Kinetics, Equilibrium And Thermodynamics Studies For Dye Removal Using Bio Sorption (Amorphophallus Paeoniifolius)

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Abstract - **The efficiency of Amorphophallus Paeoniifolius Tuber Activated Carbon (APTAC) prepared from natural source for the removal of Acid Fuchsin (AF) dye from its aqueous solution is examined in this study. Batch mode experiments conducted in different concentrations, pH, adsorbent dose, contact time and temperatures were studied in adsorption characteristics of AF dye removal on APTAC. The equilibrium data were analyzed using Freundlich, Langmuir and Temkin isotherms. Langmuir adsorption isotherm gave a good fit to the experimental data. The results proved that APTAC has a good adsorption capacity towards AF dye removal. The pseudo first order and pseudo second order kinetics data were applied to the adsorption data. The kinetic data confirmed to the pseudo second order suggesting that the rate limiting step may be chemisorption. The thermodynamic quantities such as Gibbs free energy (ΔG0), Enthalpy (ΔH0) and Entropy (ΔS0) were evaluated. The negative value of ΔG0 and negative value of ΔH0obtained indicates the spontaneity and exothermic nature of the adsorption. The changes in value of entropy suggest that the adsorption process was favorable. According to the results APTAC treated as cheapest and available bio-adsorbent to remove toxic dyes from waste water. keywords: adsorption, acid fuchsin, amorphophallus paeiniifolius tuber, activated carbon, isotherms, kinetics and thermodynamics.**

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INTRODUCTION

Adsorption technique is by far the most versatile and widely used, moreover these processes becomes economic if the adsorbent used is available and cheap in cost. The most common adsorbent materials are; alumina silica, metal hydroxides and activated carbon. Activated carbon, also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and thus to a have a very large surface area available for adsorption or chemical reactions. Adsorption technique based on activated carbon has been found as most efficacious method used for removal dyes. However, its uses are still limited because higher the quality of activated carbon, the greater its operational costs. The difficulty of regeneration is one of the major concerns associated with activated carbon [1]. One of the most important environmental problems that the industrial waste is facing today is to eliminate colour from the dye's effluent into waste water. There is a variety of dyes like acid dyes, basic dyes, azo dyes, mordant dyes, plastic dyes, etc. The effluents from these industries thus contain dyes as main pollutant [2-5]. More than 10000 different dyes are used in the textile, leather, pharmaceuticals, food, paper; paint and electroplating [6] industries in India. In recent studies, Plant wastes are inexpensive and they have no or very low economic value. In the present study activated carbon was prepared from cheap adsorbent as a new adsorbent for the removal of Acid Fuchsin dye from aqueous solutions.

MATERIAL AND METHODS

MATERIALS

Acid Fuchsin Dye (AFD) has the chemical composition as 2-amino-5 [(4-amino-3-sulfophenyl) (4-imino-3-sufo 2, 5-cyclohexadiene-1-ylidene)-methyl]-3-methyl benzenesulfonic acid. It's an organic dye and has molecular formula $C_{20}H_{17}N_3Na_2O_9S_3$. The molecular weight is 585.53 g mol^{-1} (λ_{max} = 543 nm). AFD also called acid violet 19 or Fuchsin Acid, is used for staining procedure [7] and other industrial purpose [8]. Its structure given in Fig 1.

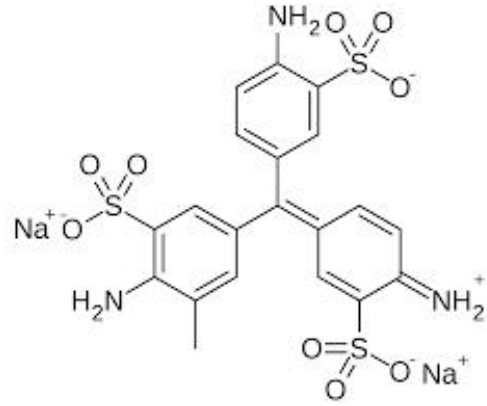

Fig 1. Structure of Acid Fuchsin

PREPARATION OF ADSORBENT

The (APT) *Amorphophallus Paeoniifolius* Tuber was used as an adsorbent were collected from Chennai. The unwanted materials like impurities, soils, dust etc., were removed extensively by washing it in running tap water. It was followed by washing it with distilled water. The washed material was dried under sun light for ten days, it was grinded in mixer. This grinded powder was oven dried at 50°C for 24hrs. The powder APT was weighed accurately is taken in beaker which contains 1:1 H_2SO_4 acid is then allowed to soak for two days and then washed with distilled water in order to attain neutral pH. The prepared adsorbent is transferred to beaker and dried in a muffle furnace at 450°C for 3hrs.The black powder obtained in the above method is called as activated carbon, which is used for further analysis.

PREPARATION OF ADSORBATE

The synthetic dye Acid Fuchsin (AF) were purchased from Kavin laboratories in Chennai. A stock solution of (1000mg/L) was prepared by dissolving 1.0 g of dye in distilled water. Distilled water was used for preparing all the solution and reagents.

