagulation, reverse osmosis, nano filtration, adsorption using activated materials etc., are used for the removal of dye from waste water. Adsorption has been found to be an efficient and economic process for the treatment of dyeing industry effluent[1].

Many researchers have been working for the preparation of low-cost adsorbents. Exploration of good low cost adsorbent may contribute to the sustainability of the environment and offer promising benefits for the commercial purpose in future. Abundance and low cost of agricultural by products and useless plant materials makes them good precursor for the preparation of activated carbon.

Activated carbon was already prepared from agricultural waste and waste plant materials like rice husk[2], peanut hull[3], orange waste[4], palm shell[5], coconut shell waste[6], tropical wood[7], saw dust[8], pinus pinaster bark[9], corncob[10], eucalyptus bark[11], pine saw dust[12], pistachio shells[13], Babool wood[14] etc. The cost of activated carbon prepared from waste materials are negligible when compared to the commercial activated carbon.

The extent of adsorption depends on the nature of adsorbent especially its porosity and high surface area. Two methods are used to increase the porosity, they are physical and chemical activation process. Physical activation refers to the carbonization of precursor followed by activation of the resulting char in presence of N_2, CO_2 and Steam. Chemical activation involves the addition of compounds like H_3PO_4, H_2SO_4, other acids, salt solutions like $ZnCl_2$, KOH etc. prior to carbonization. Chemical activation has more advantages15 over physical activation with respect to higher yield, more surface area and better development of porous structure, oxygenated surface complexes in carbon.

The purpose of the present work is to evaluate the sorption of Reactive Red 4 (Anionic-Reactive dye) from its aqueous solution using Euphorbia antiquorum L wood activated carbon prepared by H_3PO_4 impregnation method. About the precursor, it is wide spread throughout peninsular India, it can be found growing up to an altitude of 800 m. One of the largest armed tree in Euphorbias with an average height of

5 - 7 m., it has been known to attain gigantic proportions if left undisturbed. The odour of its latex is pungent and lingering. Easily propagated from seed or vegetatively and the most important point about this plant is it does not have any economical importance.

EXPERIMENTAL

Adsorbent:

Euphorbia antiquorum **L** wood used as precursor for the preparation of activated carbon. The wood cut into pieces of 2 cm to 3 cm size, dried in sunlight for 10 days. The dried material soaked in a boiling solution of 10 % H_3PO_4 for one hour and kept at room temperature for 24 hours. After 24 hours the wood material separated, air dried and carbonised in muffle furnace at 400°C. The carbonised material was powdered and activated in a muffle furnace at 800°C for a period of 10 minutes. Then the material was washed with plenty of water to remove residual acid, dried, sieved to a desired particle size and stored in a tight lid container for further adsorption studies. The characteristics of the activated carbon are studied as per the standard procedures[15,16] and few important parameters are given in table 1.

Adsorbate:

All the chemicals used are reagent grade. A Reactive dye (Reactive Red 4) having molecular formula $C_{32}H_{19}O_{14}N_8S_4Na_4Cl$ (Mol Wt: 995.23) with CI No.18105, (E. Merck, India) was chosen as the adsorbate. The structure of Reactive Red 4 is given in figure 1. A stock solution containing 1000 mg of the dye per litre was prepared by dissolving the dye in double distilled water and was used to prepare the adsorbate solutions by appropriate dilution as required. Inorder to simplify the discussion the prepared activated carbon is designated as EAAC and the dye Reactive Red 4 is designated as RR4.

Adsorption studies :

The adsorption experiments were carried out by agitating 100 mg of adsorbent with 200 ml of dye solution of 25 to 100 mg/L concentration at 200 rpm in a temperature controlled orbital shaker(REMI make). The mixture was withdrawn at specified interval then centrifuged using electrical centrifuge (Universal make) at 5000 rpm for 10 minutes and unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make Bio-UV visible spectrometer (BL-198) at 517 nm. The effect of pH was studied by adjusting the pH of the adsorptive solution by using 0.1 N NaOH and 0.1 N HCl. All the experiments conducted in duplicate and mean of the two values are taken for calculation.

Desorption studies :

Desorption studies as a function of pH were conducted to analyze the possibility of reuse the adsorbent for further adsorption and to make the process more economical. After adsorption experiments the dye loaded carbon washed gently with double distilled water to remove any un-adsorbed dye if present. Desorption studies were conducted using several such carbon samples. 500 mg of the dye loaded carbon agitated above the equilibration time with 50 ml of double distilled water of various pH and the desorbed dye was estimated as stated in the adsorption studies[17].

RESULTS AND DISCUSSION

Effect of agitation time and initial dye concentration:

The amount of RR4 removed by EAAC increases from 47.14 to 110.57 mg/L while increasing the initial concentration from 25 to 100 mg/L. At 25 mg/L of initial concentration a maximum of 94.29 % of dye removal was observed as shown in the figure 2. In all the range of concentrations under investigation, rapid uptake noticed in the initial 20 minutes of contact time and the adsorption rate decreases there after and finally reaches equilibrium at 90 minutes. The initial rapid uptake is due to the concentration gradient created by the vacant adsorbent surface between adsorbate in solution and adsorbate on the carbon. The increase in dye concentration eases the resistance and makes more contact between dye and solvent.

