



Estimation of Acid Red 114 adsorption using Ceiba Pentandra wood bark based activated carbon modified using phosphoric acid

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ABSTRACT

The use of low-cost and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. This paper deals with the removal of Acid Red 114 from aqueous solutions using activated carbons prepared from agricultural waste materials such as Ceiba Pentandra wood waste which is converted into thermally activated carbon (CPAC) using H₃PO₄. Optimum conditions for Acid Red 114 removal was found to be pH 6, adsorbent dosage = 100mg/L of solution and equilibrium time=240mins. Higher removal percentages were observed at lower concentrations of Acid Red 114. The adsorption isotherm data fitted well to Langmuir equation. Kinetic studies showed that the adsorption followed both pseudo - second-order and Elovich equation. The thermodynamics parameters such as ΔG , ΔH and ΔS were also evaluated. The activated carbons prepared were characterized by FTIR and SEM analysis.

Key words: Acid Red 114, Ceiba Pentandra wood waste, isotherm data, Kinetic studies and thermodynamics parameters.

INTRODUCTION

Dyes represent one of the most problematic groups of the organic pollutant, among the different pollutants of aquatic ecosystems. They are discharged into wastewater from industrial branches, such as the dye manufacturing, textile finishing, paper, leather, plastic, photo degradation, biodegradation and oxidizing agents. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms. Therefore, the removal of textile dyes from water and waste-water is one of the most significant environmental problems. Among several chemical and physical methods, adsorption is one of the most effective and popular techniques for the removal of dyes from water^[1-4]. Certain natural materials such as banana pith^[5], rice husk^[6], papaya seeds^[7], orange peel, banana peel^[8], Caulerparacemosa var. cylindracea^[9], Caulerpalentillifera^[10-12] and Posidoniaoceanica^[13-19] have been used for the treatment of wastewaters .

The present study aims to present the usage of a natural environmental waste, Ceiba Pentandra bark for the removal of acid red 114 dyes . It is known that the Ceiba Pentandra a bark which is a soft wood and their usage in the very limited. The present study offers an alternative evaluation of the waste wood. Actually, the present study aims to evaluate a natural environmental waste as a useful material for cleaning another waste from the

environment. Effective parameters such as adsorbent dosage, initial dye concentration, pH, kinetics and thermodynamic studies were carried out in the present paper.

EXPERIMENTAL SECTION

2.1 Adsorbate

Acid Red 114, supplied by Hindustan Ciba-Geigy, Mumbai was used as an adsorbate. The chemical formula of Acid Red 114 is $C_{37}H_{28}N_4Na_2O_{10}S_3$ with molecular weight of 830.8g/mol. The chemical structure of the dye is shown in the Fig.1. Deionized water was used to prepare all the reagent and solutions.

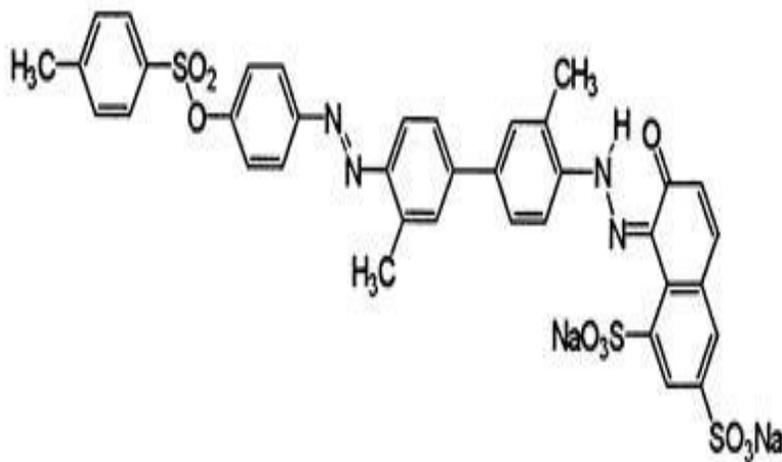


Fig. 1 Structure of Acid Red -114

2.2 Preparation of Activated Carbon:

Ceiba Pentandra wood waste (CPAC) was used as a precursor for the preparation of activated carbon using phosphoric acid activation method. The wood was cut into small pieces of 2 to 3 cm in size, dried in the sun light for 10 to 20 days to remove moisture from the material. Then the dried material was soaked with phosphoric acid in the ratio of 1:1 at $80^{\circ}C$ for 48 hours. After 48 hours the material was crushed well using mortar and this crushed material was kept aside for 12 hours. Then the material was washed well with hot water until a neutral pH is attained. The neutralized material was dried at $110^{\circ}C$ for 24 hours. The dried mass was subjected to carbonization process at $800^{\circ}C$ for about 10 minutes. The material was followed by thermal activation at $400^{\circ}C$ for about 10 minutes in technical nitrogen, N_2 99.99 purity. The final product was grounded well and used and stored in air-tight container for further adsorption studies. The characterization details have already been explained in the previous paper (20).

2.3 Adsorption studies:

Various batch adsorption studies were carried out in 50 mL of dye solution with CPAC as adsorbent at a constant temperature of 303 K. The experiments were carried out to investigate the effects of initial AR -114 concentration (20, 40 & 60 mg/L), adsorbent dosages (100 mg) with an optimum pH of 6 in the mechanical shaker. The experiments were performed by changing one of the parameters at a time while the other parameters were fixed. The AR 114 content in solution before and after adsorption was measured by UV/visible spectrophotometer at its maximum wavelength of 524 nm. The concentration retained in the adsorbent phase (q_e , mg/g) and percentage of dye removal was calculated by using eqs (1) and (2).

$$q_e = \frac{(C_0 - C_e)V}{W} \text{----- (1)}$$

$$\text{Percentage of dye removal} = \frac{(C_0 - C_t)V}{C_0} \times 100 \text{----- (2)}$$

C_0 and C_e are the initial and equilibrium concentration of the dye in mg/L, V is the volume of the solution in L, W is the weight of the adsorbents in mgs and C_e is the concentration of the dye at equilibrium.