BATCH ADSORPTION EXPERIMENT

The experiment was carried out by the batch adsorption method, the removal of dyes was studied under various temperature (298K,308K,318K,328K) using the batch technique to investigate the effect of operational parameters such as pH, initial dye concentration, adsorbent dosage, contact time, and solution temperature. The isotherm study was carried out with different initial dye concentration from 10 to 70mg/L and carefully arranged in the orbital shaker and agitated at 150rpm speed for 30 minutes. The adsorbent dosage was varied from 0.2 to 1.0g for better adsorption. The kinetic study was done by varying time from 30 to 150 minutes. For the thermodynamic study temperature is altered from 298 to 328K. The APTAC solution was separated by centrifugation at 2000rpm for 10 minutes. Residual concentration of dye was determined using UV-visible spectrophotometer at respective wavelength. The percentage of dye removal from solution was calculated as following

The percentage of AF adsorbed was determine based on the following formula

$$\% = \frac{(Co - Ce)}{Co} X\ 100 \qquad Eq.\ 1$$

The maximum AF uptake q_e (in mg g^{-1}) was calculated as shown below

$$qe = \frac{(Co - Ce)V}{M} \qquad Eq.\ 2$$

Where C_o and C_e are initial and final AF concentration of in mg 1^{-1}, respectively M is the amount of APTAC (in g) and V is the volume of AF solution.

RESULTS AND DISCUSSION

FTIR- FOURIER TRANSFORM INFRARED SPECTROSCOPY

The FTIR spectrum of APTAC before and after adsorption Fig 2 & 2.1 of AF dye were analysed to determine the vibrational frequency changes in their functional groups of APT before adsorption in various peaks at 400-4000cm^{-1}, Changes in the vibrational and rotational movements of the molecule shows the detection of functional groups which have specific vibration frequency. For example, C=O, NH_2, -OH etc. Before adsorption of AF dye 3393.14cm^{-1} from O-H Carbohydrates groups, 2921.63cm^{-1} O-H from alcohols, 1654.62 cm^{-1} -NH_2 from amines, C-O str from amino acids, 1160.94cm^{-1} C-O str from aromatic compounds, 1007.62cm^{-1} O-H def from ketone, 765.60 cm^{-1} alkyl halides, 575.64 cm^{-1} aryl halides, 523.57 cm^{-1} -NO_2 Aryl nitro compounds.

After adsorption of AF dye, it was found that most of the functional groups the adsorbent were affected after the dye uptake process. This is judged from shifts in the position of some of the functional groups that moved at lower frequency or higher frequency or band intensity before and after AF adsorption includes 3428.81cm^{-1} from O-H Carbohydrates groups, 2919.7cm^{-1} O-H str from carboxylic groups, 1655.59 cm^{-1} from amines, 1159.97 cm^{-1} C-O str from alcohols, 997.01cm^{-1} C-H $_{def}$ from aldehyde, 853.34cm^{-1} N-H def from amines, 763.67 cm^{-1} alkyl halides, 516.82 cm^{-1} from aryl halides halogen groups respectively indicates involving of these groups for AF binding to APT.

SEM – Scanning Electron Microscope

The SEM images of the APTAC sample Fig 3 revealed a great number of the pores in nanometre size, which were formed during the carbonization and activation process. Pore system and excellent pore morphology observed by SEM. From the SEM images it is confirmed that the particle having size in 27.96 nanometre as calculated by Image J programme. Such porosity should definitely provide APTAC with high adsorption capacity towards AF

