

# REMOVAL OF ACID DYE FROM AQUEOUS SOLUTION USING ACTIVATED CARBON PREPARED FROM *ALBIZIA AMARA POD* SHELL: DYNAMIC, EQUILIBRIUM AND THERMODYNAMICS

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## ABSTRACT

The efficiency of carbonaceous adsorbent prepared from *Albizia amara pod* shell by phosphoric acid process was tested in removing Acid Red 2(AR 2). The adsorption rate of AR 2 on *Albizia amara pod* shell waste was maximum at pH 2 and followed second order kinetic model. The treatment given by Boyd and Reichenberg was employed to identify whether the ongoing process is particle diffusion or film diffusion. Thermodynamic parameters such as enthalpy change ( $\Delta H^\circ$ ), free energy change ( $\Delta G^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were studied, and the adsorption process of AR 2 was found to be endothermic and spontaneous.

**Keywords:** *Albizia amara pod* shell waste, Activated Carbon, Acid Red 2, Kinetics, Isotherm, Particle diffusion, Film diffusion.

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## INTRODUCTION

It is reported that over 1, 00,000 commercially available dyes exist and the global annual production of synthetic dyes is more than  $7 \times 10^5$  metric tones.<sup>2</sup>The discharges of dyes, into water bodies after usage in large quantities by many industries cause carcinogenic and toxic effects and their treatment cannot depend on biodegradation alone<sup>1</sup>. Therefore, extensive research has been conducted to find an effective and efficient alternative for the removal of dyes.<sup>1</sup>AR 2 is one such effluent which causes various disorders when present in aqueous solution. Hence the treatment of waste water containing Acid Red 2 is a challenging problem.

For this process, several low cost carbon and non-conventional adsorbents were used as activated carbons<sup>3</sup>. The adsorbents were prepared by *Jatropha Curcas stem*<sup>4</sup>, Cashew nut sheath<sup>5</sup>, *Jatropha curcas seed shell*<sup>6,7</sup>, Rice hulls<sup>8</sup>, *Balsamodendroncaudatum*<sup>9</sup>, *Feronia limonia*<sup>10</sup>, eucalyptus bark<sup>11</sup> etc. In the present work, for the adsorption of Acid Red 2 the low cost, high value activated carbon prepared using *Albizia amara pod* shell waste was used. Three simplified kinetic models including pseudo first order, pseudo second order and Elovich equations were used to describe the adsorption process.

## EXPERIMENTAL

### Preparation of activated carbon

*Albizia amara pod* shell waste is collected and it was dried and cut into small pieces, the pieces were then impregnated in a phosphoric acid solution of known concentration for 24 hours. Then the resultant mass was washed with excess quantity of water and dried at 110 °C for 1 hour. Carbonization of the sample was carried out at 750 °C in a temperature programmable furnace under N<sub>2</sub> atmosphere. At the end of

carbonization, the material in the furnace was left to cool down to ambient temperature under the same N<sub>2</sub> flow rate. The carbon sample thus obtained was washed with pure distilled water and dried in the oven at 120 °C and then finely grinded.

### Kinetic Models

In order to investigate the mechanism of sorption and potential controlling steps such as mass transport, several kinetic models were tested including the pseudo first order kinetic model, the Elovich model and the pseudo second order kinetic model for a batch contact time process, where the rate of sorption of dye on to the given adsorbent is proportional to the amount of dye sorbed from the solution phase.

#### Pseudo First Order Kinetic Model

A simple kinetic analysis of adsorption, the pseudo first order kinetics and its integrated form, is given by Lagergren<sup>12</sup>.

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

Where  $k_1$  is the pseudo first order rate constant. A plot of  $\log(q_e - q_t)$  vs time enables calculation of the rate constant  $k_1$  and  $q_e$  from the slope and intercept of the plot.