3. Kinetics and Isothermal studies:**3.1 Kinetics studies:**

The term “modeling” in physicochemical processes study is quite general and ranged from simple fitting of the experimental data [21] to detailed models based on basic principles [22]. Especially, in the field of adsorption, quite different modeling approaches can be used. The typical experimental setup includes an initial concentration of adsorbate (C_0), a beaker volume (V) and a mass of adsorbent (M). The amount of adsorbate adsorbed on the adsorbent (per unit adsorbent mass) is expressed as “ q ” and evolves from $q = 0$ to an equilibrium value $q = q_e$, which corresponds to the thermodynamic equilibrium between q_e and C_e

$$C_e = C_0 - M \left(\frac{q}{V} \right) \text{-----} (3)$$

The modeling issue is focused on the quantitative description of the evolution curve $q(t)$, which is deduced by measuring experimentally the evolution of adsorbate concentration $C(t)$ from C_0 to C_e . The most extensively used models are typically those with the least physical background. The adsorption kinetic models which have been employed in green adsorption are:

(i) The so called Lagergren equation [23] (or pseudo-first order model) has the following differential form:

$$\frac{dq}{dt} = k_1 (q - q_e) \text{-----} (4)$$

After integration of Equation (4):

$$q = q_e (1 - e^{-k_1 t}) \text{-----} (5)$$

The fitting to the experimental data can be performed using linear (i.e., using $\ln(1 - \frac{q - q_e}{q_e})$) or nonlinear [i.e., using directly Equation (4)] techniques. The model is purely empirical and the only physical parameter used is the equilibrium value (q_e). The only fitting parameter is k_1 . Typically, instead of using the experimental value of q_e and find k_1 from fitting, both k_1 and q_e are found from fitting and then q_e is compared to the experimental one.

(ii) The second model used is also empirical and it usually gives better fitting results than the first model. It is called pseudo-second order model [24] and has the following governing expression:

$$\frac{dq}{dt} = k_2 (q - q_e)^2 \text{-----} (6)$$

After integration of Equation (6)

$$q = \frac{k_2 q_e t}{1 + k_2 q_e t} \text{-----} (7)$$

There are several ways to transform the relation to a linear one in order to use linear fitting techniques. The most usual is:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \text{-----} (8)$$

As in the case of the first-order model, the fitting can be done either for k_2 alone using the experimental value of q_e or for the pair (k_2, q_e). The above models are used to find the coefficients k_1 and k_2 , which are regarded as pure fitting parameters and subsequently depends on operational variables as C_0 .

(iii) The third model is the so-called Elovich model [26] which assumes a logarithmic a time dependence of the adsorbed species quantity. The governing equation in its linearized form is:

$$q = \frac{\ln(\alpha\beta) + \ln t}{\beta} \text{-----} (9)$$

Where the constants α , β are called initial adsorption and desorption rate constants, respectively. Alternatively, α is related to the rate of chemisorption and β to the surface coverage [27]. This equation has typically a poor success in fitting the data but, despite this, it is used extensively in the literature.

(iv) Another model is the intraparticle diffusion model. This model is based on the assumption that the adsorption kinetics is dominated by the intraparticle diffusion mechanism [28]. The corresponding equation can be derived for linear isotherm and constant adsorbate concentration, but it is used in literature for much more general conditions:

$$q_t = k_i t^{1/2} + C_i \text{-----} (10)$$

Where $(\text{mg/g h}^{1/2})$ is the rate parameter of stage which is obtained from the gradient of the versus $t^{1/2}$ straight line. is the boundary layer effect which means that the larger the intercept, the greater the contribution of the surface sorption in the rate-controlling step [29]. The intra particle diffusion should occur if the versus $t^{1/2}$ is linear.

3. 2. Adsorption Capacity:

The key-point of each adsorbent material is its adsorption capacity. Three isotherm models order to fit the experimental equilibrium data's,

3.2.1 Langmuir isotherm model is based on assumption that a saturated monolayer of adsorbate molecules is present on the adsorbent surface, the adsorption energy is constant and there is no migration of adsorbate molecules in the surface plane when maximum adsorption capacity occurs [30]. The linear transformation of the Langmuir equation is given in equation (11),

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \text{-----} (11)$$

Where q_e (mg/g) is the equilibrium concentration of pollutant in the solid phase; q_m (mg/g) is the maximum amount of adsorption; k_L (L/mg) is the Langmuir adsorption equilibrium constant.

3.2.2 Freundlich isotherm is used for determining the applicability of heterogeneous surface energy in the adsorption process [31]. The empirical Freundlich equation is expressed as,

$$q_e = k_f c_e^{1/n} \text{-----} (12)$$

Where $k_f(\text{mg}^{1-1/n} \cdot \text{L}^{1/n}/\text{g})$ is the Freundlich constant representing the adsorption capacity; n (dimensionless) is the constant depicting the adsorption intensity. The amount of total uptake of pollutant in equilibrium (q_e) was calculated using the mass balance equation (2).

3.3.3 Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption [32]. Linear form of Temkin equation is expressed as

$$q_e = B \ln A + B \ln C_e \text{-----} (13)$$

Where $B = RT/b$, b is the Temkin constant related to heat of sorption $q_e(\text{mg g}^{-1})$ and $C_e(\text{mg L}^{-1})$ are the amount of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively. Therefore, a plot of q_e versus $\ln C_e$ enables one to determine the constants A and B .