Availability of dye molecules in the vicinity of adsorbent also increased while increasing the concentration, which results high uptake of dye at higher concentration.

The results indicate that the adsorption reaches an equilibrium at 90 min, beyond which there is no change in the adsorption capacity and there fore 120 min. is fixed as equilibration time for isotherm studies. Similar trend was observed for the adsorption of verofix red (Reactive dye) on to chitin[18].

Effect of pH:

The effect of pH for the adsorption of RR4 on to EAAC over a pH range of 2 to 11 is shown in fig. 3. Dye adsorption decreases with increase of pH from 2 to 5 and no remarkable change there after. Low pH favors the adsorption, as decrease of pH the surface become more protonated and acquire positive charge[19] which makes it easier for the anionic dyes to bind with carbon. Poor adsorption of RR4 at higher pH value is due to the competition between the negatively charged hydroxyl ions and anionic dye for the sorption sites.

Effect of temperature:

Fig. 4 represents the uptake of RR4 on to EAAC at 30, 40 and 50°C by keeping the initial dye concentration at 50 mg/L. The equilibrium sorption capacity, q_e(mg/g) of RR4 on to EAAC increases with increase of temperature from 30 to 50°C. The amount of RR4 uptake increases from 93.88 mg/g to 95.92 mg/g while increasing the temperature from 30 to 50 °C, which indicates that the sorption of RR4 by EAAC is an endothermic process.

Kinetics of adsorption:

Kinetic models are useful for the design and optimization of effluent-treatment process. In order to investigate the mechanism of RR4 adsorption by EAAC the following three kinetic models were considered.

i. Pseudo first-order kinetic model :

The pseudo first-order kinetic model was proposed by Lagergren[20].

The integrated form of the model is

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (1)$$

Where,

q_e is the amount of dye adsorbed at equilibrium (mg/g),

q_t is the amount of dye adsorbed at time t (mg/g),

k_1 is the first-order rate constant (min $^{-1}$) and t is time (min).

Hence, a linear trace is expected between the two parameters, $\log(q_e\text{-}q_t)$ and t, provided the adsorption follows first order kinetics. The values of k_1 and q_e can be determined from the slope and intercept.

The results of first order kinetics at various initial concentrations and at various temperatures are given in table 2 (figure not shown). The pseudo first-order rate constant increases with increase of temperature. An irregular trend was noticed while increasing the concentration, which may be due to poor fit of the data with the pseudo first-order kinetic model. Large deviation noticed between the experimental q_e(exp) and calculated q_e(cal) values. Hence, the adsorption of RR4 onto EAAC not obeys the Lagergren pseudo first-order kinetic model.

ii. Pseudo second-order kinetics:

The adsorption may also be described by pseudo second-order kinetic model[21] if the adsorption does not follows the first order kinetics. The linearized form of the pseudo second-order model is -

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \qquad (2)$$

Where,
k_2 is the second-order rate constant (g/mg min).
A plot of t/q_t and t should give a linear relationship if the adsorption follows second order. q_e and k_2 can be calculated from the slope and intercept of the plot.
The pseudo second-order plot at various initial dye concentrations and temperatures are given in fig. 5 and 6 and results are given in table 2. The pseudo second-order rate constant, k_2 decreases from 9.03 x 10^{-4} to 12.74 x 10^{-4} g/mg min. when the temperature increased from 30 to 50°C. q_e(cal) and q_e(exp) are well in close at various concentrations as well at various temperatures of study. The adsorption of RR4 by EAAC is explained well by pseudo second-order kinetics with a very high correlation coefficient.

iii. Intra particle diffusion model:

In the batch mode adsorption process, initial adsorption occurs on the surface of the adsorbent. In addition, there is a possibility of the adsorbate to diffuse into the interior pores of the adsorbent. Weber and morris[22] suggested the following kinetic model to investigate the adsorption is intra-particle diffusion or not. According to this theory

$$q_t = k_d \,.\, t^{1/2} \qquad (3)$$

Where, k_d is the rate constant of the above model and is analyzed by plotting q_t vs $t^{1/2}$
A plot of q_t versus $t^{1/2}$ is given in the fig. 7. The linear portion of the plot for wide range of contact time between adsorbent and adsorbate does not pass through the origin. This deviation from the origin or near saturation may due to the variation of mass transfer in the initial and final stages of adsorption[23&24]. Such a deviation from the origin indicates that pore diffusion is the only controlling step[24]. From the fig. 7 we could see that there are two different regions before the equilibrium. The initial pore diffusion due to external mass transfer (r^2 = 0.9660 to 0.9979) followed by the intra particle diffusion (r^2 is in the range 0.9824 of to 0.9961). The high correlation coefficient in the first region proves that pore diffusion play a major role for the adsorption RR4 on to EAAC.

Adsorption isotherm:

The equilibrium existence of adsorbate between the liquid and solid phase is well described by adsorption isotherms. Experimental isotherm data collected at different temperatures were fitted in Langmuir, Freundlich and Dubinin-Raduskevich adsorption isotherm models.