#### Elovich Model

The Elovich or Roginsky – Zeldovich equation<sup>13</sup> is generally expressed as follows:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (2)$$

On integrating this equation for the boundary conditions,

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (3)$$

Where,  $\alpha$  and  $\beta$  are the initial dye adsorption rate (mg/g) and desorption constant (g/mg) respectively are obtained from the slope and intercept of linear plot of  $q_t$  vs  $\ln t$ .

#### Pseudo Second Order Kinetic Model

To describe the dye adsorption, the modified pseudo second order kinetic equation<sup>14</sup> is expressed as-

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where,  $k_2$  is the pseudo second order rate constant. A plot of  $t/q_t$  vs  $t$  enables calculation of the rate constant  $k_2$  which in turn is used to calculate the initial sorption rate  $h$  as follows-

$$h = k_2 q_e^2 \quad (5)$$

#### Adsorption Thermodynamics

Any chemical system tends to attain a state of equilibrium from one of non-equilibrium. The thermodynamic parameters, which characterize the equilibrium of the system, are the Gibbs free energy change  $\Delta G$ , the enthalpy change  $\Delta H$  and the entropy change  $\Delta S$ . These parameters were determined using the following relations<sup>15</sup>

$$K_c = C_{Ae}/C_e \quad (6)$$

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

$$\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}$$

Where  $K_c$  is the equilibrium constant,  $C_{Ae}$  is the solid phase concentration at equilibrium,  $C_e$  is the residual concentration at equilibrium,  $R$  is the gas constant in J/mole and  $T$  is the temperature in Kelvin.

## RESULTS AND DISCUSSION

### Optimum pH for adsorption

The effect of pH for the adsorption of ACID RED 2 on to activated carbon over a pH range of 2 to 11 is represented in Fig. 1. The uptake of AR 2 decreased when the solution pH was increased from 2 to 11. The uptake of AR 2 by activated carbon was increased from pH 2 to 4 and then decreased. The interaction between the sorbate and sorbent is affected by pKa of dye as well as the isoelectric point (pHpzc) of the adsorbent<sup>16</sup>. The pKa value of AR 2 is 3.2. Below the isoelectric point (pHpzc = 8.2), the electrostatic repulsion between the adsorbed molecules is minimized, resulting in a maximum adsorption. At pH below 8.2, the surface of the adsorbent may acquire a positive charge leading to an increased anionic dye adsorption due to electrostatic attraction. At pH above the pH<sub>PZC</sub> the adsorbent surface acquires a negative charge, which repels the negative anionic dye molecules. On increasing the pH, the added NaOH increases the ionic strength, which also makes more competition for adsorption sites, hence, the adsorption decreases.