RESULTS AND DISCUSSION**4.1 FTIR and SEM Analysis:**

Figure (2) is FTIR image of Acid Red 114 and CPAC before adsorption. FTIR images showed that the most prominent peaks in the spectrum originate from OH⁻ vibrations, CH₂ and CH₃ asymmetric and symmetric stretching vibrations. The peaks at (1155-1103 cm⁻¹) region related to lignin. Therefore, it is possible the cellulose, hemicelluloses as well as lignin, having many OH⁻ groups in their structure, make up most of the absorbing layer. Two strong peaks observed in the range between 2963 and 2853 cm⁻¹ are assigned to asymmetric C-H bands and symmetric C-H bands, respectively. Stretching vibration band around 1700 cm⁻¹ is assigned to carbonyl C=O group present in aldehyde, ester, ketone and acetyl derivatives. The strong band at 1600 cm⁻¹ may be due to C=C band. These specific functional groups enhance adsorption properties [33].

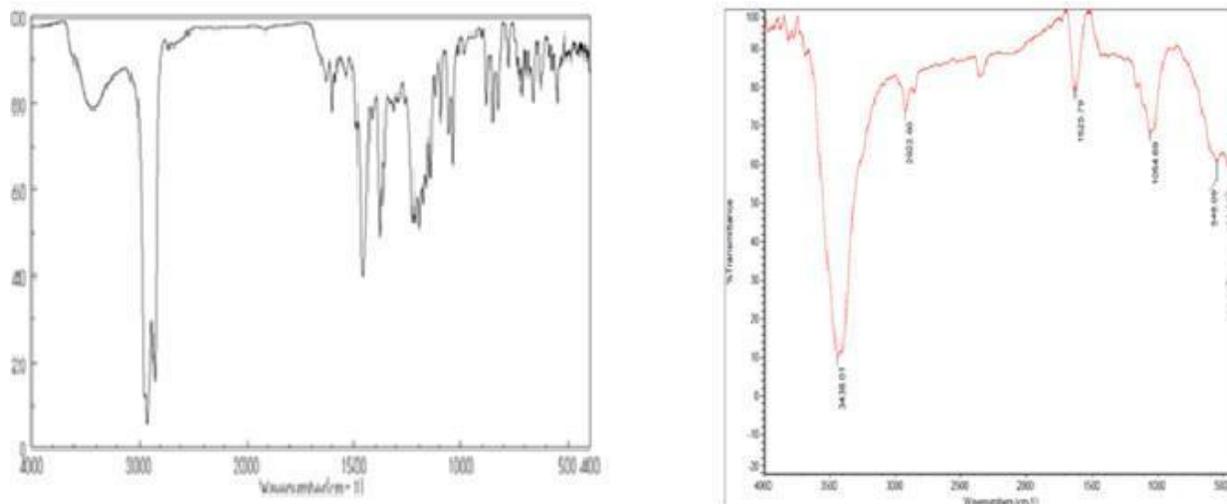


Figure 2: FTIR spectrum of Acid Red 114 and CPAC

SEM morphology:

It is widely used to study the morphological features and surface characteristics of the adsorbent materials. Typical SEM photographs are shown in Fig. 3. It reveals that the CPAC has a rough surface with more porous and caves like structure and it is supported with FTIR spectra as shown in Fig.2.