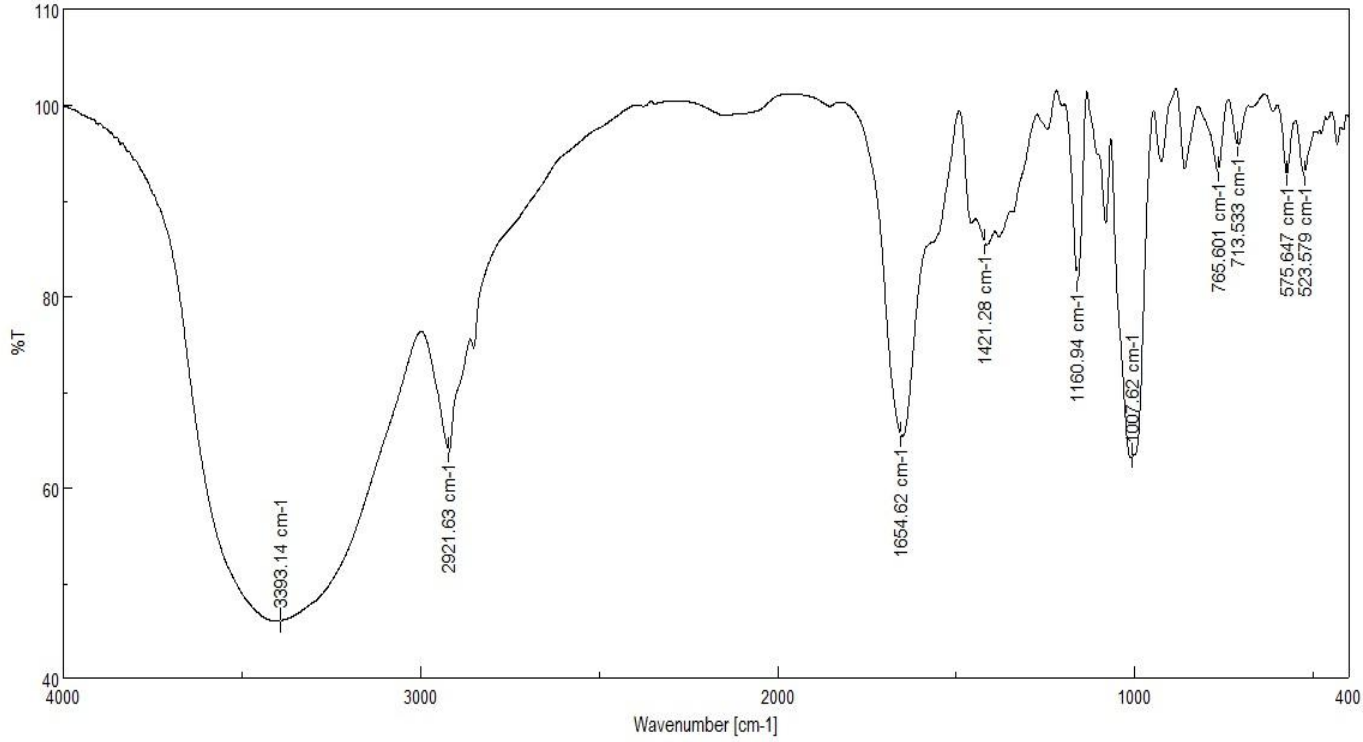

Fig 2. FTIR spectrum for before adsorption on APTAC

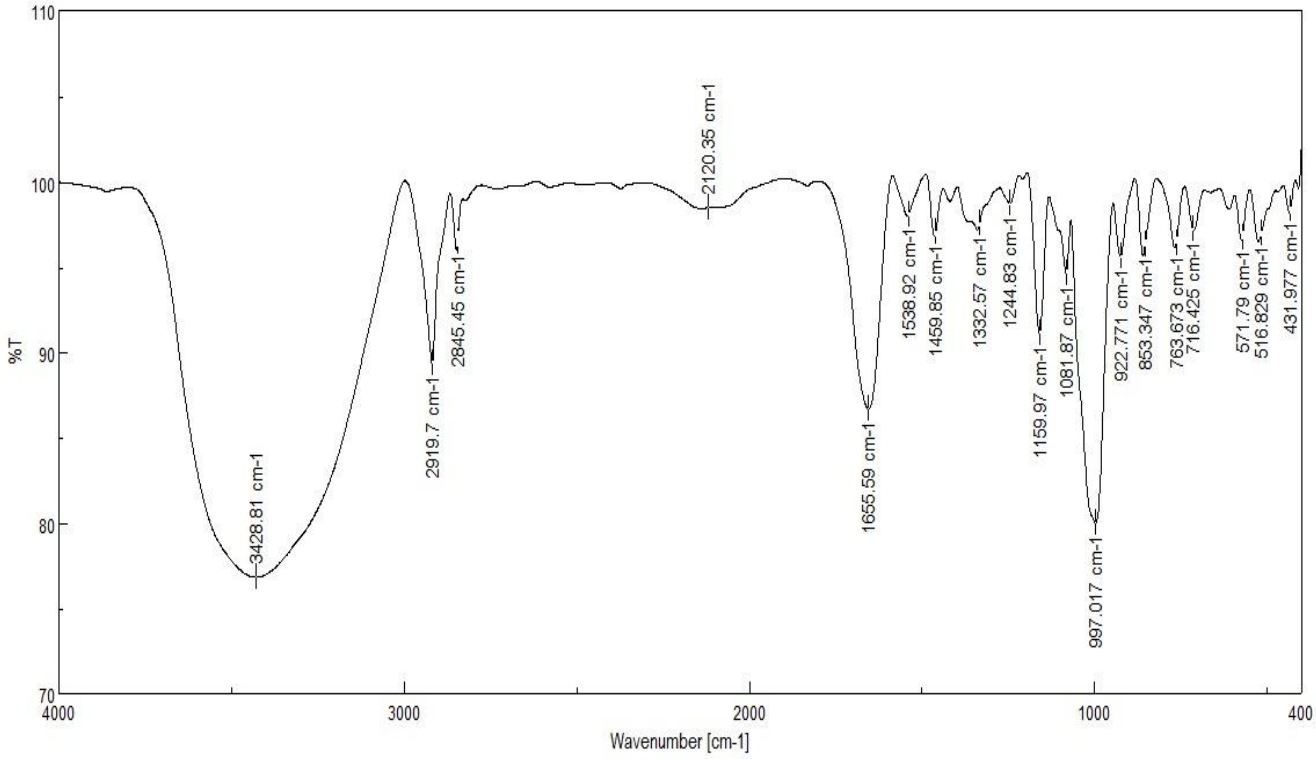

Fig 2.1 FTIR spectrum for after adsorption on APTAC

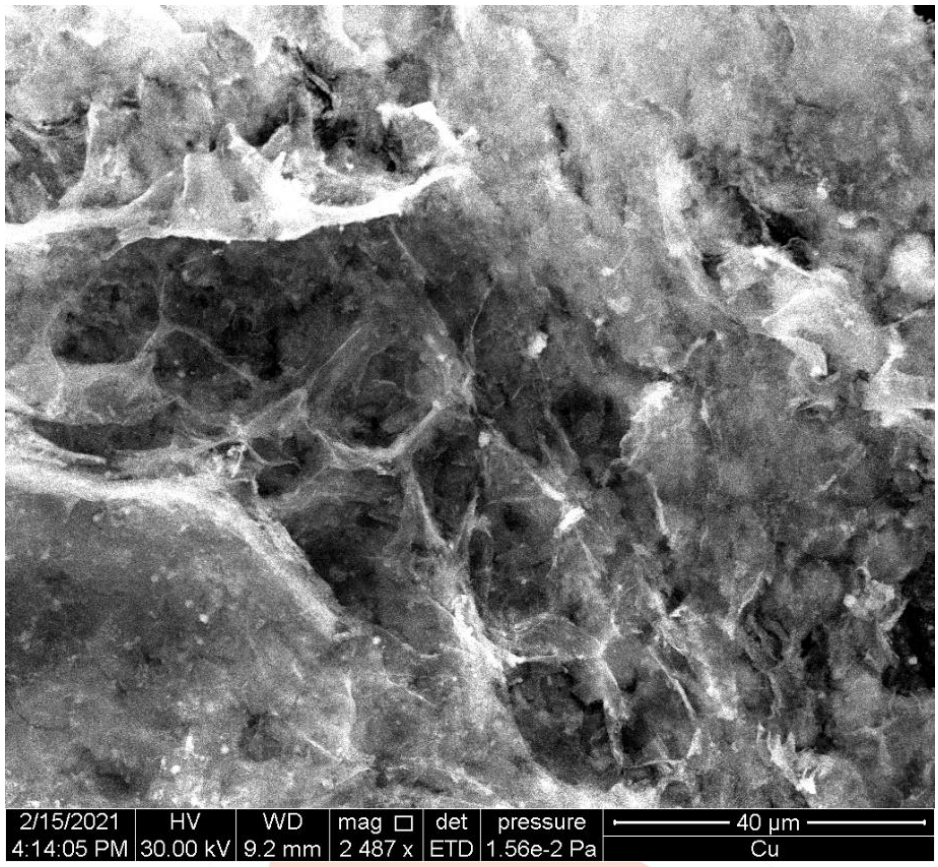

Fig 3. The SEM images of APTAC

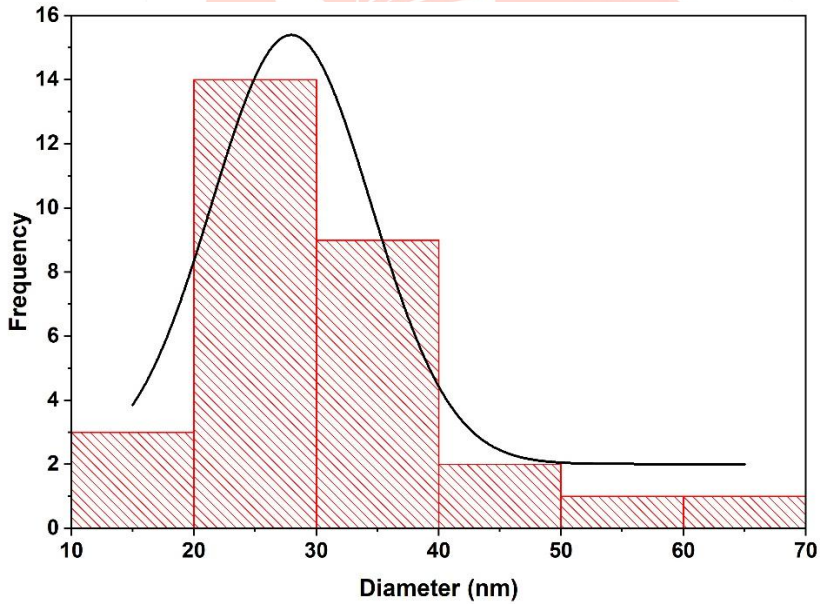

Fig 3.1. Histogram of APTAC

Effect of Adsorption process parameters on removal of AF

Effect of initial dye concentration of AF

The inference of the initial concentration of AF in the Solutions on the rate of adsorption on APTAC was investigated. The Experimental parameter was carried out with fixed adsorbent dosage, optimal pH and stably maintained temperature. The percentage removal of AF is plotted against the initial dye concentration shown in Fig (4). The percentage removal of dye increased from 66.5% to 83.13% with an increase in initial dye concentration from 10 to 50 mg/L, after that the adsorption efficiency decreased with increase dye concentration from 50 to 70 mg/L. Maximum adsorption of 83.13% was recorded for (50mg/L). This could be attributed to the increase in the driving force from higher concentration which enhances the sorption process.

