

Equilibrium Uptake and Sorption Dynamics for the Removal of Acid Dyes Using *Euphorbia tirucalli* Wood

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Abstract: The capability of activated carbon from *Euphorbia tirucalli* L wood for the adsorption of acid dyes from aqueous solution was investigated. Batch experiments were carried out for the adsorption of Acid Blue 15 and Acid Orange 10 onto activated carbon (ETAC). The removal of acid dyes from aqueous solution using ETAC was investigated in terms of initial pH, initial concentration, contact time and temperature. The results showed that maximum adsorption occurs at pH 2-3. Isotherm and kinetic experiments were carried out on different temperatures. Adsorption kinetics was well described by the pseudo- second order kinetic model with intra particle diffusion as one of the rate determining step. Equilibrium data were well represented by Langmuir and Freundlich models. Thermodynamic parameters such as change in free energy, enthalpy and entropy were also evaluated. For AB15, enthalpy change (ΔH°) and entropy change (ΔS°) were 26.830 kJ/mole, 0.1160 kJ / K /mole respectively, and those for AO10 were 15.780 kJ/mole, 0.0180 kJ/K/mole respectively. The values of ΔG° , ΔH° and Activation Energy E_a which indicate that the adsorption of acid dyes onto ETAC were a physisorption process.

Key words: *Euphorbia tirucalli*, Acid Dyes, Isotherm models, Dye removal, Activated Carbon.

Introduction

Dyes are synthetic aromatic water soluble dispersible organic colorants, having potential application in various industries. The dyestuff usage has been increased day by day due to tremendous increase of industrialization and human desire for colour¹. Most of the dyes used in textile industries are stable to light and are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin². In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic. Furthermore, the coloured effluents reduce light penetration and potentially prevent photosynthesis³⁻⁴.

Acid dyes which comprise the largest class of dye in the colour index (CI) are anionic compounds mainly used for dyeing nitrogen containing fabrics like wool, polyamide, modified acryl and silk. Most of the

acid dyes belong to azo and anthroquinone groups and give a wide range of bright colors' on textiles and are the most difficult to remove. Physical and chemical processes have been used to treat the waste water. However these processes are costly and can not be used effectively to treat the wide range of dye waste water. Adsorption is physico- chemical waste water treatment method, which has gained popularity in the waste water treatment industry due to the high quality treated effluents are produced. Activated Carbon is the most widely used adsorbent with great success because of its high adsorption capacity. But its use is limited due to its high cost. This has led to search for cheaper substitutes. The present study is undertaken to evaluate the efficiency of a carbon as adsorbent prepared from *Euphorbia Tirucalli L* wood (ETAC) treated with H_3PO_4 for the removal of acid dyes in aqueous solution. Phosphoric acid activation is a conventional method for the preparation of active carbon from lignocellulosic material. Phosphoric acid induces important changes in the pyrolytic decomposition of lignocellulosic materials as it promotes depolymerisation, dehydration and redistribution of constituent biopolymers. Various parameters affecting adsorption onto the activated carbon such as initial dye concentration, contact time, pH and temperature were studied. The adsorption data were evaluated using Langmuir and Freundlich models.

Materials and Methods

Adsorbent

Preparation of *Euphorbia Tirucalli* Activated Carbon

Dried wood pieces of *Euphorbia Tirucalli L* were carbonized with 35% H_3PO_4 for 1½ hour in muffle furnace at 550° C and activated at 800 °C for 10 minutes. The resulting carbon was washed with plenty of water until the residual acid was removed. The dried material was ground well to fine powder and sieved⁵.

Characteristics of the Adsorbent

Physico-chemical characteristics of *Euphorbia Tirucalli* Activated Carbon (ETAC) were studied as per the standard testing methods⁶⁻⁷ and shown in Table 1. The surface structure and morphology of ETAC was carried out using Scanning Electron Microscope as shown in Figure1.