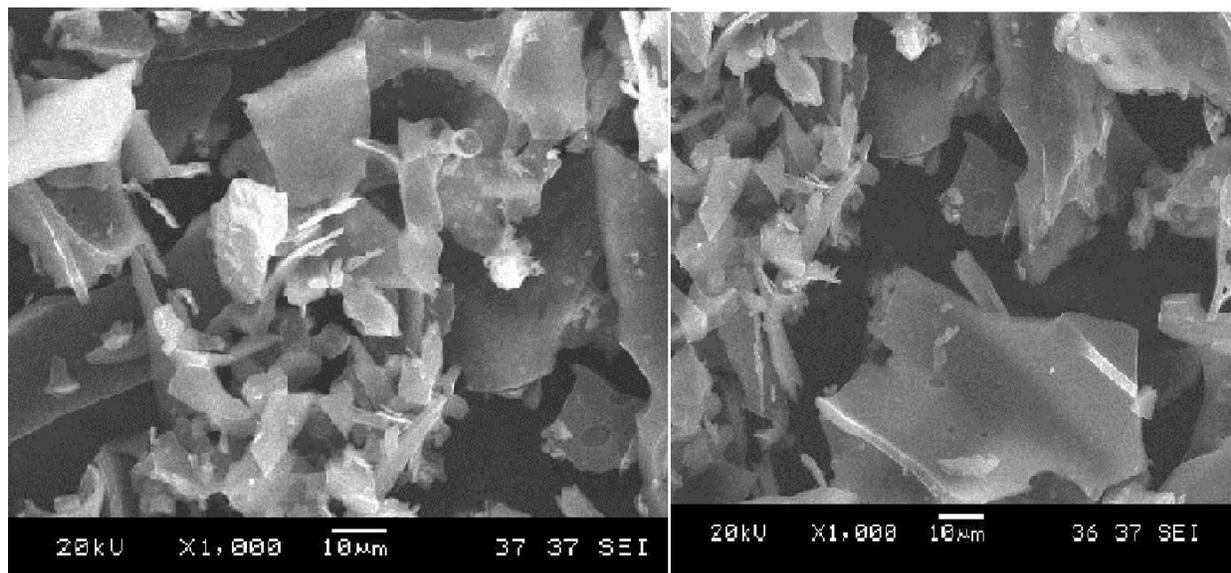


Fig 3. SEM images of CPAC in presence of N₂ atmosphere at 800⁰C

4.2. Effect of Initial Dye Concentration and Contact Time:

It is well-known that the dye concentration plays an important role in the adsorption process, which can impel strongly the solute molecules to overcome mass transfer resistance between the liquid and the solid phases [34]. Figure 4 show the effect of different initial dye concentrations (20, 40 & 60 mg/L) on the adsorption capacity of CPAC. The percentage removal of the dye decreases with increasing initial concentrations of dye for the adsorbent. Moreover, the CPAC had the capacity to remove up to 90% for 20 ppm, at an equilibrium time of 220 minutes. When the concentration increased from 20 to 40 ppm the adsorption decreased to 85% and for 60 ppm the adsorption further decreased to 83%. Even the equilibrium time of the dye also varied and increased to 240 minutes. The reasons for the decrease in the percentage of dye removal is, at low concentration the ratio of dye molecules to the number of available adsorption sites on adsorbent may be limited and consequently the adsorption process may mainly occur on the exterior surface of the activated carbon. The rate of adsorption is fast in this stage, resulting in short time. With an increase in the amount of dye molecules, the situation changes and lots of dye molecules are probably adsorbed by the interior surface of adsorbent by pore diffusion after the adsorption of the exterior surface reaches saturation.

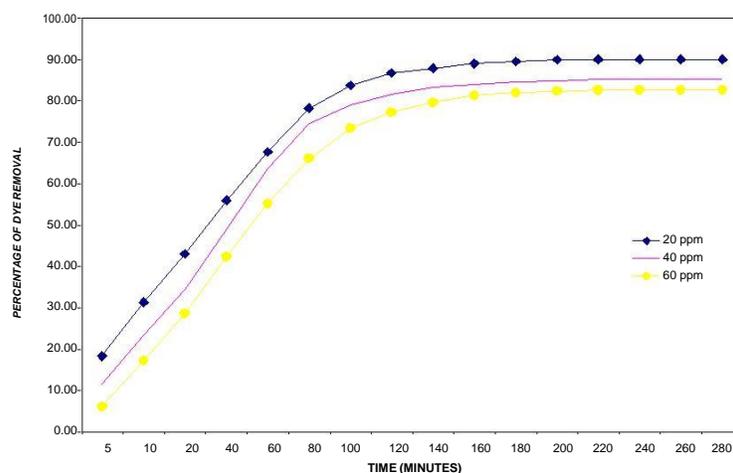


Fig (4) Effects of initial concentration on amount of Acid Red 114 adsorbed at different contact times (experimental conditions: adsorbent dosage 100 mg/ mL, temperature 303 K and initial pH 6 without adjustment) CPAC

4.3 Effect of pH:

The pH of the solution plays an important factor in the adsorption process, which may alter the surface properties of the adsorbent as well as the degree of ionization of the dye. The influence of pH on the dye adsorption onto CPAC was studied for the dye concentration (20 mg/L) and amount of adsorbent (100 mg/50 mL) in the pH range of 2–11. The results are shown in Figure 5. The amount of dye adsorbed and the percentage removal efficiency of Acid Red 114 on adsorbent decreased as the pH of aqueous solution increased from 2 to 11. There was a sudden decrease in the percentage of dye removal when pH reached 6 and the percentage removal further decreased as the pH increased. This is due to the electrostatic repulsion of the negative charge ions in the outer surface of the dye and the pH concentration in the basic medium. The protonated groups of activated carbon were mainly carboxylic group ($-\text{CO}-\text{OH}^+$) and phenolic (OH^+) [35,36]. The deprotonated groups were probably the sulphonated group of $-\text{SO}_3^-$. The strong electrostatic attraction favored the adsorption of dye onto CPAC resulting in the high removal efficiency of dyes.

When the solution reached the pH 5, the sulphonated group of the acid red 114 were almost protonated ($-\text{SO}_3\text{H}$), therefore the dye becomes neutral. Furthermore, the protonation of nitrogen atoms especially those not involved in aromatic systems was also probable [37]. The reactive dye molecules, therefore, are neutral or positive charged in acidic solution. Subsequently, the attraction between dye and CPAC decreased, resulting in the slightly decreasing of dye removal [38]. The low dye removal at highly basic solution could be due to the strong repulsion interaction

between the negatively charged CPAC and the deprotonated acid dye molecules. At the same time, hydroxide ion concentration increased with the incremental solution pH, and it could be adsorbed preferentially on the surface of the activated carbon. There was competition between OH^- and dye ions for positively charged adsorption sites. These results could be decreased evidently the removal efficiency of acid dye removal.

5. Adsorption Isotherms

The Langmuir, Freundlich and Temkin are the most commonly used models in literature describing the non-linear equilibrium between amounts of dye adsorbed on the acid treated adsorbents. The adsorption isotherm for the removal of Acid red 114 was studied using an adsorbent dosage of between 100 mg/50 ml at an initial concentration variation between 5-150 ppm. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent (q_e) and the solute concentration for the solution at equilibrium (C_e).