1. Langmuir model

The Langmuir model[25] was originally developed to describe the adsorption of gas on to solid surface. It suggests the formation of monolayer adsorption and also the surface is energetically homogeneous. The Langmuir isotherm can be expressed as;

$$q_e = \frac{Q_0 . b_L . C_e}{(1 + b_L . C_e)} \qquad (4)$$

Linear form of the rearranged Langmuir model is

$$\frac{C_e}{q_e} = \frac{1}{Q_0 . b_L} + \frac{C_e}{Q_0} \qquad (5)$$

Where, q_e is the amount of dye adsorbed at equilibrium (mg/g), C_e is the dye concentration in solution at equilibrium (mg/L), Q_0 is a constant related to adsorption capacity (mg/g) and b_L is Langmuir constant related to energy of adsorption L/mg.

The constants Q_0 and b_L can be calculated from the slope and intercept of the plot of C_e/q_e vs C_e.
The results of Langmuir plot (fig. 8) are given in table 3. Langmuir adsorption capacity increases from 222.22 to 227.27 mg/g while increasing the temperature from 30 to 50°C. The high adsorption capacity is

due to high surface area and porosity of the adsorbent. Comparable results were reported for the adsorption of reactive red 23 by waste wood pallets[26].

The essential characteristics of Langmuir isotherm can be expressed by dimensionless constant called equilibrium parameter, R_L[27].

$R_L = 1/(1+b_L.C_0)$ (6)

Where, b_L is the Langmuir constant and C_0 is the initial concentration (mg/L). The value of R_L indicates the nature of the adsorption process as given below

$R_L > 1$ Unfavourable
$R_L = 1$ Linear
$0 < R_L < 1$ Favourable
$R_L = 0$ Irreversible

The R_L value ranges between zero and one for the range of temperatures studied indicate that the adsorption is favourable.

2 . Freundlich model

It is a most popular model for a single solute system, based on the distribution of solute between the solid phase and aqueous phase at equilibrium[28]. The Freundlich equation is expressed as;

$$q_e = k_f C_e^{1/n} \qquad (7)$$

Where, K_f is the measure of adsorption capacity and n is the adsorption intensity

Linear form of Freundlich equation is

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad (8)$$

A plot of log q_e vs log C_e gives a linear trace with a slope of 1/n and intercept of log k_f.

When 1/n is >1.0, the change in adsorbed concentration is greater than the change in the solute concentration.

The Freundlich model is suitable for use with heterogeneous surface but can describe the adsorption data over a restricted range only. It is often found that when the Freundlich equation is fitted to data at higher and intermediate concentrations, since the Freundlich equation does not approach Henry's Law of ideal dilute solutions.

The Freundlich parameters k_f and n calculated by the plot of log q_e versus C_e (figure not shown) are given in table 3. The Freundlich constant, k_f increases with increase in temperature. The value of n is greater than 1.0 indicating the adsorption RR4 on to EAAC is favourable. Similar results were reported for the adsorption of RB5 dye on to chitosan[29]. Langmuir model is more appropriate to explain the nature of adsorption with correlation coefficient of 0.9969 to 0.9994 rather Freundlich model shows poor fit (r^2 = 0.9299 to 0.9530).

3 .Dubinin-Radushkevich isotherm

The isotherm proposed by Dubinin[30] has the following form

$$q_e = q_D . e^{-B\varepsilon^2} \qquad (9)$$

Linear form of Dubinin-Radushkevich isotherm is

$\ln q_e = \ln q_D - B\varepsilon^2$ (10)

Where,

q_D is the theoretical saturation capacity (mg/g)

B is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2) and

ε is polanyi potential which is related to the equilibrium as follows;

$\varepsilon = RT \ln(1+1/C_e)$ (11)

Where, R is the Universal gas constant (8.314 J/mol K)

A plot of ln q_e vs ε^2 gives a linear trace and the constants q_D and B calculated from the slope and intercept respectively. The mean free energy of adsorption E calculated from B using the following equation

$$E = 1/ (2B)^{1/2} \qquad (12)$$

Based on this energy of activation one can predict whether an adsorption is physisorption or chemisorption. If the energy of activation is <8 KJ/mol, the adsorption is physisorption and if the energy of activation is 8 – 16 KJ/mol, the adsorption is chemisorption in nature[31]. The activation energy of adsorption increases with temperature. At 30 and 40°C, E is <8, hence, the adsorption is physisorption in nature. At 50°C, E is 10 kJ/mol indicates the adsorption is chemisorption in nature(normally chemisorption will occur at high temperature).

Thermodynamics of adsorption:

Thermodynamic parameters like ΔH°, ΔS° and ΔG° were measured based on van't Hoff's plot.

$$\ln k_L = \frac{\Delta S^O}{R} - \frac{\Delta H^O}{R}\frac{1}{T} \qquad (13)$$

Where,

k_L is the Langmuir equilibrium constant,

ΔH° and ΔS° are the standard enthalpy and entropy changes of adsorption respectively.

