Mechanistic study of dye adsorption on to a novel non-conventional low-cost adsorbent

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ABSTRACT

*Activated carbons are known for their high adsorption capacities. In this study, an activated carbon with high adsorptive capacity was prepared from **Euphorbia antiquorum L** wood. Impregnation with H_3PO_4 solution followed by activation at 800° C results an activated carbon with a surface area of 918 m^2/g and more developed porosity. The prepared adsorbent was used for the adsorptive removal of four categories of dyes. Various kinetic models were applied for the analysis of the adsorption process and pseudo second order model fits well for the adsorption system. Based on the results of kinetic models, Intra particle diffusion model and energy of adsorption, a four stage pore diffusion mechanism was illustrated.*

Keywords: Activated carbon, Adsorption, Dyes, Kinetics.

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INTRODUCTION

Water pollution due to the discharge of dyeing industry effluent is a major concern now a days. 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 was proved an efficient and economical process to treat dyeing industry effluent. In recent years, many natural waste materials have been investigated to assess their suitability as an adsorbent. Exploration of a good low cost adsorbent may contribute to the sustainability of the environment and also offer promising benefits for commercial purpose in future.

Recently some agricultural wastes and forestry products have been developed as adsorbents. Activated carbon prepared from different materials like agricultural wastes[1,2], oil palm waste[3], babool seed[4], eucalyptus bark[5], pine saw dust[6], pistachio shells[7], etc.,

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In this investigation an attempt was made to prepare an activated carbon from ***Euphorbia antiquorum* L** wood by H_3PO_4 activation method (EAC). About the precursor plant, it is wide spread throughout peninsular India, it can be found growing in the regions of an altitude of 800 m from the sea level. It is one of the largest armed trees in the Euphoria's with an average height of 5-7 m, it has been known to attain gigantic proportions if left undisturbed. The plant does not have any economical importance.

MATERIALS AND METHODS

2.1 Adsorbent
The precursor wood was cut into pieces of 2 - 3 cm size, dried in sunlight for 10 days. The dried material soaked in a boiling solution of 10 % H_3PO_4 for 1 hour and kept at room temperature for 24 hours. After 24 hours, the wood material was separated, air dried and carbonized in muffle furnace at 400°C for 20 minutes. The carbonized material was powdered, activated in a muffle furnace at 800°C for a period of 10 minutes and used for further adsorption studies.

2.2 Adsorbate
All the chemicals used are Analytical (AR) grade. The details of the selected dyes are given in Table 1. The batch mode adsorption experiments were carried out in 250 ml tight lid reagent bottle (Borosil-R) by agitating 100 mg of adsorbent with 200 ml of the aqueous dye solution of desired concentration. The contents of the flasks were agitated by placing them in a temperature controlled orbital shaker (REMI Make). The mixture was withdrawn at specified interval and then centrifuged using electrical centrifuge (Universal make) at 5000 rpm for 10 minutes and un-adsorbed supernatant liquid was analyzed for the residual dye concentration using Bio UV-visible spectrometer (Elico make : BL-198) by fixing the λmax as the absorption wavelength.

Table 1 - Details of dyes selected for the adsorption studies

S.No	Selected dye	Molecular formula	Mol. Wt.	C.I. Number	λmax
1	Acid Blue 92	$C_{26}H_{16}N_3Na_3O_{10}S_3$	695.59	13390	571
2	Basic Red 29	$C_{19}H_{17}ClN_4S$	368.88	11460	511
3	Reactive Red 4	$C_{32}H_{19}ClN_8Na_4O_{14}S_4$	995.23	18105	517
4	Direct Blue 53	$C_{34}H_{24}N_6Na_4O_{14}S_4$	960.82	23860	611