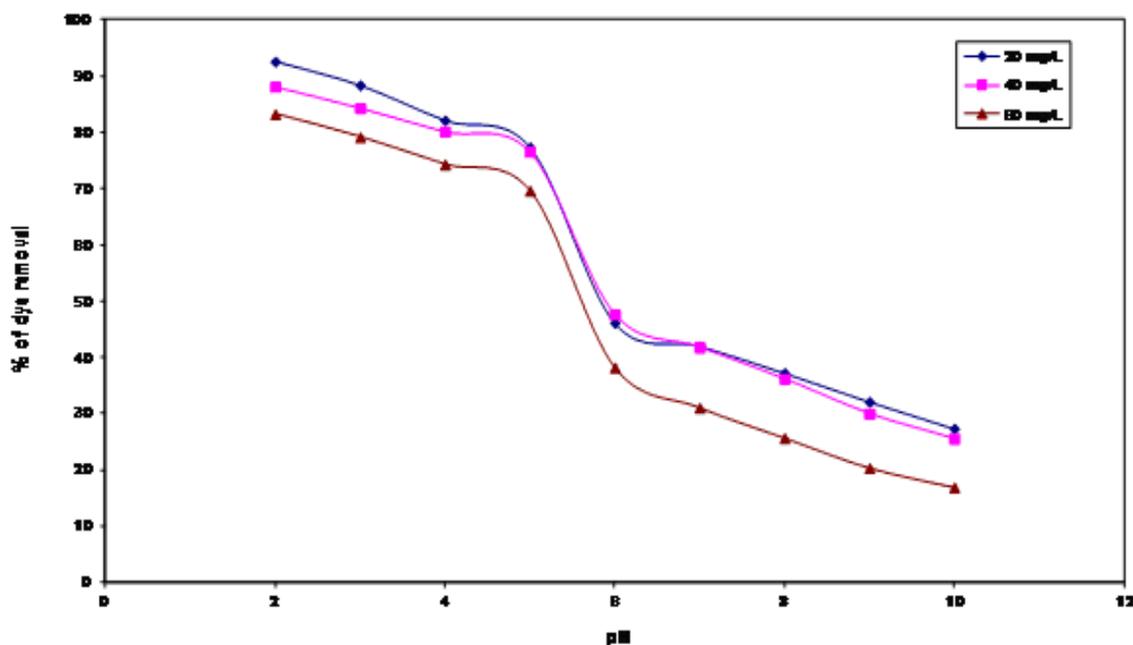


Fig. - 1: Influence of pH on Acid Red 2 Adsorption

Table-1: Kinetic Model Values for the Effect of Initial concentration variation of Acid Red 2 on to *Albizia amara* pod shell waste Activated Carbon

| Conc. mg/L | Pseudo First Order Values |        | Elovich Values    |               |        | Pseudo Second Order Values |                  |              |        |
|------------|---------------------------|--------|-------------------|---------------|--------|----------------------------|------------------|--------------|--------|
|            | $k_L$ /min                | $R^2$  | $\alpha$ mg/g/min | $\beta$ g/min | $R^2$  | $q_e$ mg/g                 | $k_2$ g/ mg /min | $h$ g/mg/min | $R^2$  |
| 20         | 0.0466                    | 0.8715 | 0.7349            | 0.3356        | 0.9708 | 10.05856                   | 0.0052           | 3.1058       | 0.9761 |
| 40         | 0.0474                    | 0.7579 | 0.5320            | 0.1783        | 0.9654 | 9.5462                     | 0.0069           | 1.1068       | 0.9631 |
| 60         | 0.0494                    | 0.9599 | 12.796            | 0.1852        | 0.9475 | 8.9982                     | 0.0081           | 0.0392       | 0.9974 |