Table.1 Physico-chemical characteristics of ETAC

S.No	Properties	ETAC
1	pH	6.48
2	Conductivity, $\mu S/cm$	0.187
3	Moisture content, %	10.4
4	Ash, %	10.8
5	Volatile matter, %	22.2
6	Bulk density, g/ml	0.56
7	Specific gravity	1.18
8	Porosity, %	52.54
9	Methylene Blue value, mg/g	405
10	Iodine Number, mg/g	932
11	Surface area(BET), m^2/g	857.85

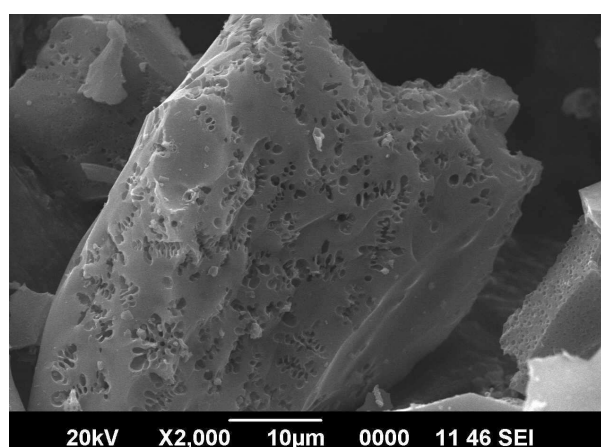


Figure 1 SEM image of ETAC

Adsorbate

The dye used in this experiment are Acid Blue 15 (M.Wt:775.95, Mol. Formula: $C_{42}H_{46}N_3NaO_6S_2$, λ_{max} : 570 nm) Acid Orange 1015 (M.Wt:452.38, Mol. Formula: $C_{16}H_{10}O_7N_2S_2Na_2$, λ_{max} : 478 nm) Nature: anionic dye used without further purification. The structure of Acid Blue15 and Acid Orange10 are shown in Figure 2a and 2b respectively.

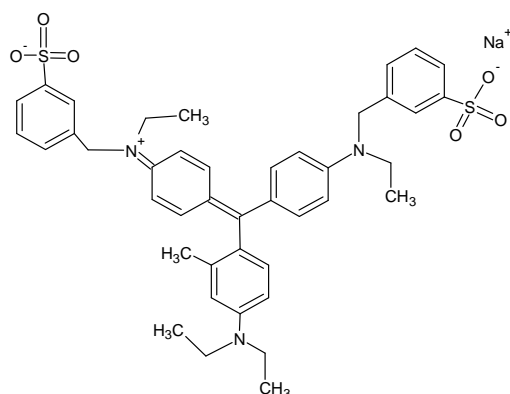


Figure 2a Structure of Acid Blue15

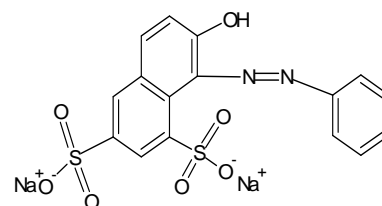


Figure 2b Structure of Acid Orange10

The stock solution was prepared by dissolving 1gm of dye in water and made up to the 1000 ml using double distilled water. The concentration of the dye solution was determined by using spectrophotometer at their respective wavelengths.

Experimental Procedure

Batch adsorption experiments were carried out by agitating 200ml of dye solution with 0.1gm of prepared activated carbon in an orbital shaker (REMI make) at different temperatures. After a predetermined contact time, the mixture was withdrawn, centrifuged and analyzed for residual dye concentration using Elico make UV- Vis spectrophotometer.

$$\% \text{ of dye removal} = (C_0 - C_e) / C_0 \times 100$$

Desorption studies were carried out using spent carbon. After desorption experiment the dye loaded carbon agitated with double distilled water at various pH and dye desorbed was estimated as stated in the adsorption studies⁸.