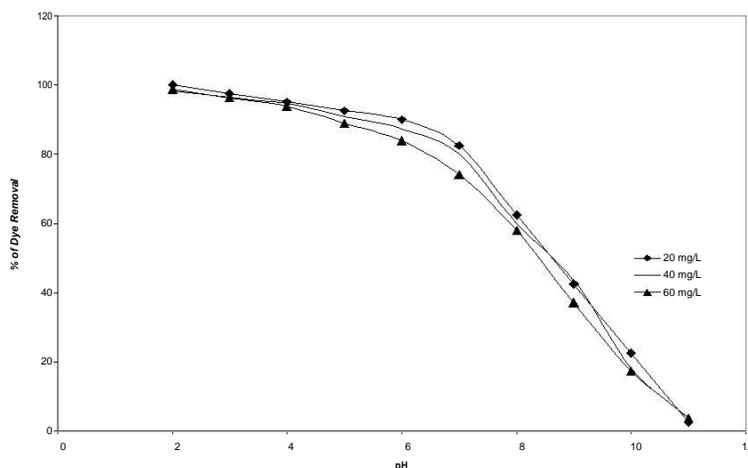


Fig 5. Effect of pH in the removal of Acid red 114 on CPAC

5.1 Langmuir Adsorption Isotherm:

The Langmuir adsorption isotherm has been traditionally used to quantify the performance of different adsorbent. The Figure 6 was employed to determine the value of Q_0 (mg/g) and K_L (L/mg) from slope and intercept, respectively. The data obtained with the correlation coefficients (R^2) was listed in Table 2. The Q_0 value increased with increase in temperature and the values were 60.91, 64.43 and 69.45 $\text{mg}\cdot\text{g}^{-1}$ for CPAC. The data related to the equilibrium obeyed well with the Langmuir models. The R^2 values were 0.9925, 0.9914 and 0.9939 for the respective temperatures. The R_L values also show that they undergo monolayer of adsorption. There are numerous biomass material which are used as precursor to develop activated carbon and their comparison were shown in the table 3.

Table 1 Comparison of adsorption capacities on activated carbon from waster biomass materials

Dye	Adsorbent	Q_0 mg.g-1	Reference
Basic blue 9	Apricot shell	4.81	[39]
Basic blue 9	Walnut shell	3.53	[39]
Basic blue 9	Coconut coir	15.59	[40]
Reactive Orange	Sugare Pith	3.48	[41]
Direct blue 106	Pomegrante peel	58.14	[42]
Acid red 114	Gingelly seed shell	102.24	[40]
Acid red 114	Cotton seed shell	158.85	[40]
Acid red 114	CPAC	60.91 (303K) 64.43 (318K) 69.45 (333K)	This work

5.2 Freundlich Adsorption Isotherm:

The values of the Freundlich constants (K_F) and (n), the correlation coefficients (R^2) are obtained from the Figure 7. The values of K_F are 5.33, 8.52 and 12.22 $\text{mg}\cdot\text{g}^{-1}$ at 303, 318 and 333 K, respectively for CPAC which shows that

they have high adsorption capacity. Furthermore, the values of n are greater than 1, reflecting the favorable adsorption for the adsorbent. It is evident from these data that the surface of the adsorbent is made up of heterogeneous adsorption patches, R^2 values are also compared (Table 3). From the results it was clearly observed that both models were well suited for adsorption of AC 114 on CPAC, but the regression factor as well as the calculated and experimental values correlates more correctly with the Langmuir values, on this basis it could be concluded that, AR 114 form monolayer on the surface of CPAC.

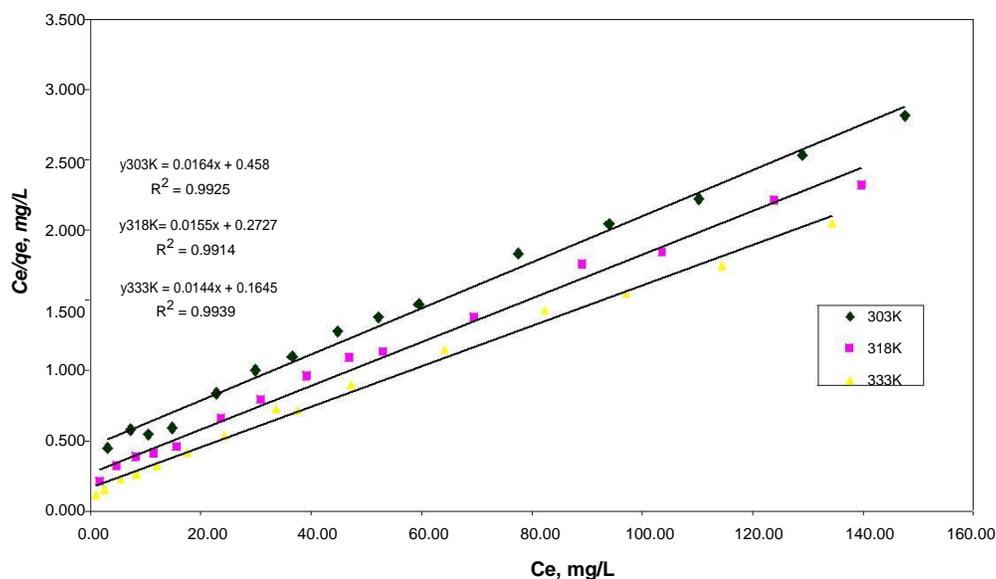


Figure 6 .Langmuir isotherm for adsorption of acid red 114 on CPAC (experimental conditions: adsorbent dosage 100 mg/50 mL, dye concentration =20 mg/L and initial pH=6 without adjustment and temperature, 303K,318K and333K)

Table 2. Estimated parameters of Langmuir isotherms for adsorption of Acid Red 114 on CPAC at an adsorbent dosage of 100 mg/50 mL

Temperature K	Q^0 mg/g	K_L l/mg	R^2
303	60.90621	2.183627	0.9925
318	64.43401	3.667452	0.9914
333	69.44913	6.07778	0.9939

Table 3. Estimated parameters of Freundlich isotherms for adsorption of Acid Red 114 on CPAC at an adsorbent dosage of 100 mg/50 ml

Temperature K	n	K_f	R^2
303	2.05946	5.33301	0.9376
318	2.3882	8.5223	0.9455
333	2.66922	12.2198	0.9454