a) Acid Blue 92

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b) Basic Red 29

c)   Reactive Red 4

d) Direct Blue 53
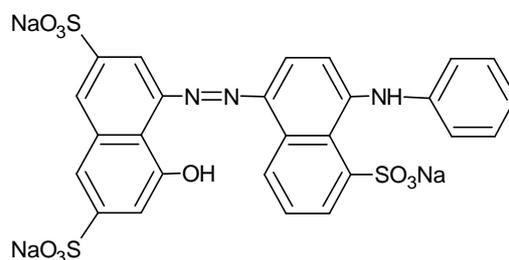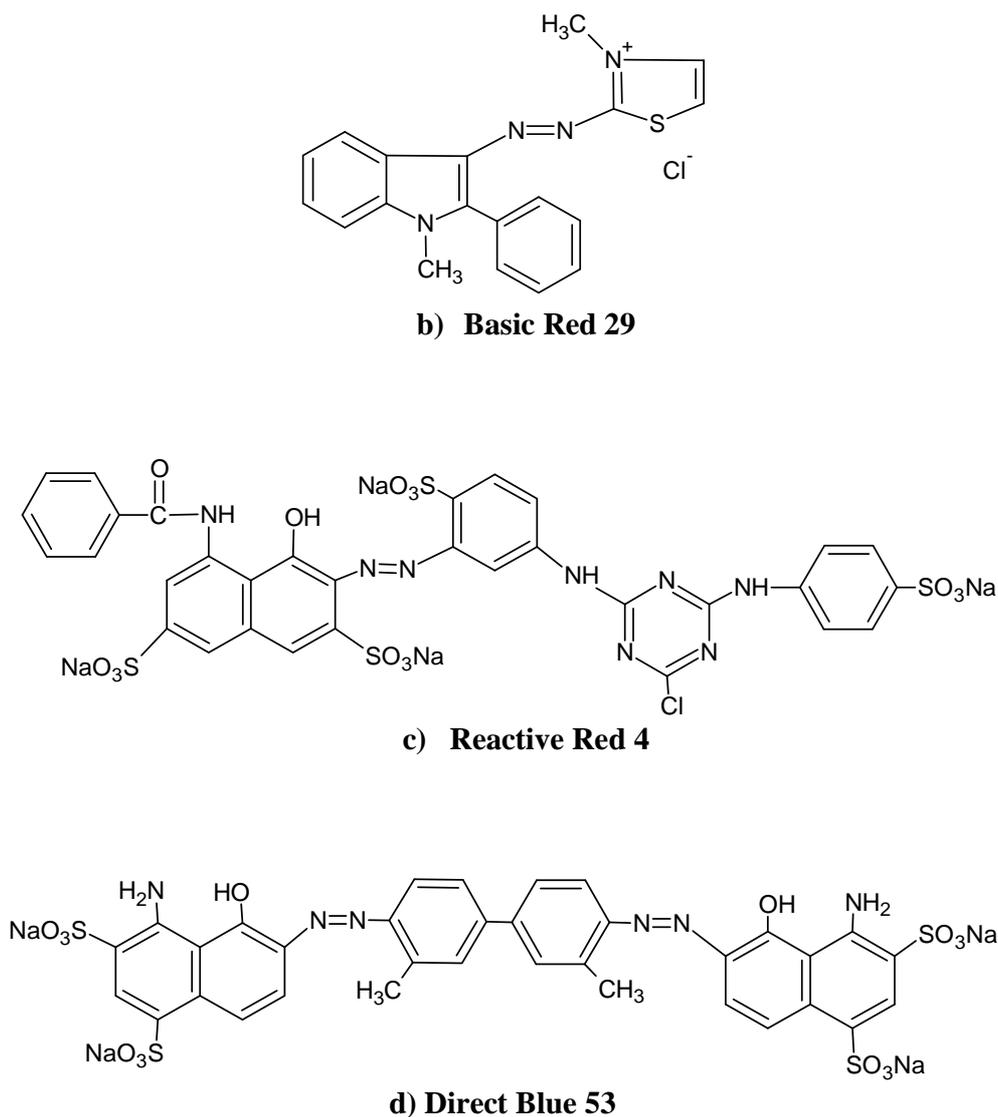
Fig. 1 - Structure of the dyes selected for adsorption studies

2.3 Kinetic Models of Adsorption
Many kinetic models have been proposed by various researchers in the past to elucidate the mechanism of solute adsorption. The rate and mechanism of adsorption is controlled by various factors like physical and/or chemical properties of adsorbent, mass transfer process, etc.

2.3.1 Pseudo First Order Kinetic Model
Lagergren[8] suggested a first order equation for the sorption of liquid/solid system based on solid adsorption capacity. The Lagergren rate equation is the most widely used adsorption rate equation for the adsorption of adsorbate from aqueous solution.

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

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).

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 calculated from the slope and intercept of the plot are given in Table 2 (Plots are not shown).

2.3.2 Pseudo Second Order Kinetics

The adsorption may also be described by pseudo second order kinetics[9], if the adsorption does not follow the first order kinetics. The second order kinetic model is represented as:

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

Where,

k_2 is the second-order rate constant (g/mg min) and t is time (min)
and q_e is the equilibrium adsorption capacity (mg/g).