Result and Discussion

Effect of Initial Dye Concentration and Contact Time

The experimental results of adsorptions of Acid Dyes (AB15, AO10) on the ETAC at various initial concentrations (25, 50, 75 and 100 ppm) with contact time are shown in the Figure 3a and 3b. The percentage adsorption decreased with increase in initial dye concentration, but the actual amount of dyes adsorbed per unit mass of carbon increased with increase in dye concentration. The amount of dye adsorbed increased from 44.35 mg/g to 164.71 mg/g for AB15 and 47.22 mg/g to 171.72 mg/g for AO10, revealed that the adsorption is highly dependent on initial concentration of dye. This is because that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low. However, at high concentration the available sites of adsorption becomes lesser and hence the percentage removal of dye gets decreased with increase in initial concentration^{9- 10}. Further in Figures 3a and 3b, the curves are single and continuous, leading to saturation, suggesting the possible monolayer coverage of the dyes on the carbon surface.

Effect of pH

The pH is one of the most important factors controlling the adsorption of dye onto the adsorbent. The experiments were carried out at initial dye concentration of 50 mg/lit and at different initial pH, the results show that there was a change in percentage removal of dye with change in pH and maximum adsorption 86.2% for AB15 and 89.1% for AO10 occurs at pH=2 as shown in Figure 4. Higher pH causes a decrease in percentage of dye removal from 90 to 56% and 93.9 to 58.9% for AB15 and AO10 respectively.

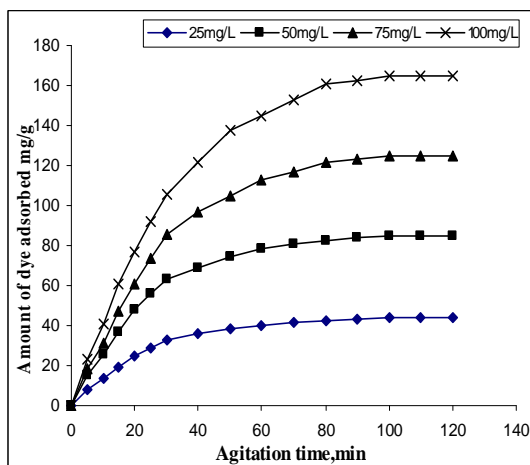


Figure 3a Effect of initial dye concentration and contact time for the adsorption of AB15

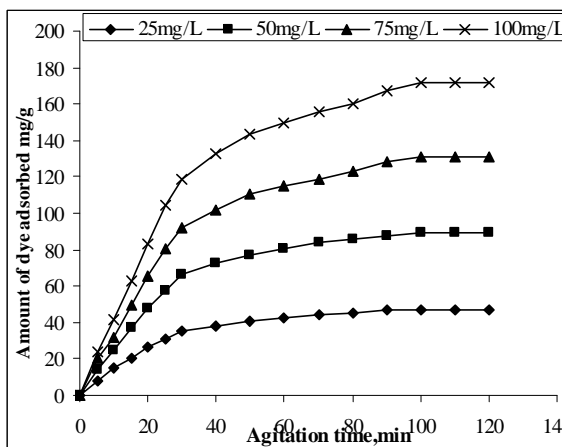


Figure 3a Effect of initial dye concentration and contact time for the adsorption of AO10

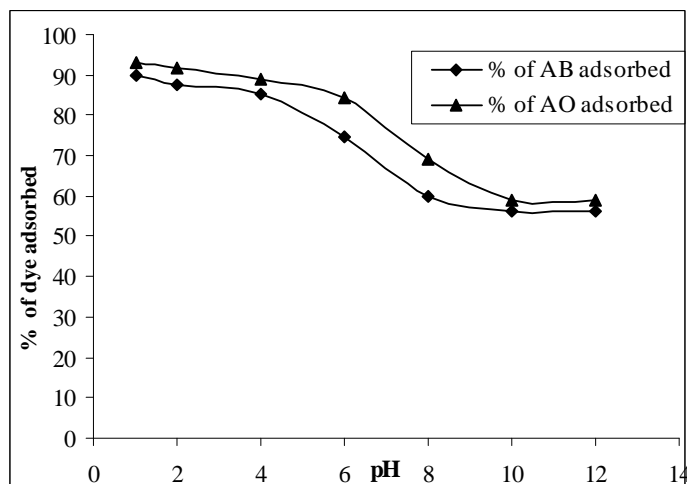


Figure 4 Effect of pH

Effect of Temperature

The adsorption capacity of the carbon increased with increase in temperature of the system from 30 - 45⁰C. The increase in the equilibrium adsorption capacity of Acid dyes indicates that a high temperature favours the dye removal. The percentage removal of both the dyes increased from 85.06 to 91.95% and 89.04 to 95.89% for AB15 and AO10 when the temperature increased from 30 -45⁰C respectively. From the above results it is clear that adsorption equilibrium is a thermo dependent process. The enhanced adsorption of acid dyes with temperature may be due to increased mobility of dye molecules and enlargement of pore size due to activated diffusion which causes pores to widen and deepen there by creating more surfaces for adsorption. Similar results are also reported by other researchers^{11- 12}.