The values of ΔH° and ΔS° are calculated from the slopes and intercepts of the linear plot of ln k_L Vs 1/T (figure not shown) and the values are given in table 4. The free energy of specific adsorption ΔG° (kJ/mol) is calculated from the following expression

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (14)$$

The mean adsorption enthalpy ΔH° was found to be 2.800 kJ/mol, indicates that the bonding between RR4 and EAAC surface is very weak. The positive enthalpy proves that the adsorption process is endothermic in nature. The ΔG° decreased from -3.225 kJ/mol to -3.622 kJ/mol with increase in temperature from 30 to 50 °C. Negative value of ΔG° indicates that the adsorption process is favourable and spontaneous in nature.

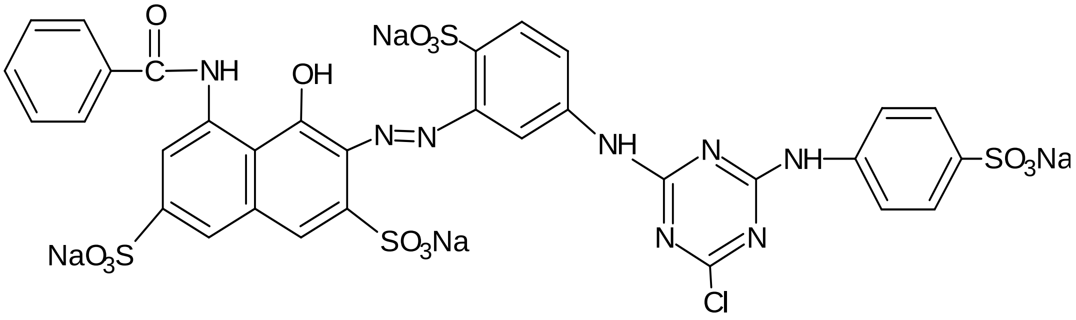

Fig. 1 Structure of Reactive Red 4 (C.I No., 18105; F.W., 995.23; λmax., 517 nm)

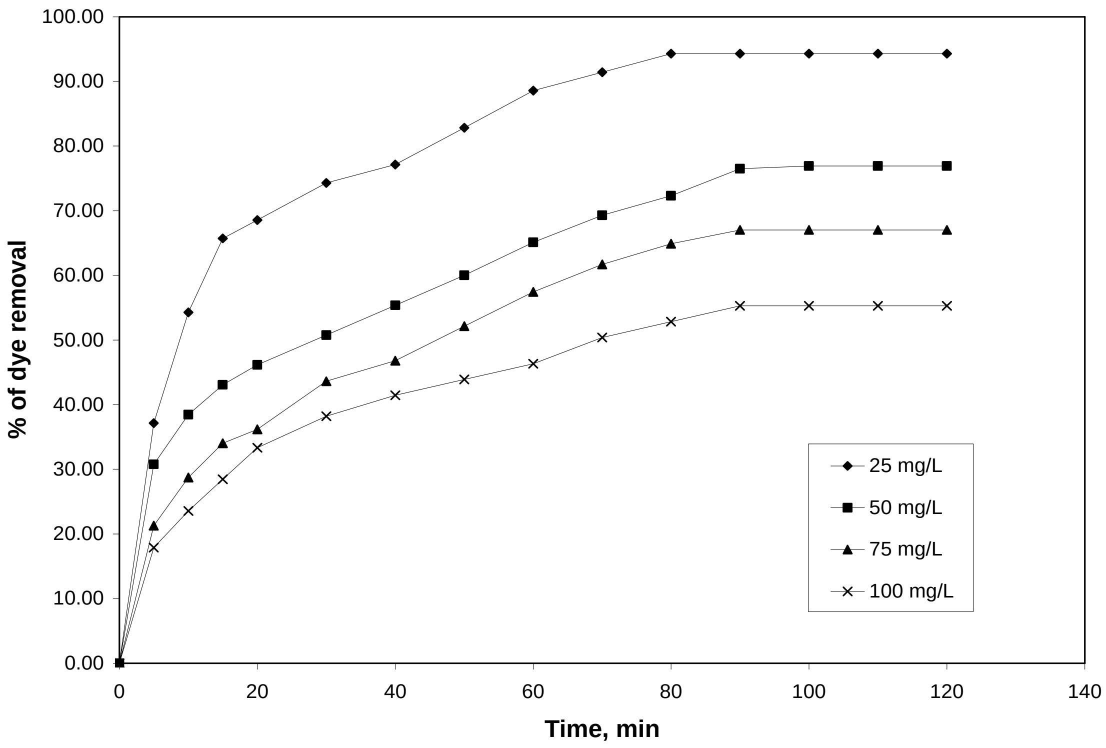

Fig. 2 Effect of agitation time for the adsorption RR4 on to EAAC at 30°C (pH, 8.50; adsorbent dosage, 100 mg; adsorbent size, 300 to 850 µm