A plot of "t/q_t" and "t" should give a linear relationship if the adsorption follows second order. The values of q_e and k_2 calculated from the slope and intercept of the plot are given in Table 2 (Plots are not shown).

2.3.3 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[10] suggested the following kinetic model to investigate whether the adsorption is intra particle diffusion or not. According to this theory,

$$q_t = k_d \cdot t^{\frac{1}{2}} \qquad \text{…(3)}$$

where, k_d is the intra particle diffusion rate constant and is calculated by plotting "q_t" vs "$t^{\frac{1}{2}}$" is given in Table 2 (Plots are not shown).

RESULTS AND DISCUSSION

Detailed results of various kinetic and isotherm model for the adsorption of the four selected dyes were published in our earlier publications [11-14]. This paper analyzes the possible mechanism of adsorption based on the summarized results (Table 2)

In adsorption process of dye on the solid surface, the dye species migrate towards the surface of the adsorbent. This type of migration proceeds till the existence of concentration gradient of the adsorbate species in the bulk of the solution to the surface of the adsorbent. Once equilibrium is attained, the migration of the solute species from the solution stops. At this situation, it is possible to measure the magnitude of distribution of the solute species between the liquid and solid phases. This kind of distribution is a measure of the efficiency of the chosen adsorbent for the adsorption of particular solute.

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When a powdered solid adsorbent is in contact with a solution containing dyes, the dyes first migrate from the bulk of the solution to the surface of the liquid film. This surface exerts a diffusion barrier. This barrier may be very significant or less significant. The involvement of a significant quantum of diffusion barrier indicates the dominant role taken up by the film diffusion in the adsorption process. Furthermore, the rate of an adsorption process is controlled either by external diffusion, internal diffusion or by both types of diffusions.

Table 2 - Results of various kinetic models & enthalpy of adsorption

Dye	Parameter		1st Order		2nd Order		ID Model		ΔH° (KJ/mol)
			k_1 (min^{-1})	r^2	k_2 x 10^{-4} (g/mg/min)	r^2	k_{id} (mg/g/min$^{1/2}$)	r^2	
Acid Bule 92	IC, mg/L	25	0.0454	0.986	8.70	0.992	2.03	0.879	1.693
		50	0.0339	0.958	2.79	0.993	6.16	0.977	
		75	0.0325	0.988	1.55	0.987	9.63	0.996	
		100	0.0339	0.981	0.96	0.976	13.2	0.993	
	Temp., °C	30	0.0339	0.984	2.79	0.991	6.66	0.972	
		45	0.0366	0.991	4.36	0.999	6.31	0.999	
		60	0.0364	0.984	6.00	0.999	5.23	0.999	
Basic Red 29	IC, mg/L	25	0.0465	0.968	23.64	0.993	2.741	0.981	1.589
		50	0.0444	0.991	10.31	0.989	6.825	0.977	
		75	0.0451	0.969	6.078	0.984	10.539	0.985	
		100	0.0355	0.979	3.741	0.972	13.345	0.999	
	Temp., °C	30	0.0444	0.991	10.31	0.989	6.825	0.977	
		45	0.0401	0.976	14.09	0.996	5.281	0.992	
		60	0.0472	0.950	18.04	0.997	4.973	0.983	
Reactive Red 4	IC, mg/L	25	0.0424	0.957	25.05	0.995	2.741	0.967	2.800
		50	0.0295	0.963	9.03	0.982	6.825	0.998	
		75	0.0359	0.941	5.419	0.978	10.539	0.991	
		100	0.0329	0.963	5.579	0.984	13.345	0.991	
	Temp., °C	30	0.0295	0.963	9.03	0.982	6.825	0.998	
		45	0.0304	0.906	12.56	0.989	5.224	0.959	
		60	0.0325	0.933	12.74	0.991	5.168	0.974	
Direct Blue 53	IC, mg/L	25	0.0679	0.995	41	0.997	2.441	0.999	2.555
		50	0.0507	0.982	20.16	0.996	4.319	0.954	
		75	0.0509	0.991	14.17	0.995	6.585	0.977	
		100	0.056	0.970	9.042	0.998	10.502	0.968	
	Temp., °C	30	0.0504	0.936	20.93	0.999	3.188	0.974	
		45	0.0469	0.922	28.63	0.997	3.189	0.989	
		60	0.0392	0.970	25.54	0.997	4.122	0.996	

As high correlation co-efficient was observed for pseudo first order and pseudo second order kinetic models, it was impossible to conclude which adsorption mechanism actually occurred and which was responsible for the specific adsorption.