Adsorption Kinetic Study

The prediction of the adsorption kinetics of dye from aqueous system is important in order to design a suitable treatment system. In order to analyse the adsorption kinetics of Acid dyes AB15, AO10 on ETAC, the following kinetic equations have been studied. This study includes i) Adsorption rate study, ii) Intra particle diffusion study.

Pseudo-First Order Kinetics

The first order equation is the simplest one and is the most widely used for the adsorption of a solute from a liquid solution. The rate equation¹³ is

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad \dots (1)$$

which was further integrated to

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad \dots(2)$$

where q_e and q_t are the amounts of dye adsorbed at equilibrium and time t (min), k_1 is the rate constant (min⁻¹). Linear plot of $\log(q_e - q_t)$ versus t gives the value of k_1 and q_e (figure not shown). The adsorption data fitted poorly with pseudo-first order kinetic model. Hence the adsorption does not follow first order rate expression.

Pseudo Second Order Kinetics

Adsorption of dyes on porous material has been observed that evolution of the adsorbed amount with time follows pseudo second order kinetics¹⁴

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots (3)$$

The values of k_2 and q_e can be calculated from the plot of t/q_t versus t and presented in Table 2. The k_2 is the second order rate constant (g/mg min) and q_e is the equilibrium adsorption capacity (mg/g). h is the initial adsorption rate (mg/g min), as $t=0$ can be defined as $h = k_2 q_e^2$. The second order rate constant decreases from 7.34×10^{-4} g/mg min to 1.146×10^{-4} g/mg min for AB15 and 6.69×10^{-4} g/mg min to 1.18×10^{-4} g/mg min for AO10 with increase in initial dye concentration. The correlation coefficient r^2 ranges from 0.9925 to 0.9865 for AB15 and 0.9926 to 0.9823 for AO10. From the results, it is concluded that the adsorption of acid dyes on ETAC can be explained by second order kinetics which describes the adsorption much better than pseudo-first order kinetics. Figure 5a and 5b shows the second order plot for the adsorption of AB15 and AO10 onto ETAC.

Table 2 - Kinetic Model values for adsorption of Acid Dyes onto ETAC

Dyes	Concn mg/L	First Order Kinetics			Second Order Kinetics			Intra Particle Diffusion model	
		k_1 (min ⁻¹)	q_e (cal) (mg/g)	r^2	$k_2 \times 10^{-4}$ (g/mgmin)	q_e (cal) (mg/g)	r^2	k_{id} (mg/g min)	r^2
AB15	25	0.0428	45.656	0.9956	7.34	55.248	0.9925	4.2943	0.9214
	50	0.0458	92.811	0.9924	3.72	106.38	0.9902	8.2976	0.9190
	75	0.0462	155.88	0.9770	1.67	169.49	0.9837	12.754	0.9418
	100	0.0462	215.19	0.9622	1.14	227.27	0.9865	16.959	0.9541
AO10	25	0.0467	51.594	0.9628	6.69	59.171	0.9926	4.5746	0.9239
	50	0.0437	89.04	0.9905	3.08	114.94	0.9861	8.8000	0.9204
	75	0.0389	139.65	0.9747	1.69	175.43	0.9844	13.104	0.9381
	100	0.0377	183.65	0.9795	1.18	232.55	0.9823	17.349	0.9429