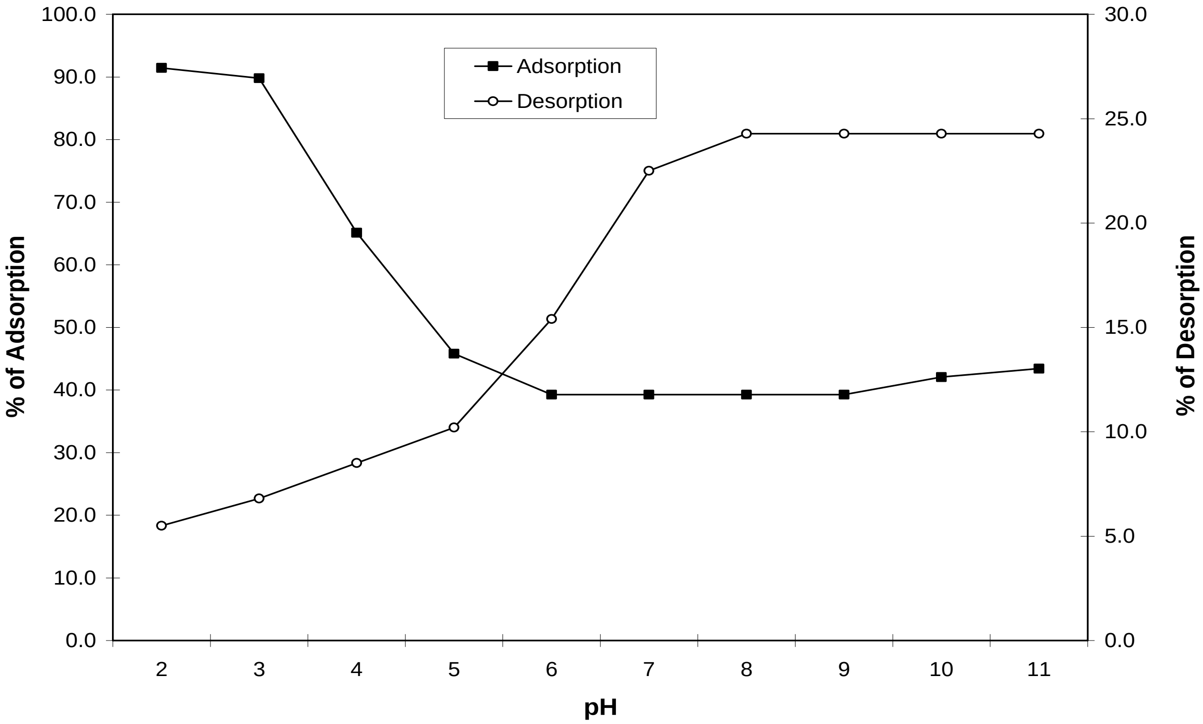

Fig. 3 Influence of pH on the adsorption & desorption of RR4 on to EAAC at 30°C

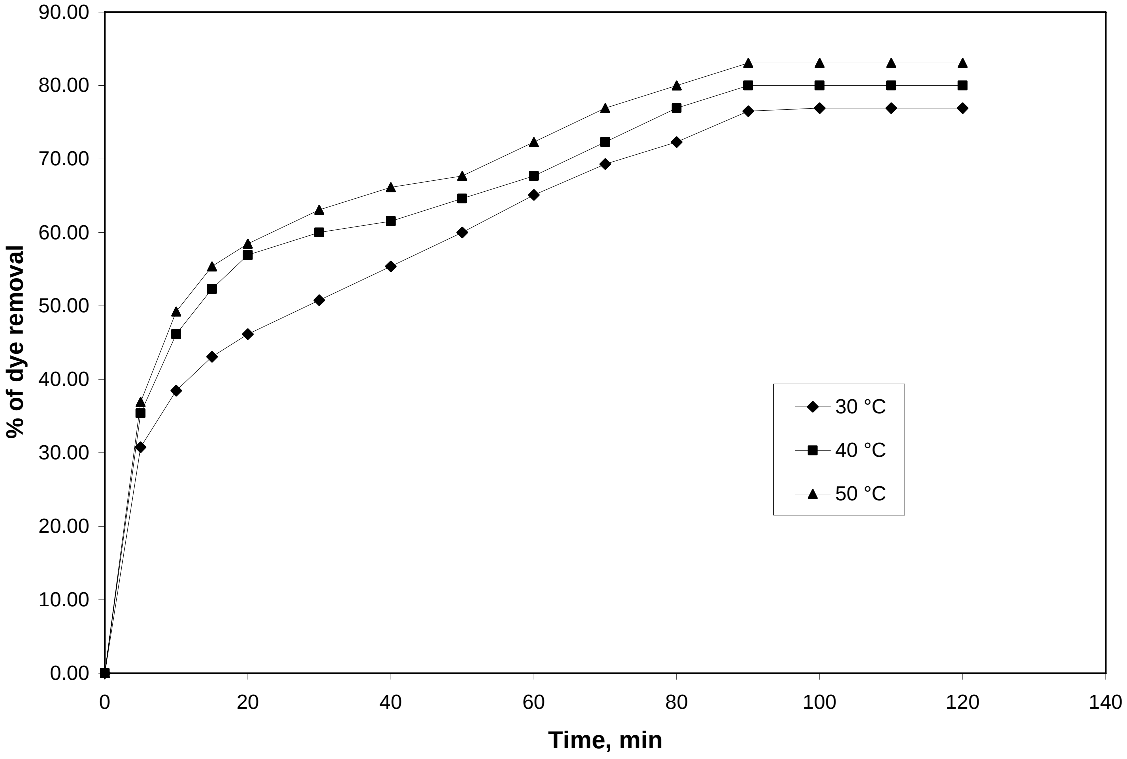

Fig. 4 Effect of temperature for the adsorption RR4 on to EAAC (initial concentration, 50 mg/L; pH, 8.50; adsorbent dosage, 100 mg; adsorbent size, 300 to 850 µm)