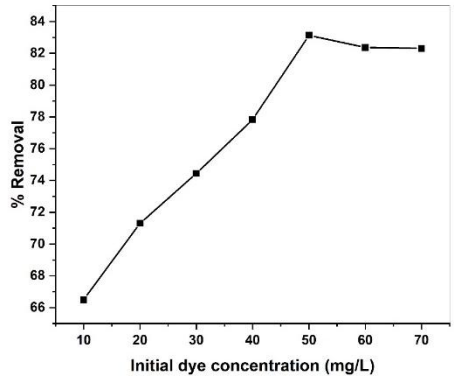

Fig 4. Effect of Initial AF dye concentration on the adsorption of APTAC.

Effect of Adsorbent Dosage

The effect of adsorbent dosage on the removal of the AF from aqueous solution was determined using variable quantities of APTAC adsorbent ranging from 0.2 g to 1.0 g at fixed volumes 50 (ml) with initial dye solution 50 mg/L under constant parameters. The results are shown fig (5). The highest percentage of AF removal was achieved using 0.2g APTAC. At elevated levels of APTAC the amount of AF removal gets decreased. The observed decrease in AF dye removal with increase adsorbent dosage from 82.77% to 76.74%. This phenomenon attributes to overlapping or aggregation of adsorption sites resulting in an increase total adsorbent surface area with respective initial dye concentration

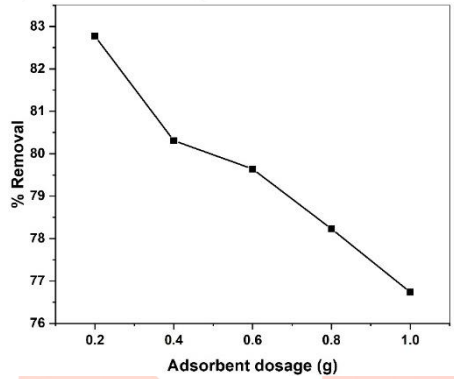

Fig 5. Effect of adsorbent dose on removal of AF

Effect of pH study

To study the effect of initial pH onto adsorption, the pH of AF solution was varied from 4 to 9. The results of the variation in AF percentage removal with increase in pH is shown fig (6). As the solution pH was increased 4 to7 the percentage removal of AF increased 76.74 to 83.50 % for APTAC, after that the adsorption efficiency is decreased. Uptake of dyes mainly depends upon pH of the adsorbent. The pH of APTAC found to be slightly acidic since its surface filled with positive charged particles. The increase in the percent dye removal with increase in pH from 4 to 7 for APTAC might be ascribe to the electrostatic attraction between positively charged adsorbent surface and negatively charged dye molecules [9]. An increase pH beyond 7 for APTAC, percentage removal decreased probably due to electrostatic repulsion between negatively charge adsorbent surface and positively charge dye molecules.

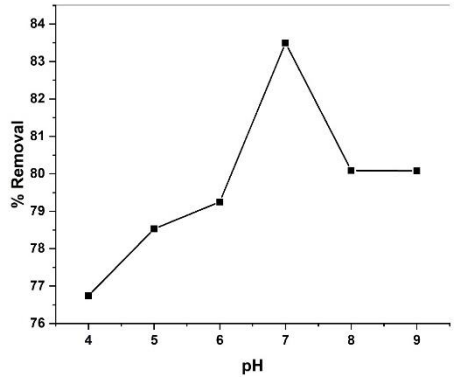

Fig 6. Effect pH on the adsorption of AF onto APTAC

Effect of contact time: -

To identity the effect of contact time an experiment was conducted by mixing 50 ml of Acid Fuchsine solution (50 mg/l concentration) with 0.2g of APTAC adsorbent at constant pH 7 with varying time intervals of (30,60,90,120 and 150) minutes respectively. The contact time effect on the acid fuchsine adsorption onto APTAC is depicted in fig (7), which correlates relationship between the percentage adsorption and adsorption time. The figure shows that the removal efficiency is equilibrium time dependent. It is evident that the amount of adsorption is rapid in the initial stages and decrease with increase

in contact time. The fact which is inferred from the above process states large number of vacant sites were available for adsorption, moment equilibrium attained at particular contact time due to desorption removal get decreased further.