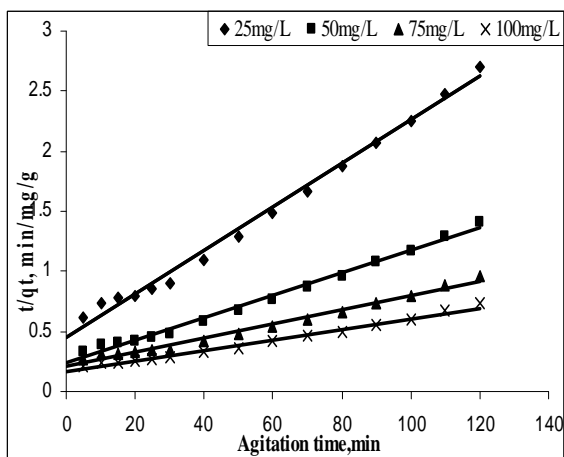


Figure 5a Pseudo Second Order plot for the adsorption of AB15

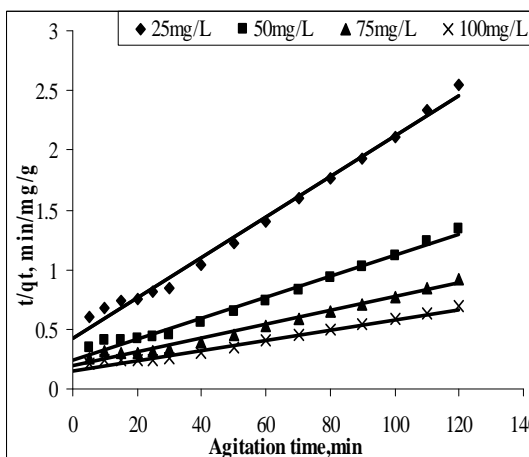


Figure 5a Pseudo Second Order plot for the adsorption of AO10

Intra particle Diffusion Model

It is important to determine the rate determining step in adsorption studies. Since the particles are vigorously agitated during the experiment, there is a possibility that transport of adsorbate ion from the solution into the pores of adsorbent is the rate limiting step. The rate limiting step might be film or intra particle diffusion¹⁵ and was tested by plotting the graph between amount of dye adsorbed q_t and $t^{1/2}$. Figure 6a and 6b shows the intra particle diffusion plot for the adsorption of AB15 and AO10 onto ETAC.

The adsorption curve followed by two portions and suggested that the adsorption process proceeds by surface adsorption and intra particle diffusion. The initial portion indicates the boundary layer diffusion effect, while the final linear portions are due to intra particle or pore diffusion effect. The rate constant for intra particle diffusion coefficient K_{id} determined from slopes of the plot. Further more, the linear portions of the curve do not pass through the origin, indicates that intra particle diffusion is not the only rate determining step. This indicates that mechanism of dye removal is complex and both surface adsorption as well as intra particle diffusion contributes to the rate limiting step¹⁶.