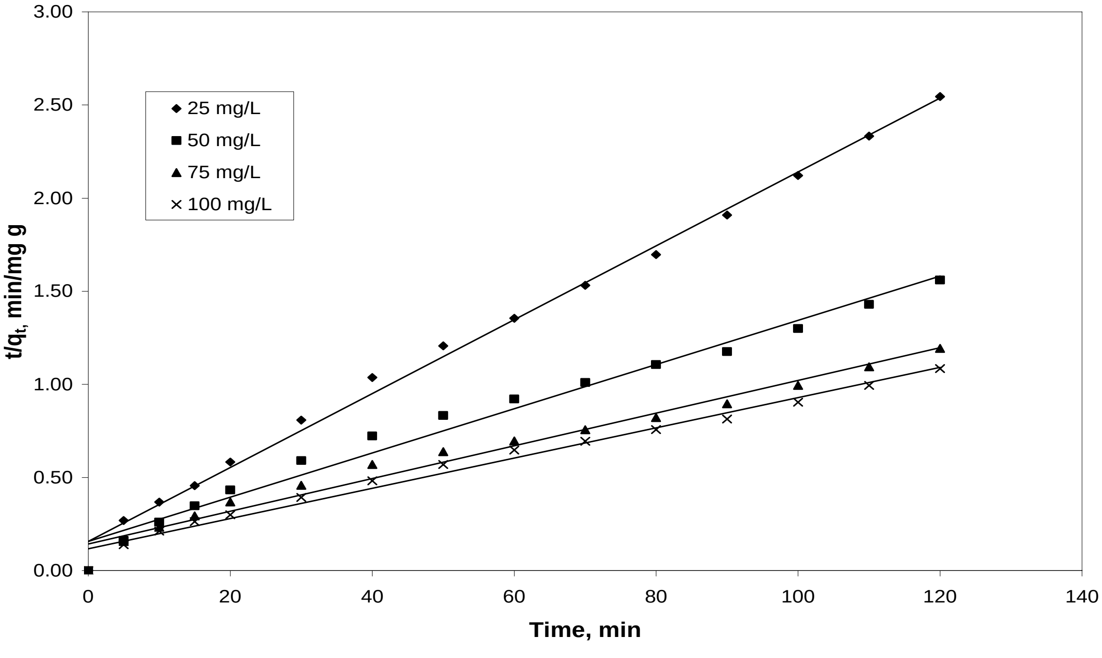

Fig. 5 Pseudo second order plot for the adsorption RR4 on to EAAC at 30°C (pH, 8.50; adsorbent dosage, 100 mg; adsorbent size, 300 to 850 µm)

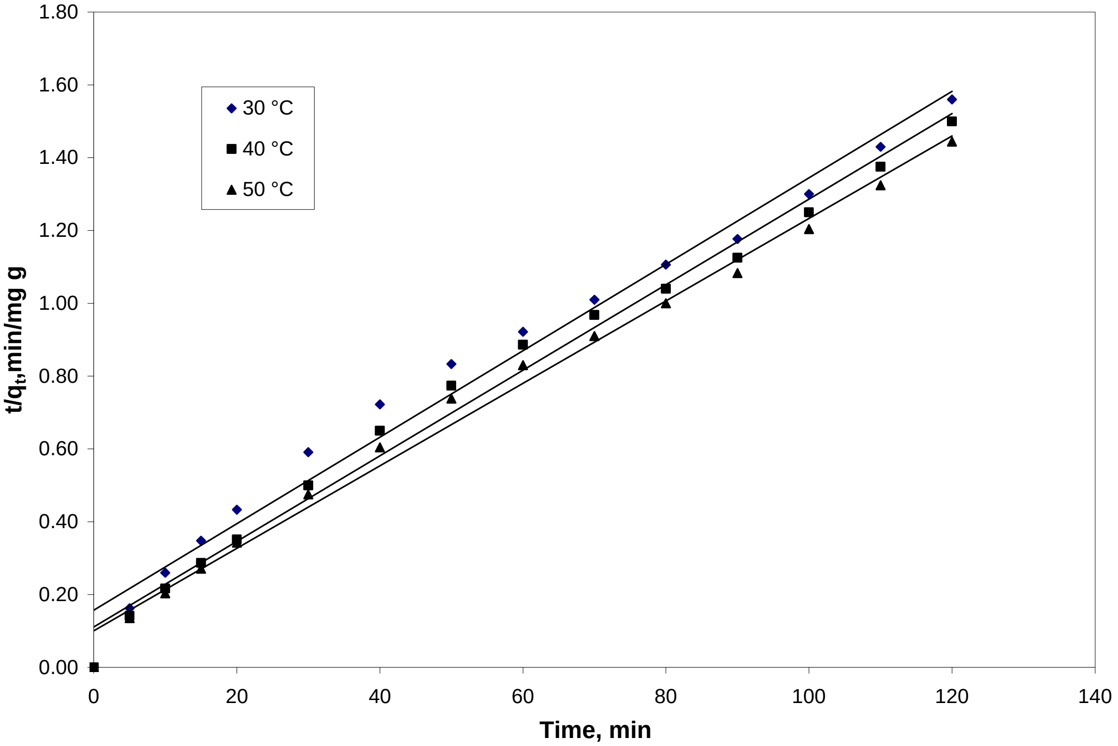

Fig. 6 Pseudo second order plot for the adsorption RR4 on to EAAC at various temperatures (pH, 8.50; adsorbent dosage, 100 mg; adsorbent size, 300 to 850 μm)