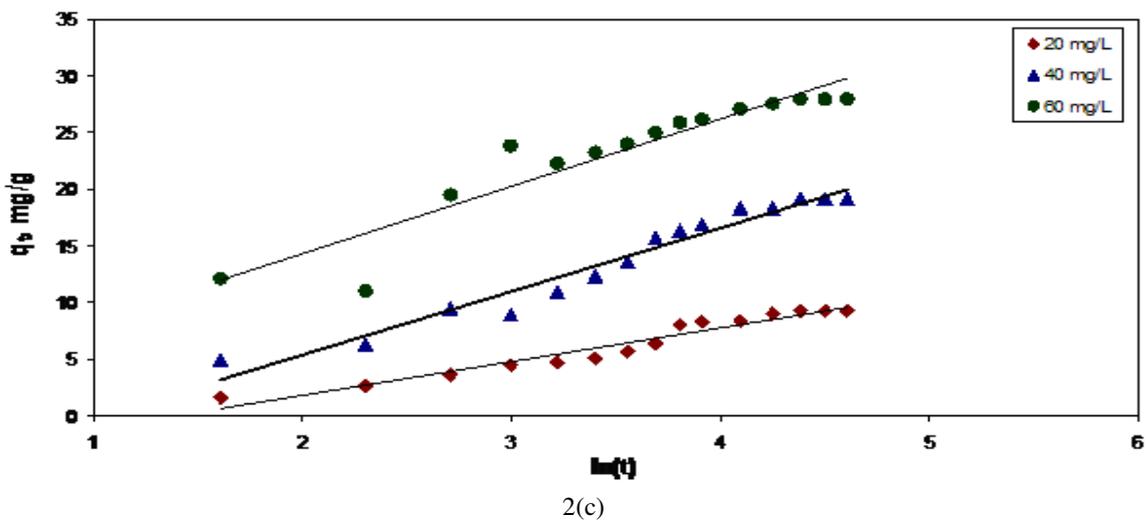
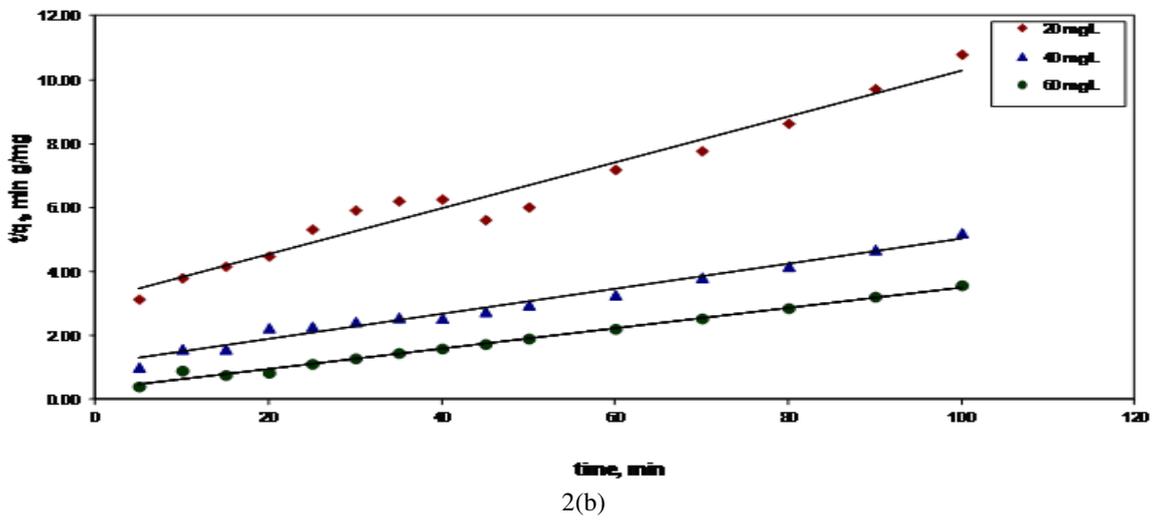
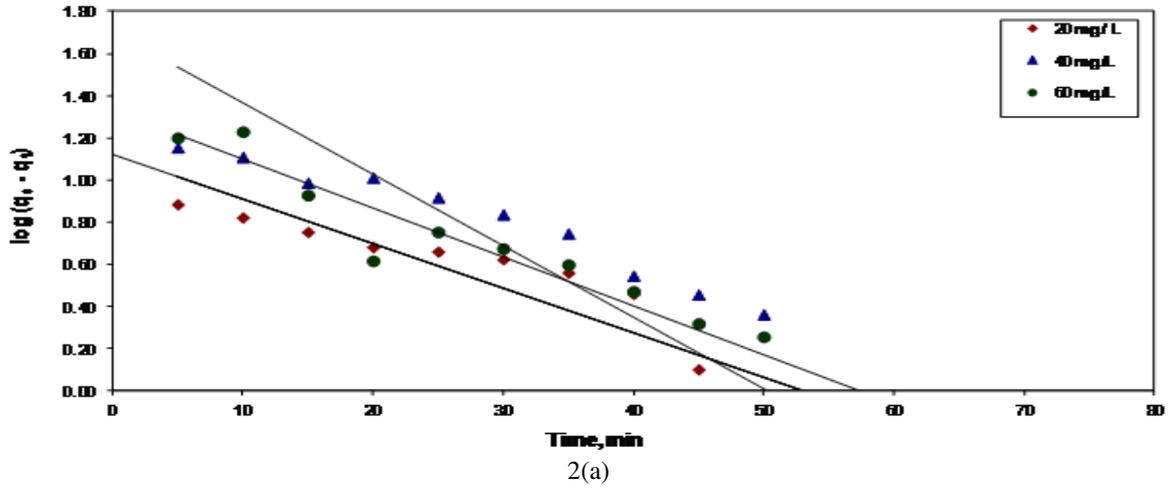