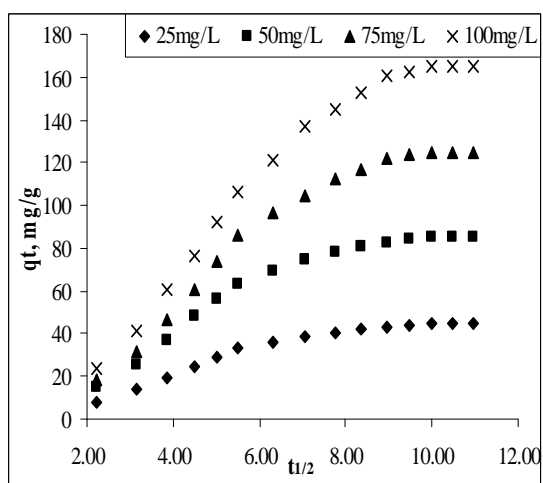


Figure 6a Intraparticle Diffusion model for the adsorption of AB15

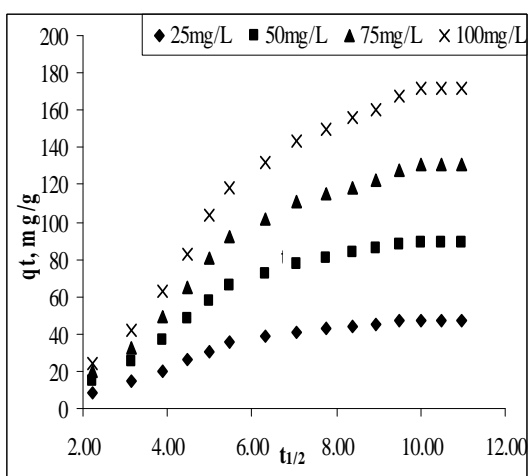


Figure 6b Intraparticle Diffusion model for the adsorption of AO10

Isotherm Models

Adsorption isotherm usually describes the equilibrium relationship between adsorbent and adsorbate ie the ratio between the quantity of dye adsorbed and that remaining in aqueous solution at a fixed temperature at equilibrium. The distribution of dye between the adsorbent and the dye solution at equilibrium is important in establishing the capacity of the adsorbent for dye removal from aqueous solution.

The experimental data obtained were evaluated by various isotherm models incorporating Langmuir and Freundlich models.

Table 3 - Comparison of the coefficients of Isotherm parameters of Acid dyes

Dyes	Temp °C	Isotherm Models					
		Langmuir			Freundlich		
		Q ₀ (mg/g)	b (L/mg)	r ²	N	k _f (mg ^{1-1/n} L ^{1/n} g ⁻¹)	r ²
AB15	30	200.00	0.1377	0.9920	2.3452	36.2576	0.8746
	35	208.33	0.1621	0.9957	2.4962	42.2668	0.9062
	40	212.76	0.1857	0.9970	2.5819	47.2063	0.9133
	45	222.22	0.2054	0.9980	2.5960	51.0152	0.8998
AO10	30	227.27	0.1447	0.9973	2.3668	43.2818	0.9437
	35	238.09	0.1478	0.9980	2.3866	45.8880	0.9572
	40	238.09	0.1693	0.9979	2.4881	50.4196	0.9589
	45	243.90	0.1790	0.9987	2.5220	52.9785	0.9528

Langmuir Isotherm

The Langmuir Isotherm assumes that adsorption take place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption¹⁷. The linear form of Langmuir isotherm is presented by the following equation

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot b_L} + \frac{C_e}{Q_0} \quad \dots (4)$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q₀ and b_L are constants related to adsorption capacity energy of adsorption (L/mg). Plotting C_e/q_e against C_e, straight line was obtained, where Q₀ was calculated from the slope, whereas with b_L was found from the intercept.

The Langmuir isotherm fits the experimental data very well may be due to the homogeneous distribution of active sites onto the surface. Langmuir adsorption capacity increases from 200 mg/g to 222.22 mg/g for AB15 and 227.27 mg/g to 243.90 mg/g for AO10. The Figure 7a and 7b shows the Langmuir isotherm for the adsorption of AB15 and AO10 onto ETAC.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter R_L¹⁸.

$$R_L = 1 / (1 + bC_0)$$

Where C₀ is the highest initial solute concentration. R_L value indicated the type of adsorption isotherm to be either unfavourable (R_L > 1), favourable (R_L < 1), linear (R_L = 1) or irreversible (R_L = 0). Langmuir model is more appropriate to explain the nature of adsorption with correlation coefficient of 0.992 to 0.998 for AB15 and 0.9973 to 0.9987 for AO10.