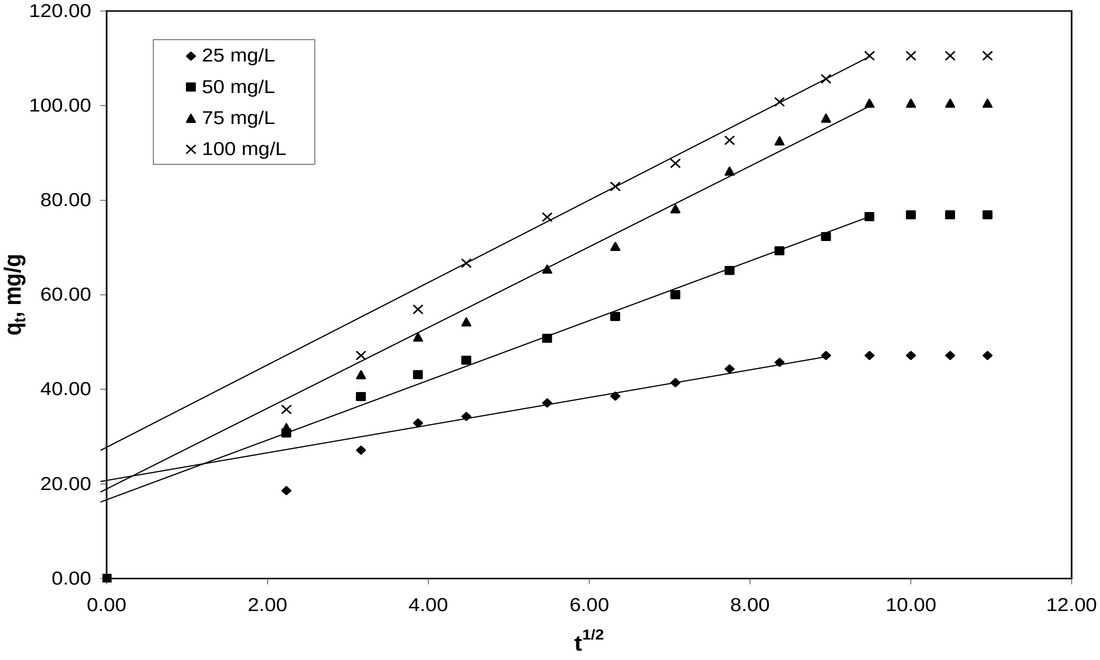

Fig. 7 Intra particle diffusion plot for the adsorption RR4 on to EAAC at 30°C (pH, 8.50; adsorbent dosage, 100 mg; adsorbent size, 300 to 850 μm)