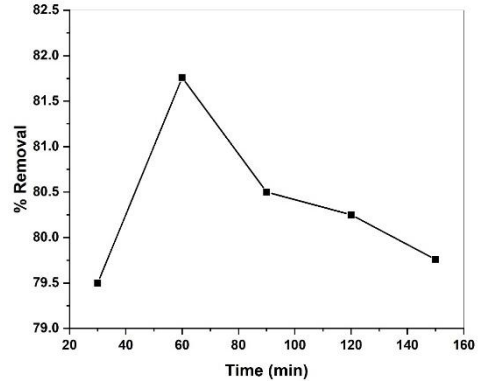

Fig 7. Effect of contact time adsorption for the AF onto APTAC

Effect of temperature

Temperature is an important parameter that influence dye adsorption, the effect of temperature on the percentage removal of Acid fuchsine onto APTAC is shown in fig (8). The percentage removal adsorption decreased from 92.20% to 91.77% with the temperature increased from 298K to 328K. This decrease in adsorption efficiency with increase in temperature is attributed mainly to the fact that the physical bonding between the dye (adsorbate) and the active sites of the adsorbent is weakened as the temperature rises. Furthermost the dye solubility increases also causing the interaction between the solute and solvent to become stronger than between the solute and adsorbent. This therefore makes it more difficult for the solute (i.e., dye) to adsorb [10].

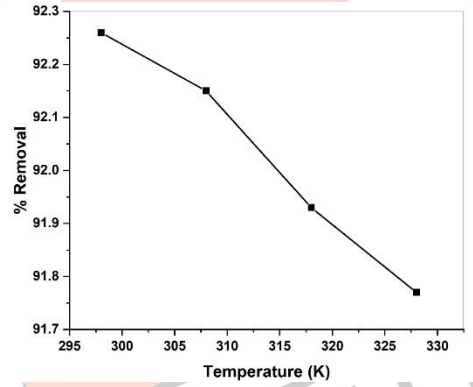

Fig 8. Effect of temperature on the adsorption of AF onto APTAC

ADSORPTION ISOTHERM

An adsorption isotherm indicates how adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes [11]. In the present experimental work, the isothermal results were analysed using well known expression for Langmuir, Freundlich and Temkin isotherms. The applicability of the isotherm models to the adsorption study was compared by judging the correlation coefficient R^2 values.

Langmuir Isotherm

Langmuir adsorption model corresponds to a saturated mono layer of the solute molecules on the adsorbent surface. Langmuir isotherm model assumes the uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Langmuir adsorption model based on the physical hypothesis that there is no interaction between adsorbed molecules and the adsorption energy over the entire coverage surface. Also, there is no transmigration of the adsorbate in the plane of the surface of the adsorbent [12]. Expression of the model is given by equation (4)

$$\frac{1}{qe} = \frac{1}{qmKlCe} + \frac{1}{qm} \qquad \text{e. (4)}$$

Where q_e is the amount of adsorbed dye at the equilibrium (mg g^{-1}), K_L (L mg^{-1}) and q_m (mg g^{-1}) are Langmuir constant related to energy adsorption and maximum adsorption capacity respectively. A graph was plotted $1/q_e$ against $1/c_e$ results in a straight lion with a slope of $(1/q_m)$ and intercept $(1/q_m)$.

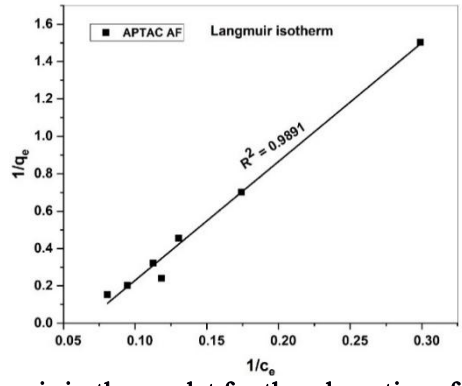

Fig 9. 1. Langmuir isotherm plot for the adsorption of AF onto APTAC

The essential characteristic of the Langmuir isotherm can be expressed in term of dimensionless constant separation factor R_L that is given equation (5).

$R_L = 1/1+K_LC_O$ Eq.5

The values of R_L indicates the type of isotherm to be either favourable ($0 < R_L > 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The values of R_L were found to be 0.0304 suggesting the isotherm is to be favourable at the concentration studied.

Freundlich isotherm

The Freundlich model is described by a formula Assuming heterogeneous multilayer adsorption on heterogeneous Surfaces. The Freundlich model also assumes interaction between the Adsorbates and that adsorption capacity increases with the analyte Concentration. The formula describing the Freundlich model is shown [13]

$\log q_e = \log K_F + 1/n \log C_e$ Eq.6

Where K_F is the reaction constant reflecting adsorption Capacity (in 1 mg-1), and 1/n indicates dimensionless exponent of the Freundlich model to show adsorption intensity (it is calculated from the slope and intercept of log q_e versus log Ce plot).