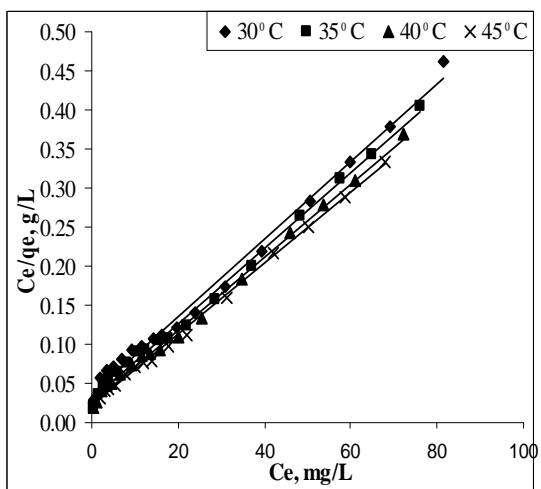


Figure 7a Langmuir Model for the Adsorption of AB15

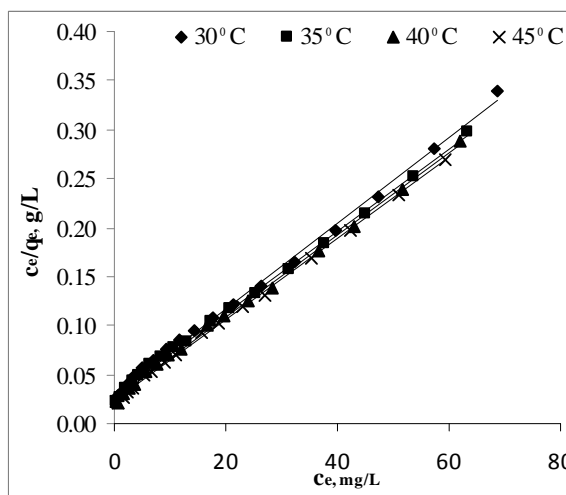


Figure 7a Langmuir Model for the Adsorption of AO10

Freundlich Model

The Freundlich isotherm is the earliest known equation describing the adsorption process. The Freundlich isotherm¹⁹ is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor 1/n. Hence linearised form of Freundlich equation can be written as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \dots (5)$$

Where K_f is the measure of adsorption capacity, n is the adsorption intensity and are calculated from intercept and slope linear plot of $\log q_e$ versus $\log C_e$ (figures not shown). The value of $1/n$ is below one for both dyes indicating that the adsorption of acid dyes on ETAC is favourable. But it poorly fits with the experimental data with correlation coefficient 0.8746 to 0.8998 for AB15 and 0.9437 to 0.9538 for AO10.

Thermodynamic Parameters

Thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) of adsorption were calculated from the binding constant which obtained from Langmuir equation using the following relations,

$$\Delta G^\circ = -RT \ln K \quad \dots\dots (6)$$

$$\ln K = \Delta S^\circ/R - \Delta H^\circ/RT$$

The ΔH° values were calculated from the slopes of linear variation of $\ln K$ versus $1/T$ and the results are presented in table 4. The negative value of ΔG° indicates high affinity of dye to the surface of ETAC. The Gibbs free energy change (ΔG^0) is an indication of spontaneity of a chemical reaction therefore it is an important criterion for spontaneity. The values of ΔG^0 for all the three dyes were within the range of -20 and 0 kJ /mole, indicating that the physisorption is the dominating mechanism. The positive values of ΔS^0 confirming physical adsorption nature and increased randomness at the solid-solution interface during adsorption and indicate affinity of the dye onto adsorbents²⁰. The bonding between acid dyes and ETAC surface is weak, since ΔH° value is found to be 26.830 kJ /mole for AB15 and 15.78 kJ /mole for AO10.

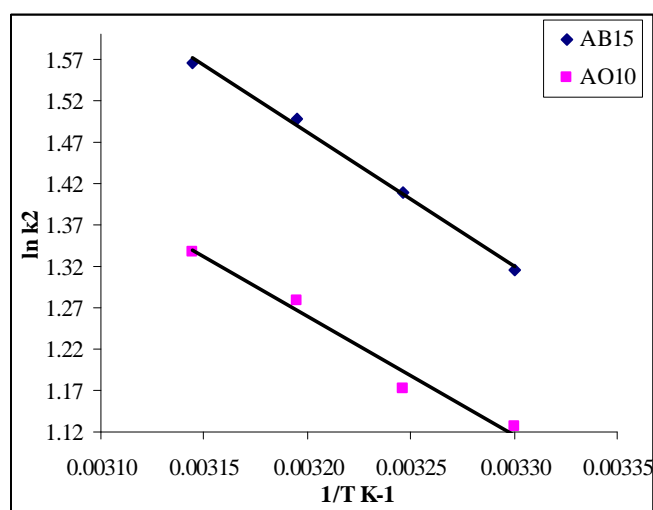


Figure 8 Arrhenius plot for the Adsorption of Acid dyes

Table 4 - Thermodynamic Parameters at different Temperatures

Dyes	Temp°C	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° kJ/K/mol	Ea kJ/mole	ΔH_x kJ/mole
AB15	30	-8.387	26.830	0.1160	13.4703	29.503
	35	-8.969				
	40	-9.550				
	45	-11.131				
AO10	30	-8.773	15.780	0.0810	11.8499	22.1859
	35	-9.178				
	40	-9.584				
	45	-9.989				