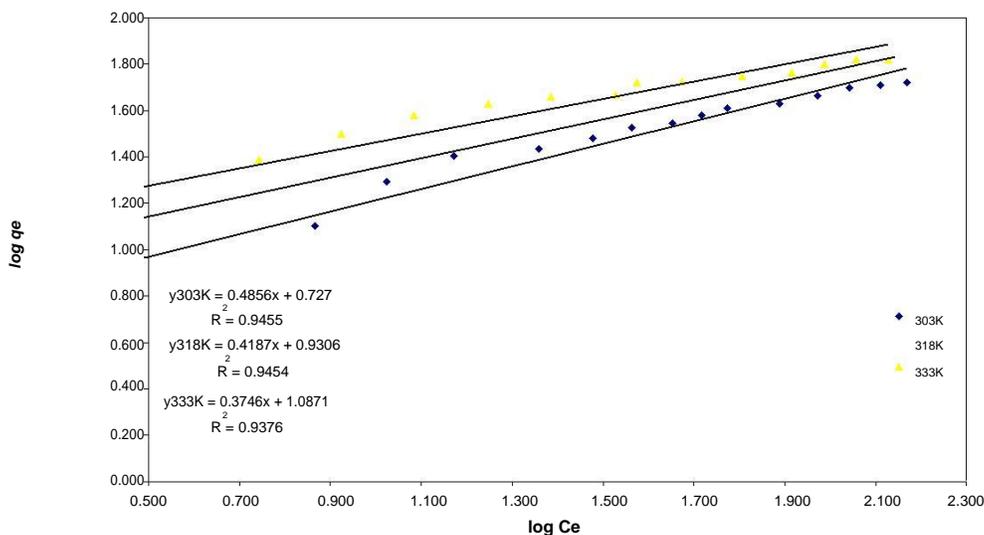


Figure 7. Freundlich isotherm for Acid red 114 adsorption onto CPAC (experimental conditions: adsorbent dosage 100 mg/50 mL, dye concentration =20 mg/L and initial pH=6 without adjustment and temperature, (303K, 318K and 333K))

5.3 Temkin isotherm:

Temkin isotherm constants were evaluated from the plot of $\ln C_e$ versus q_e . Fig. 8, and the value of K_T , the equilibrium constant, was found to increase from 0.46 to 1.76 when the temperature increased from 303 K to 333 K. Thinakaran et al.^[40] have reported a similar trend in their studies on removal of dye AR114 by activated carbons from seed shells. Table 4 gives a clear data for Temkin isotherm plot. The potential of the CPAC for the Acid Red 114 as seen from the Temkin isotherm showed a reasonable fit with a linear coefficient of determination R^2 values.

Table 4. Estimated parameters of Temkin isotherms for adsorption of Acid Red 114 on CPAC at an adsorbent dosage of 100 mg/50 ml

Temperature K	K_T	R^2
303	0.4558419	0.9895
318	0.8871749	0.9859
333	1.7162459	0.9911

6. Sorption Kinetics:

The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid–solution interface including the diffusion process. The models are explained as follows,

6.1 Pseudo-first-order:

The data obtained were analyzed with the Lagergren pseudo -first order kinetic model. The plot of $\log (q_e - q_t)$ versus t is shown in Figures 9. The values of k_1 and q_e were determined from the slope and intercept respectively as presented in Table 5. The result indicated that the data were not strongly correlated with R^2 ranging from 0.9929, 0.9954 and 0.9982 for the dose and or the concentration of 20ppm. Also the theoretical values obtained from the equation did not yield reasonable values. Thus the rate of removal of Acid Red 114 from solution into the CPAC does not follow the pseudo-first-order equation. Indeed this is the general trend in most adsorption studies reported in the literature ^[43-46]

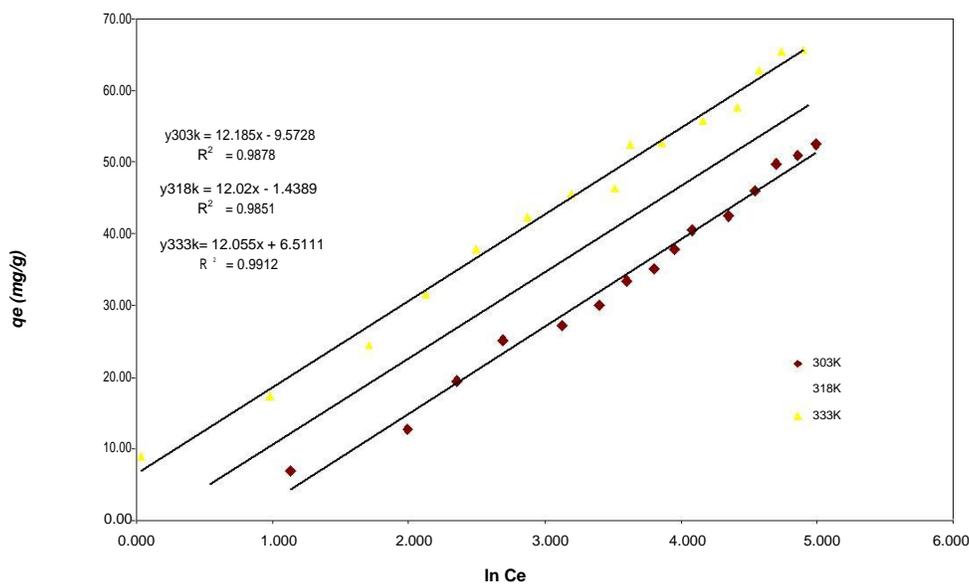


Figure 8. Temkin Isotherm for Acid red 114 adsorption onto CPAC (experimental conditions: adsorbent dosage 100 mg/50 mL, dye concentration =2 mg/L and initial pH=6 without adjustment and temperature, (303K,318K and 333K)