Fig.-2(a), 2(b), 2(c): Pseudo first order plot, Pseudo second order plot, Elovich plot for Initial Concentration variation

Table-2: Kinetic Model Values for the effect of Temperature on Acid Red 2 adsorption on to *Albizia amara pod* shell waste Activated Carbon

| Temp.<br>°C | Pseudo First Order Values |        | Elovich Values |               |        | Pseudo Second Order Values |                |              |        |
|-------------|---------------------------|--------|----------------|---------------|--------|----------------------------|----------------|--------------|--------|
|             | $k_L$ /min                | $R^2$  | $\alpha$ g/min | $\beta$ g/min | $R^2$  | $q_e$ mg/g                 | $k_2$ g/mg/min | $h$ g/mg/min | $R^2$  |
| 30          | 0.0677                    | 0.9659 | 4.7807         | 0.5506        | 0.9443 | 10.3418                    | 0.0068         | 0.7273       | 0.9993 |
| 45          | 0.0542                    | 0.9889 | 4.6583         | 0.5974        | 0.9677 | 9.7733                     | 0.0087         | 0.8319       | 0.9993 |
| 60          | 0.0801                    | 0.8362 | 4.1706         | 0.6260        | 0.9568 | 9.2468                     | 0.0105         | 0.9038       | 0.9991 |

### Effect of initial concentration on kinetic rate constants and rate parameters

The batch adsorption studies were performed at 30 °C and at pH 4.0. 50 mg of adsorbent was mixed with known initial concentration (20, 40, 60 mg/L) of AR 2 solution and agitated. The rate constants and rate parameters at different initial dye concentrations are presented in Table 1 showed that the rate constants decreased with better increase in initial dye concentration. An analysis of the data reveals that the influence of the initial concentration of AR 2 has very little influence on the pseudo second order rate constant. It also reveals that the influence of the initial concentration of AR 2 on the Elovich and Pseudo first order rate constant is neither appreciable nor very little (Fig.-2a, 2b, 2c).

### Effect of Temperature on kinetic rate constants and rate parameters

The temperature effect on the biosorption capacity of dried *Albizia amara pod* shell wastewas examined at 30, 45 and 60 °C using initial dye concentration of 20 mg/L at pH 6 and is shown in Fig. 3a, 3b, 3c. From the slope of the linear trace, the rate constants were calculated and the results are presented in the Table 2. The data obtained separately for each of the kinetic models from the slopes of plots show a better compliance with the pseudo second order equation, the  $R^2$  values for the linear plots being greater than 0.985 showed that the kinetic data fitted best with pseudo second order kinetic equation.

### Mechanism for sorption of AR 2 on to *Albizia amara pod* shell Waste

The mathematical treatment as suggested by Boyd *et al.* and Reichenberg<sup>17,18</sup> was used to identify whether the ongoing process is particle diffusion or film diffusion. These mathematical models also helped in determining the mechanism of the undergoing process. An established fact is that when a solid chemical substance adsorbs over the porous adsorbent, three types of diffusion processes takes place in following three consecutive steps<sup>19</sup>:

1. Transport of the ingoing adsorbate ions to external surface of the adsorbent (film diffusion),
2. Transport of the adsorbate ions within the pores of the adsorbent except for a small amount of adsorption, which occurs on the external surface (particle diffusion) and
3. Adsorption of the ingoing adsorbate ions on the interior surface of the adsorbent.