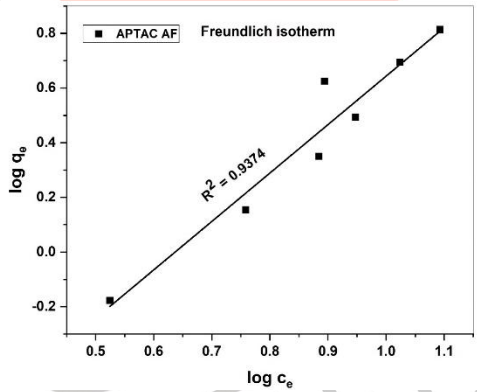

Fig 9.2 Freundlich isotherm plot for adsorption of AF onto APTAC

Temkin isotherm

The Temkin isotherm model assumes that the Adsorption energy decrease linearly with the surface coverage due to adsorbent-adsorbate interaction. The linear form of Temkin Isotherm model is described as follows [14]

$q_e = \frac{RT}{BT} lnKT + \frac{RT}{BT} ce$ Eq.7

Where BT is the Temkin constant related to the heat of sorption (KJ/mol), KT is the equilibrium binding constant Corresponding to the maximum binding energy (L/g), T is the Absolute temperature(K) and R is the gas constant (8.314×10^{-3} KJ/mol K).

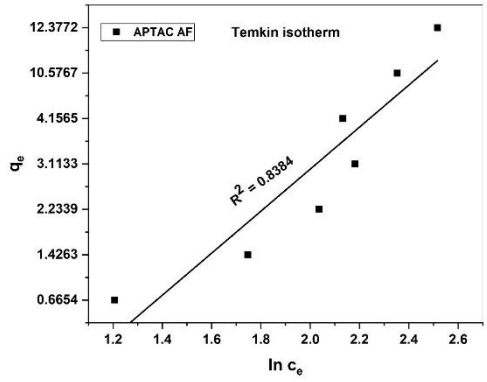

Fig 9.3 Temkin isotherm plot for the adsorption of AF onto APTAC

Fig 9.1, 9.2, and 9.3, displays the Langmuir, Freundlich, and Temkin isotherms for our adsorption experiments. The calculated parameters for the all isotherms along with R^2 values are shown table (1). The Langmuir isotherm model was well

fitted and has good agreement with experimental data better than Freundlich and Temkin isotherm models. The results also confirmed by the high R^2 value for the Langmuir model (0.9891) compared with Freundlich (0.9374) and Temkin (0.8384) isotherm models. The Langmuir isotherm fit well because homogeneous distribution of active sites onto APTAC surface. This finding was similar to other studies on the sorption of AF dye on different sorbent.

Table 1. Isotherm parameters for removal of AF adsorption onto APTAC

Adsorption Isotherm	*Parameters*	*Acid Fuchsin*
Freundlich Isotherm	K_F (mg/g)	0.0744
	1/n	1.7715
	n	0.5644
	R^2	0.9783
Langmuir Isotherm	K_L (mg^{-1})	0.0639
	q_m (mg/g)	2.4618
	R_L	0.2383
	R^2	**0.9891**
Temkin Isotherm	K_T (mol/g)	0.2364
	B_T (mol/kJ)	8.4649
	R^2	0.8384

ADSORPTION KINETICS

Adsorption kinetics studies the relationship between adsorption capacity and reaction time. Thus, its main concern is adsorption speed dynamic equilibrium mass transfer and diffusion rates. Analysis of these parameters helps to understand adsorption process rates as well as adsorption mechanism. The pseudo-first-order model and pseudo-second-order model were used to investigate the adsorption kinetics of the AF dye on APTAC.

The linear form of the pseudo-first-order kinetin model is represented by the following equation.

$$\text{Log } (q_e\text{-}q_t) = \log q_e - K_1/2.303.\ t \qquad \text{Eq.8}$$

Where qe and qt are the values of amount of the dye adsorbed per unit mass on the adsorbent at equilibrium at various time respectively. K_1 is the pseudo first order adsorption rate constant (min-1). The values of K_1 are determined from slope and intercept respectively of the linear plot of log (qe-qt) versus t. Fig 10 .1. Where the values are given in table (2).

The linear form of the pseudo-second-order model is given by equation (9) [15]

$$t/qt = 1/K_2\ q_e^2 + t/q_e \qquad \text{Eq. 9}$$

Where K_2 is the pseudo-second-order adsorption rate constant (g/mg 1min) and qe is the amount of dye adsorbed (mg/g) on the adsorbent equilibrium. The initial adsorption rate (h = mg g^{-1}) is expressed as

$$h = K_2 qe^2$$

The plot of t/qt versus t gives a linear relationship which allows computation of K_2 h and calculated qe shown fig 10.2

The kinetic adsorption results of AF by APTAC under various condition from the related plots and the results are listed in table (2). The applicability of these model is based on the judgment on the respective correlation coefficient (R^2) and agreement between the experimental and calculated value of qe. The correlation coefficient R^2 (0.3571) values obtained for pseudo-first-order kinetic model were relatively low hence this model has very poor correlation coefficient for the fit data.