The selected adsorbent is a mesoporous, hence the mesoporous carbon can accommodate multilayer dye adsorption due to its high pore width when compared to the size of dye molecules [13] (width of mesopore is 2 to 10 times more than the width of dye molecules). Based on the results of Intra particle diffusion model, all the four selected dyes shows high correlation co-efficient in the first region of the plot. This behaviour substantiates that pore diffusion plays a

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significant role in the adsorption. A simple adsorption mechanism to understand the kinetics and isotherms of the dye adsorption onto EAC is proposed as follows:

Ionic adsorption mechanism related to chemisorption is not considered because the energy of adsorption and the $\Delta H°$ value for all the four selected dyes very strongly substantiates the physisorption mechanism. Firstly, dye particles diffuse into the mesopores of EAC, and are then adsorbed in the mesopores then micropores and finally pore interior. The mesopore diameter shrinks and the pore length becomes short because of the dye adsorption. The narrow mesopore hinders the dye diffusion into the pore interior and micropores. Dye particles are adsorbed on EAC in the form of a multilayer not a monolayer. This assumption is needed because the second layer of dye is adsorbed onto the first layer of dye. Therefore, adsorption rate is not a first order.
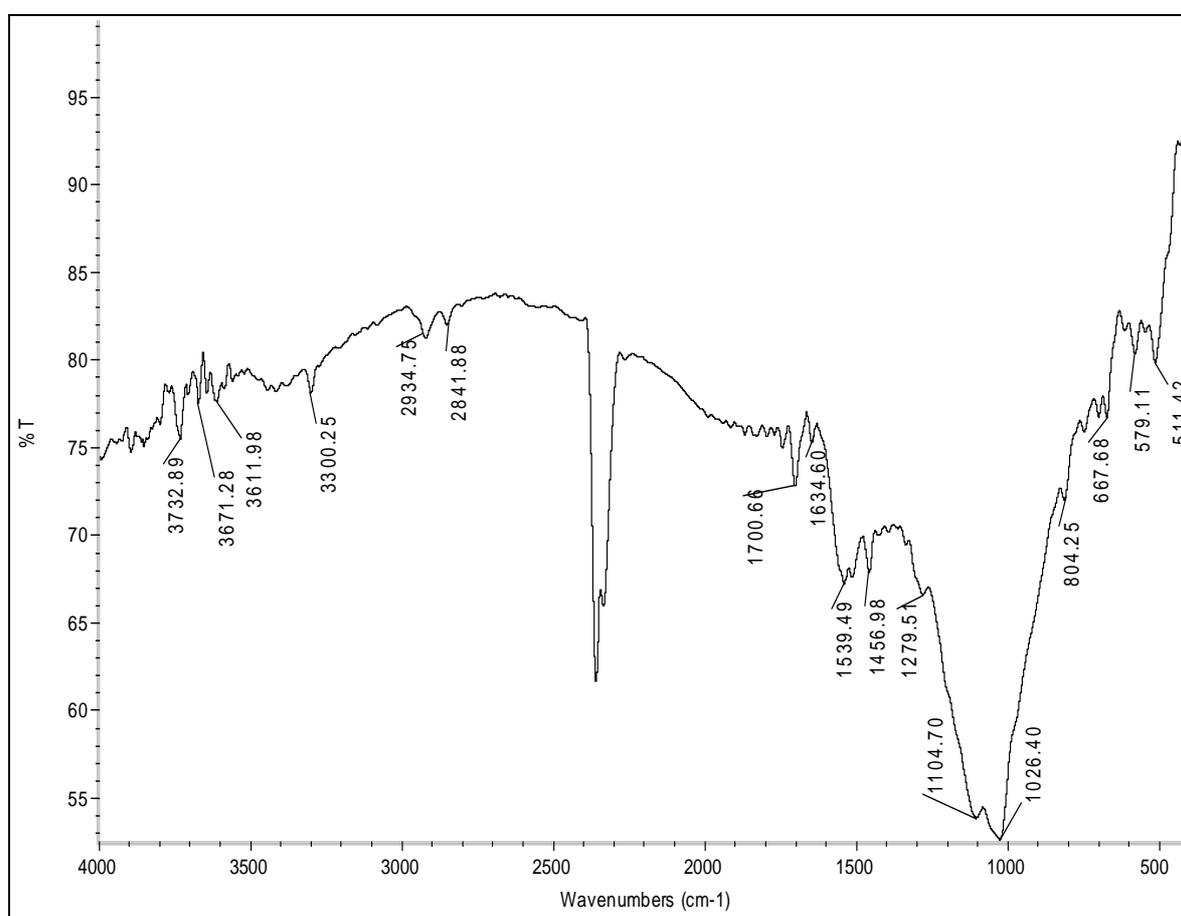
Fig. 2 – FTIR Spectra of EAC