The third step is very fast and cannot be considered as a rate-determining step, while for the adsorption carrying out via remaining two steps, the following three possibilities exist.

**Case 1:** External transport > internal transport, where rate is governed by particle diffusion.

**Case 2:** External transport < internal transport, where the rate is governed by film diffusion.

**Case 3:** External transport = internal transport, which accounts for the transport of the adsorbate ions to the boundary and may not be possible within a significant rate, which later on gives rise to the formation of a liquid film surrounded by the adsorbent particles with a proper concentration gradient.

To investigate the actual process involved in the present adsorption, the quantitative treatment of the sorption dynamics was founded in accordance with the observation of Reichenberg<sup>18</sup>, as described by the following equation:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-Dn^2\pi^2 t}{r^2}\right) \quad (8)$$

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-n^2 \beta_t] \tag{9}$$

Where F is the fractional attainment of equilibrium at time t and is obtained by using following equation and n is the adsorption intensity of the adsorbate.

$$F = \frac{q_t}{q_e} \tag{10}$$

Where q<sub>t</sub> and q<sub>e</sub> are the amounts adsorbed at time t and at equilibrium respectively.

On the basis of F values, the corresponding values of B<sub>t</sub> were obtained from Reichenberg’s table<sup>18</sup> and the linearity test was carried out by plotting B<sub>t</sub> with respect to time for both the solutions at different time intervals and at 30 °C, 45 °C and 60 °C. The linearity test of B<sub>t</sub> versus time plot drawn for different concentrations is employed to distinguish between film diffusion and particle diffusion. From the slope of the straight line obtained from time versus B<sub>t</sub> graph, the B value (time constant) was calculated. The values of the effective diffusion coefficient (D<sub>i</sub>) were calculated at different temperatures using the following equation:

$$B = \frac{\pi^2 D_i}{r^2} \tag{11}$$

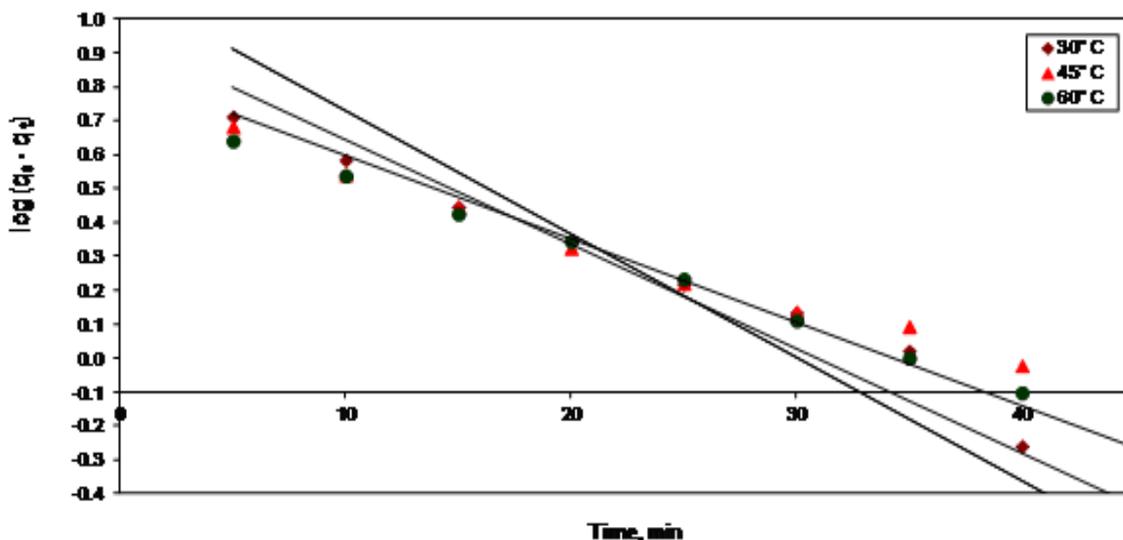
Here r is the radius of adsorbent particle. The D<sub>i</sub> values are given in the Table-3.