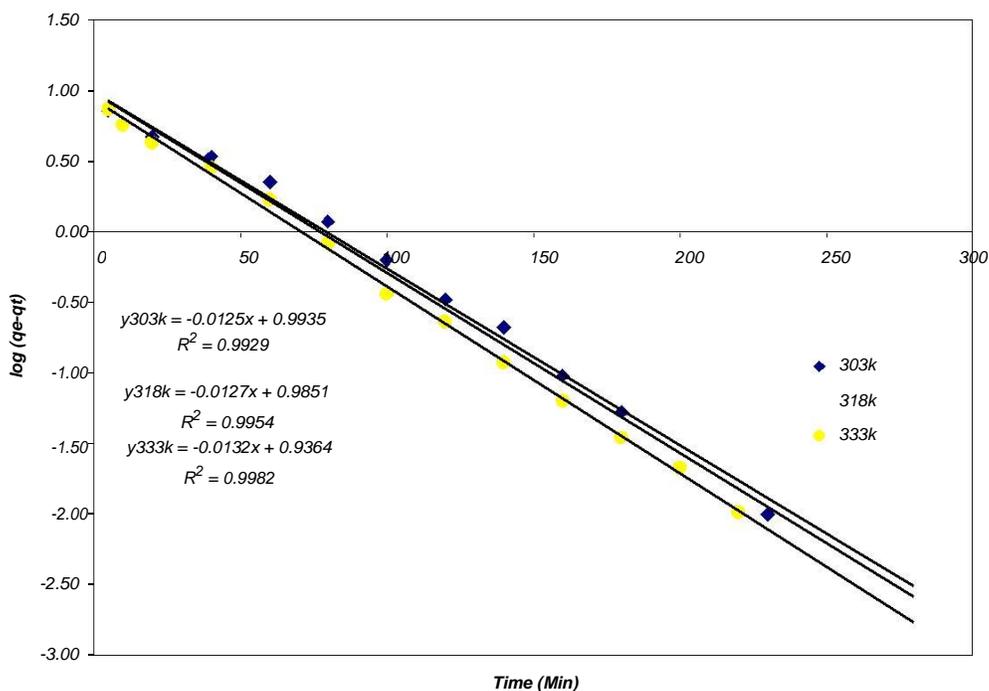


Figure 9. Pseudo-first order kinetics for the adsorption of AR114 dye onto CPAC (experimental conditions: adsorbent dosage 100 mg/50 mL, dye concentration =20 mg/L and initial pH=6 with adjustment of temperature 303k,318k and 333k)

6.2 Pseudo-second-order:

The results obtained when the data was subjected to the Pseudo-second-order equation are shown in Figures 10 and the values are tabulated in Tables 5 which corresponding to the dosage and concentration respectively. The data

applied showed very high correlation coefficients value. The calculated values of q_e were also close to the experimental data. This confirms that the adsorption process followed the pseudo-second-order model. A similar phenomenon has been observed in the adsorption of methylene blue onto rice husk [47], and methylene blue onto activated carbon prepared from rattan sawdust [48].

6.3 Elovich model:

The Elovich equation is widely used to describe the chemisorptions of gases on solid surfaces. The dye adsorption fits the Elovich model. The correlation coefficients values obtained, R^2 , were between 0.9677, 0.966 and 0.9548, indicating that the Elovich expression could fit properly the experimental data. The applicability of the simple Elovich equation for the present kinetic data is generally in agreement with other researcher's results that the Elovich equation was able to describe properly the kinetics of acid dye adsorption on activated carbons prepared from CPAC. The similar behavior of the trend was also absorbed and reported by Thinakaran et al [40]. The values of α , β and R^2 is reported in the table 5.

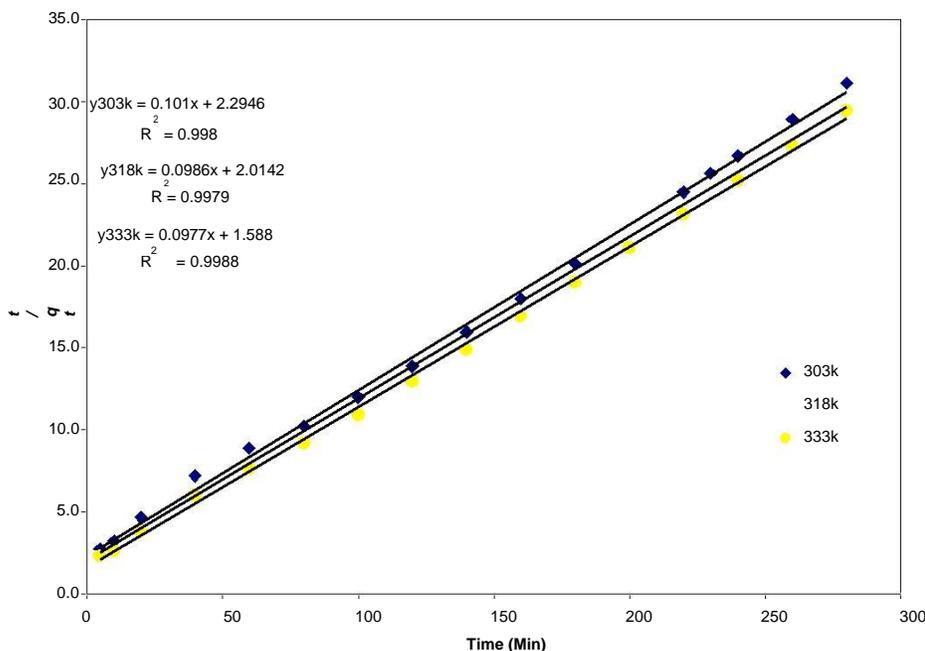


Figure 10. Pseudo-second order kinetics for the adsorption of AR114 dye onto CPAC (experimental conditions: adsorbent dosage 100 mg/50 mL, dye concentration =20 mg/L and initial pH=6 with adjustment of temperature 303k,318k and 333k)