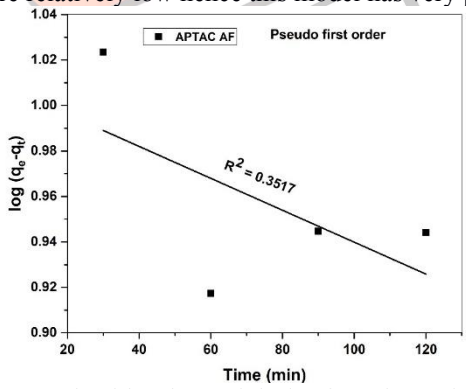

Fig 10.1 Pseudo-first-order kinetic model plot for adsorption of AF onto APTAC

The pseudo-second-order rate constant K_2 and qe determined from the model as well as correlation coefficient presented in table (2). The observed R^2 (0.9999) values are very high for the pseudo-second-order kinetic model, where the values of qe_{cal} are good agreement with qe_{exp}. It is therefore evident that pseudo-second-order model is the best fit kinetic model in describing the adsorption process AF onto APTAC.

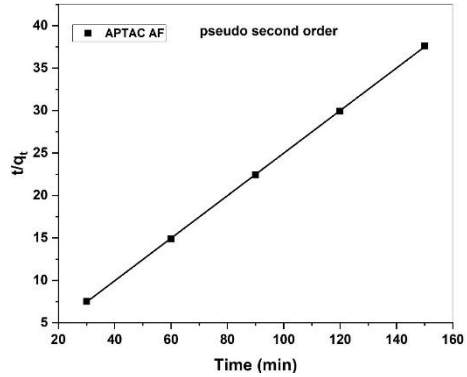

Fig 10.2. Pseudo-second order kinetic model for adsorption of the AF onto APTAC

ADSORPTION THERMODYNAMICS

Thermo dynamical parameters are important in adsorption studies, they provide a better understanding of the effect of temperature on the adsorption process. The standard changes in Gibb's energy (ΔG^O) enthalpy (ΔH^O) and entropy (ΔS^O) were calculated using the following

$$\Delta G^O = - RT\ln K \quad \text{Eq.10}$$

$$\text{Log } K = \Delta S^o/2.303R - \Delta H^o/2.303RT \quad \text{Eq.11}$$

Where R is the universal gas constant (8.314 J) T is the absolute temperature (k) and K is the equilibrium constant. Plots of ln K vs 1/T should be a straight line as shown in fig (11). All the thermodynamic parameters were tabulated in table (3). During the adsorption process the negative values of ΔG^o for the experimental temperature indicate spontaneous and favourable AF adsorption onto the surface of APTAC. The negative enthalpy (ΔH^o) values obtained indicate the adsorption process was exothermic in nature. The positive entropy change (ΔS^o) values of corresponds to an increase in the degree of randomness.

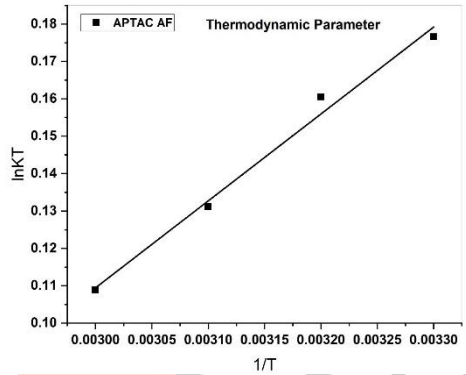

Fig 11. Thermodynamic parameter plot for the adsorption of AF onto APTAC

Table2. Adsorption Kinetic Model for AF Adsorbing by APTAC

Kinetic Model	*Parameter*	*Results*
Pseudo 1st Order	K_1 (min^{-1})	0.0016
	q_e (mg/g)	10.2352
	R^2	0.3517
Pseudo 2nd Order	h ($mg.g^{-1}$ min^{-1})	15.6739
	q_e (mg/g)	3.9920
	R^2	0.9999

Table3. Thermodynamics Parameter

Temperature (K)	*ΔG^o (J. Mol^{-1})*	*ΔH^o (KJ. Mol^{-1})*	*ΔS^o (J. Mol^{-1}. K^{-1})*	*R^2*
298	-0.4375	-4.4497	11.2546	0.9890
308	-0.41009			
318	-0.3468			
328	-0.3468			

CONCLUSION

Based on the results shown, APTAC can be used as a very efficient and cheap adsorbent for the removal of dyes from waste water. The adsorption of AF dye was examined at different experimental conditions like initial dye concentration, dosage, pH, contact time and temperature respectively. As overall result shows that the Langmuir adsorption isotherm model best fits as the Freundlich and Temkin isotherm model. Kinetic study reveals that the adsorption reaction follows pseudo second order kinetic model. The thermodynamic results predict the negative value of ΔG^o which indicates that the adsorption processes of

AF dye onto APTAC surface are spontaneous and thermodynamically more favourable. The negative value of ΔH^o indicates that the nature of the adsorption process is exothermic and the positive value of ΔS^o suggest increasing randomness at the adsorbent solution interface during the adsorption process. Further it can be concluded that APT are abundant in our country, further it can be used for the removal of AF dye from industrial waste water. The future work is going to be based on dye removal using green synthesized nano activated carbon.

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