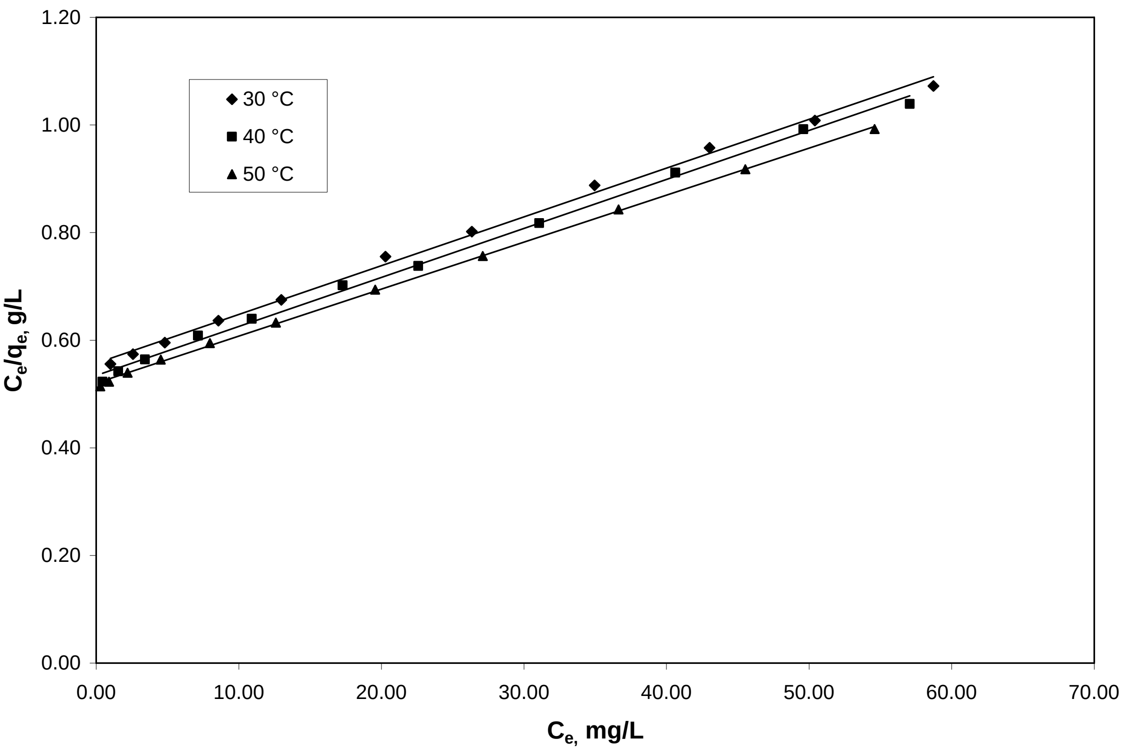

Fig. 8 Langmuir isotherm for the adsorption RR4 on to EAAC at various temperatures (pH, 8.50; agitation time, 180 min; adsorbent dosage, 100 mg; adsorbent size, 300 to 850 µm)

Table 1: Properties of EAAC

S.No	Properties	Values
1	Bulk density, g/mL	0.48
2	Porosity, %	55.32
3	pH_{ZPC}	6.82
4	Surface area (BET), m^2/g	918
5	Methylene Blue Value, mg/g	375
6	Iodine Number, mg/g	955

Positive values of ΔS° suggested good affinity of the dye towards the adsorbent and the adsorption is spontaneous in nature[32].

Desorption Studies:

Desorption increases with increase of pH from 2 to 8 and there is no considerable change in desorption above pH 8. As shown in fig. 3, the maximum percentage of desorption observed at pH 8 was 24.28 %.

CONCLUSIONS

Activated carbon for the adsorption of dye from its aqueous solution can be conveniently and economically prepared from Euphorbia antiquorum L wood by H_3PO_4 impregnation followed by carbonization. The uptake of dye increased from 47.14 mg/g to 110.57 mg/g while increasing the initial dye concentration from 25 mg/L to 100 mg/L. A maximum of 94.29 % of dye was removed at 25 mg/L of initial dye concentration. The adsorption of RR4 increases from 93.88 mg/g to 95.92 mg/g while increasing the temperature from 30 to 50°C, which indicates that the sorption process is endothermic in nature. The pseudo second-order kinetic model describes the adsorption much better with very high correlation coefficient. The role of pore diffusion for the adsorption is well explained with the help of Intra particle diffusion model. The Langmuir adsorption capacity increases from 222.22 mg/g to 227.27 mg/g with increasing the temperature from 30 to 50°C. Langmuir model is more appropriate to explain the nature of adsorption with high correlation coefficient. The positive $\Delta H°$ value suggests that the adsorption is endothermic in nature.

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Table-3: Results of various isotherm plots for the adsorption of RR4 on to EAAC

Temperature °C	**30**	**40**	**50**
Langmuir			
Q_0 (mg/g)	222.22	217.39	227.27
b (L/mg)	0.0162	0.0172	0.0169
k_L	3.589	3.743	3.845
r^2	0.9969	0.9976	0.9994
Freundlich			
n	2.5445	2.9824	3.2310
k_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	46.441	61.688	76.173
r^2	0.9410	0.9530	0.9299
Dubinin-Raduskevich			
q_D (mg/g)	1.00	1.00	1.00
E (KJ/mol)	3.333	5.773	10.000
r^2	0.8752	0.7789	0.7746

Table 4: Thermodynamical parameters for the adsorption RR4 onto EAAC

Temperature, °C	**ΔH° kJ/mol**	**ΔS° J/K/mol**	**ΔG° kJ/mol**
30	2.800	19.886	- 3.225
40			- 3.423
50			- 3.622

Table-2: Calculated kinetic parameters for the adsorption of RR4 onto EAAC at various initial concentrations

Concentration					Temperature		
(mg/L)	25	50	75	100	°C 30	40	50
First order kinetics							
k_1 (min $^{-1}$)	0.0424	0.0295	0.0359	0.0329	0.0.274	0.0304	0.0325
$q_e$cal (mg/g)	35.65	60.63	97.76	95.87	58.19	54.78	57.07
$q_e$exp.(mg/g)	47.14	76.92	100.53	110.57	76.92	80.00	83.08
r^2	0.9567	0.9626	0.9409	0.9630	0.9570	0.9064	0.9327
Second order kinetics							
k_2 x 10^{-4} (g/mg min)	25.05	9.025	5.419	5.579	9.03	12.56	12.74
h	6.3898	6.3735	6.9979	8.5034	6.3735	9.0253	9.9800
$q_e$cal(mg/g)	50.51	84.03	113.64	123.46	84.03	84.75	88.50
r^2	0.9951	0.9816	0.9778	0.9840	0.9816	0.9887	0.9912
Intra particle diffusion model							
k_{id} (mg/g min)	2.741	6.825	10.539	13.345	6.471	5.224	5.168
r^2	0.9670	0.9979	0.9907	0.9906	0.9979	0.9593	0.9740