The adsorption sites are heterogeneous. It is known that the surface chemical structures of EAC are not homogeneous. The FT-IR spectra of EAC (Figure 2) shows the presence of various functionalities which supports the surface heterogeneity. Finally figure 3 illustrates the possible four stage mechanism of dye adsorption by EAC.

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Stage I: Diffusion of dye from bulk
of the solution to adsorbent

Stage II: Pore Diffusion

Stage IV: Multilayer adsorption of
dye molecules

Stage III: Monolayer adsorption of
dye molecules
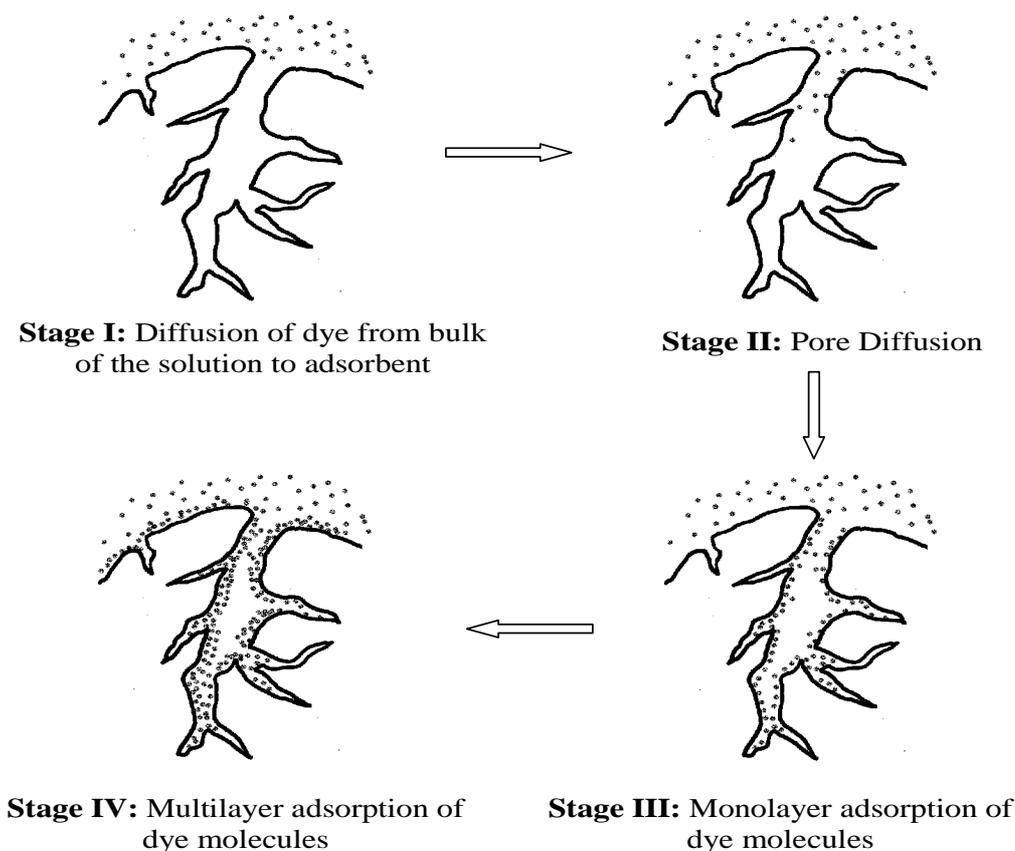
Fig. 3 – Proposed four stage mechanism of dye adsorption

CONCLUSION

The precursor *E. antiquorum* **L,** a worthless (waste) plant was conveniently and economically used for the preparation of activated carbon. The selected adsorbent is highly mesoporous, can accommodate multilayer dye adsorption due to its high pore width. The pore diffusion plays a significant role in the adsorption than film diffusion. Based all the results four stage dye adsorption mechanism was arrived.

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