Activation Energy

The second order rate constant of the dye adsorption is expressed as a function of temperature by Arrhenius relationship.

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad \dots (7)$$

Where E_a and A refers to Arrhenius activation energy and Arrhenius factor obtained from the slope and intercepts of a graph by plotting $\ln k_2$ vs $1/T$ as shown in Fig 8. The activation energy was found to be 13.4703 kJ/ mole and 11.8499 kJ/mole for AB15 and AO10 respectively. The minimum value of E_a for sorption of AO10 onto ETAC indicated the higher adsorption. The physisorption usually have energies in the range of 5-40 kJ/mole, while higher activation energies 40-800 kJ/mole suggests chemisorption²¹. The activation energy <40 KJ/mole for Acid dyes indicate the physisorption.

A similar result has been observed for the adsorption of reactive dye on palm oil industry waste²², reactive orange on loofa activated carbon²³, adsorption of acid dyes on the surface of Nirgudi leaf powder²⁴.

Isosteric Heat of Adsorption

Isosteric Heat of Adsorption ΔH_x is defined as the heat of adsorption determined at constant amount of adsorbate adsorbed. It is the basic requirements for the characterization and optimization of an adsorption process and also very important for equipment and process design.

The isosteric heat of adsorption at constant coverage is calculated using Clausius-Clapeyron equation²⁵⁻²⁶

$$\ln Ce = \frac{\Delta H_x}{RT} + K \quad \dots (8).$$

Where C_e is the equilibrium dye concentration in solution (mg/L), ΔH_x is the isosteric heat of adsorption (kJ/mole). The isosteric heat of adsorption is calculated from the slope of the plot $\ln C_e$ versus $1/T$ and the results are presented in Table 4. The magnitude ΔH_x of provides an information about the nature and mechanism of the process. For physical adsorption ΔH_x should be below 80 kJ/mole and for chemical adsorption it ranges between 80-400 kJ/mole²⁷. The values of ΔH_x for the adsorption of acid dyes onto ETAC are 29.503 kJ/mole and 22.1859 kJ/mole which is within the range of physisorption and suggested that the adsorption process is physisorption.

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of spent carbon and the dye. High percentage of desorption 23% occurs at the pH range of 8 to 9. Desorption increases with increase in pH from 2 to 10. The high desorption at higher pH is due to the common ion effect suggests that dil. NaOH could be the suitable reagent for the regeneration of carbon.

Conclusion

The present investigation showed that ETAC is a promising adsorbent for the removal of Acid dyes from aqueous solution over a wide range of concentration. The amount of dye adsorbed was influenced by initial dye concentration, contact time, pH and temperature. Adsorption behaviour was well described by a monolayer Langmuir type isotherm and Freundlich isotherm. Langmuir model is more appropriate to explain the nature of adsorption with high correlation coefficients. The adsorption capacity of ETAC was determined as 200 mg/g and 227.27 mg/g for AB15 and AO10 respectively. The experimental data indicates that the adsorption kinetics follow the second order kinetics with intra particle diffusion as one of the rate limiting steps. The adsorption of Acid dyes (AB15, AO10) increases with temperature indicates that adsorption process is endothermic in nature. From the thermodynamic parameters ΔG° , ΔH° and ΔS° values, it is suggested the adsorption is favourable and spontaneous in nature. Activation energy which is below 40 kJ/mole for both acid dyes and isosteric heat of adsorption also supports that the adsorption of acid dyes on ETAC is an endothermic physical process.

Acknowledgement

The first and third authors thank UGC, New Delhi for providing financial assistance under major research project scheme to carryout this research work.

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