Table 5. Isotherm Parameters for the adsorption of Acid red 114 onto CPAC

Dye	Temperature K	Pseudo first order kinetics		Pseudo second order kinetics				Elovich Model		
		kL min ⁻¹	R ²	q _e ,mgg ⁻¹	K ₂ mgg ⁻¹ min ⁻¹	h, mgg ⁻¹ min ⁻¹	R ²	α, mgg ⁻¹ min ⁻¹	β gm ⁻¹	R ²
ACID RED 114	303	0.02882	0.9929	9.9014	0.4358	0.4358	0.998	2.8464	0.26	0.9677
	318	0.02935	0.9954	10.1394	0.01959	0.4965	0.9979	3.0984	0.26	0.968
	333	0.03044	0.9982	10.2346	0.01516	0.6297	0.9988	3.4831	0.27	0.9548

6.4 Intra Particle diffusion:

The intra-particle diffusion was also involved for adsorption of Acid red 114 onto CPAC as shown in Figure 11. Previous studies showed that such plots may present a multilinearity, which indicates that two or more steps occur. The first sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intra-particle diffusion is rate limited. The third portion is final equilibrium stage, where the intra-particle diffusion starts to slow down due to extremely low concentration in the solution [49]. The diffusion model plot shown in Figure 11 suggests two stage adsorption process, surface adsorption and intra-

particle diffusion. The first portion of the plot indicates boundary layer effect, i.e., surface adsorption while the second

linear portion is due to the intra-particle/pore diffusion within the pores of the carbon [50]. The slope of the linear portion indicated the rate of the adsorption. The lower slope corresponds to a slower adsorption process. Figure 11 shows that the slope of the first portions (0.4693, 0.4534 and 0.4365 for CPAC, respectively) is greater than second portions, hence it may be concluded that the uptake is initially faster and then slows down. It is likely that initially the adsorbate is transported to the macropores and mesopores and then it is slowly diffused into micropores [51] and also extremely low dye concentration left in the solution. These suggest that in the adsorption of Acid Red 114 over the CPAC was controlled by external mass transfer followed by intra particle diffusion mass transfer.

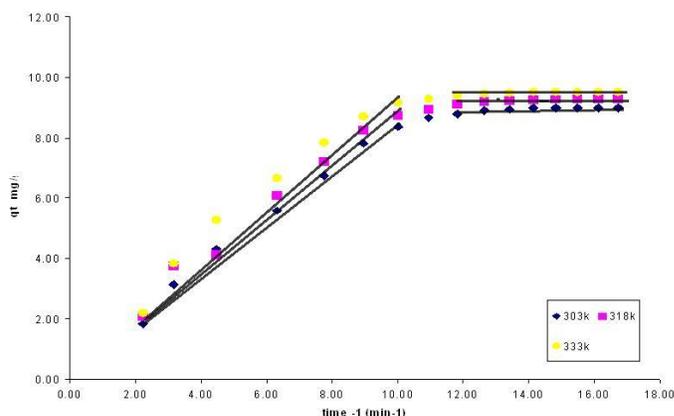


Figure 11. Intraparticle diffusion kinetic model for Acid Red 114 adsorption on CPAC (experimental conditions: adsorbent dosage 100 mg/50 mL, Dye concentration 20 mg/L, temperature 303 K, 318 K and 333 K and initial pH 6 without adjustment)

6.5 Thermodynamic Study

Experiments were conducted at different temperatures (303, 318 and 333 K). The thermodynamic parameters, namely, change in standard enthalpy (ΔH), standard entropy (ΔS), and standard Gibbs free energy (ΔG) for the present system, were determined using following expressions; Thermodynamic parameters can be calculated from the following equation-

$$\Delta G = -RT \ln K_0 \quad \text{-----(17)}$$

$$K_0 = C_{\text{solid}}/C_{\text{liquid}}$$

$$\log K_0 = \Delta S / (2.303RT) - \Delta H / (2.303RT) \quad \text{-----(18)}$$

The ΔH and ΔS values obtained from the slope and intercept of Van't Hoff plots. The values of ΔH , ΔS and ΔG were calculated. Positive values of ΔH and ΔS suggest endothermic reaction, while the negative values of free energy change (ΔG) indicate that the adsorption is spontaneous (Table 4). The negative values of ΔG indicated the spontaneous nature of the adsorption process. The magnitude of ΔG also increased with increasing temperature indicating that the adsorption was more favorable at higher temperatures. The adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system [52-53]

Table 4 : Thermodynamic Parameters for the adsorption of Acid Red 114 dye onto CPAC

TEMP (K)	ΔH J/K/Mole	ΔS J/K/Mole	ΔG J/K/Mole
303	5.1885	96.2985	-1695.2
318			-3025.2
333			-4590.9

CONCLUSION

The result of the work is summarized as follows,

- *Ceiba Pentandra* wood waste (CPAC) is a promising adsorbent for the removal of the Acid red 114 from the water. About 100 mg of the CPAC removes 90% of the dye with the dye concentration of 20 ppm.
- The optimum pH adopted for the dye removal was 6 and their p_{zpc} was 5. The dye reached the equilibrium time within 240 minutes.
- The experimental data produced perfect fit for Langmuir isotherm showing that the surfaces of the adsorbents were homogeneous, specific and uniform in nature for both the adsorbents.
- The values also had a good agreement with Freundlich isotherm model.
- The mechanism of the dye –CPAC interactions is likely to be very complicated involving a wide range of sites differing in a number of aspects including energy consideration.
- The adsorption followed Pseudo second order kinetics for CPAC with the interaction over the first hour.
- Intra particle model of the dye followed 2 step mechanism processes.
- The thermodynamic parameters show that the reaction is endothermic in nature and the negative value of ΔG shows that the reaction is spontaneous for the adsorbent.
- The above results clearly show that both the adsorbent have almost the same behavior in both kinetics and isothermal studies. They followed Pseudo second order model, Langmuir isotherm and are exothermic in nature.

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