The plot of 1/T versus log D<sub>i</sub> was found linear with negative slope indicating thereby the increase in the mobility of the ions. This is due the fact that with the rise in temperature the mobility of the ion increases, which consequently decreases the retarding force acting on the diffusing ions. The values of energy of activation E<sub>a</sub>, entropy of activation ΔS<sup>#</sup> and pre exponential constant D<sub>o</sub> were calculated using the following equations.

$$D_i = D_o \exp \left[ \frac{E_a}{RT} \right] \tag{12}$$

$$D_o = 2.72 d^2 \frac{kT}{h} \exp \left[ \frac{\Delta S^\#}{R} \right] \tag{13}$$

Where d is the average distance between the successive exchange sites and is taken as 5Å, R, h and k are the gas, plank and Boltzmann constants respectively. The values of E<sub>a</sub>, D<sub>o</sub>, ΔS<sup>#</sup> and other parameters are given in the Table-3. The negative values of ΔS<sup>#</sup> reflect that no significant change occurs in the internal structure of choosing adsorbent using the adsorption process.



3(a)

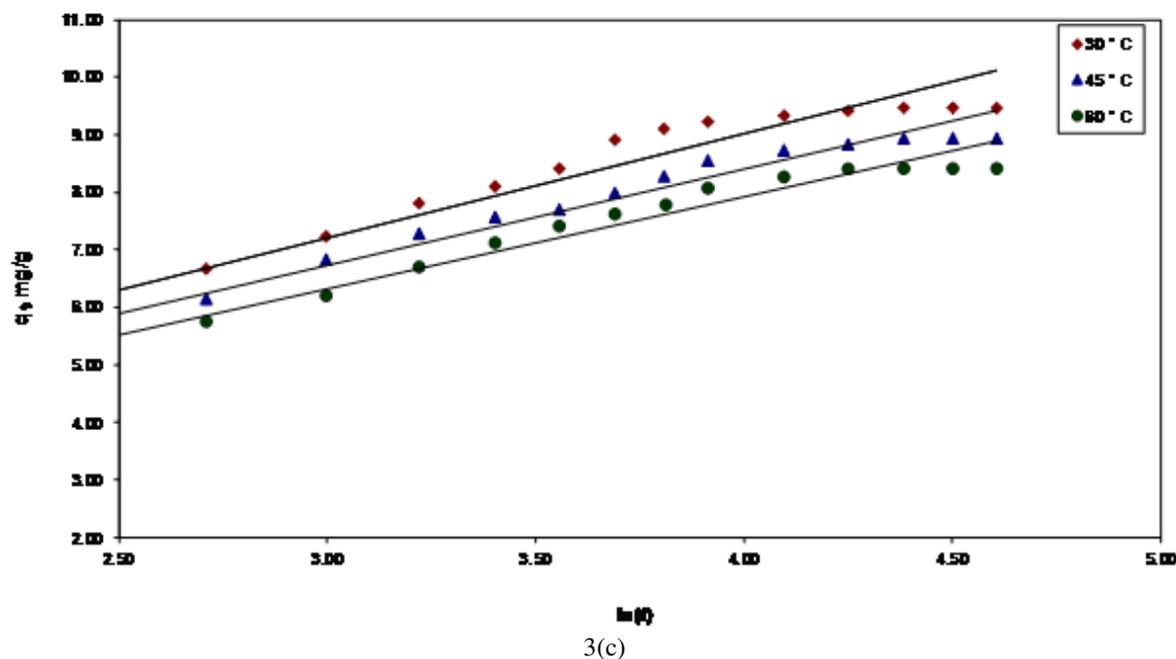
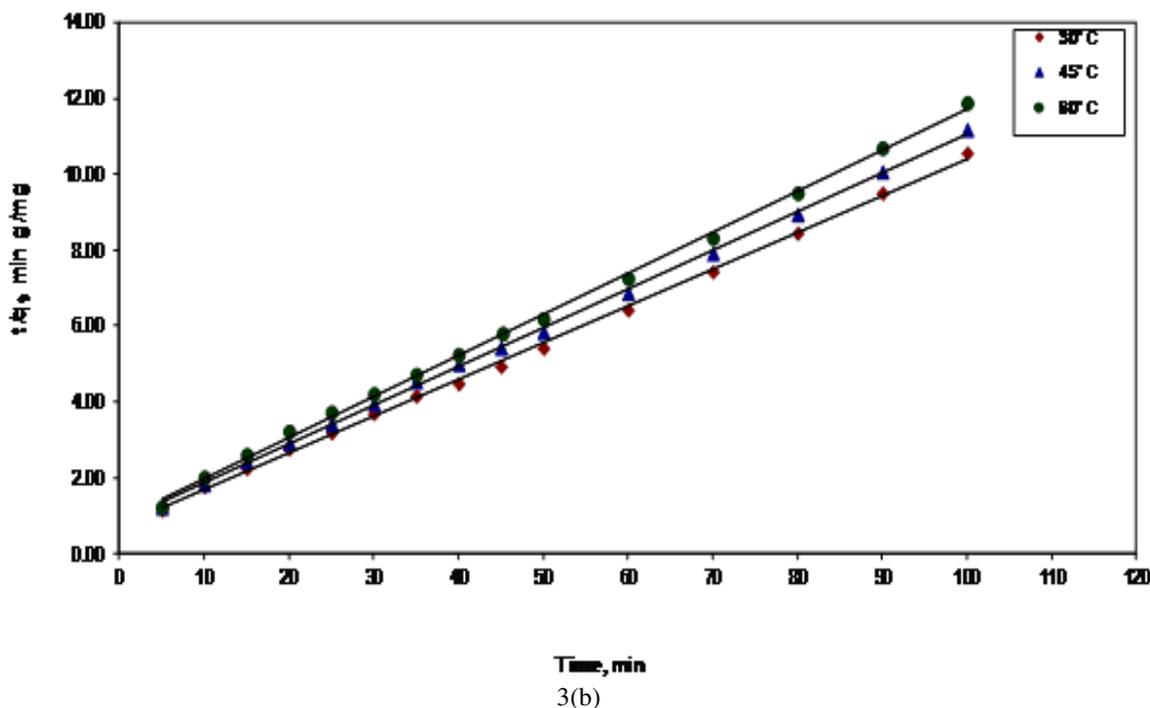


Fig.-3(a), 3(b), 3(c): Pseudo first order plot, Pseudo second order plot, Elovich plot for Temperature variation

**Thermodynamic Parameters**

$\Delta H$  and  $\Delta S$  values were obtained from the slope and intercept of Van't Hoff plot ( $\ln K_c$  vs  $1/T$ ). A batch adsorption study was carried out with AR 2 solution at  $pH \approx 4.0$  and by varying the temperature (303K, 318K and 333K). The initial concentration of AR 2 solution used was maintained to be 20 mg/L with 50 mg of the adsorbent. Table 4 gives the value of  $\Delta G$ ,  $\Delta S$  and  $\Delta H$  for the adsorption of AR 2. The negative values of free energy change ( $\Delta G$ ) indicate the feasibility and spontaneous nature of the adsorption of

Acid Red 2 species. The positive  $\Delta H$  values of the process suggest the endothermic nature of the absorption of AR 2 onto activated *Albizia amara pod* shell waste carbon. The positive value of  $\Delta S$  is due to the increased randomness during the adsorption of AR 2.

Table- 3: Values of energy of activation  $E_a$ , entropy of activation  $\Delta S^\ddagger$ , pre-exponential constant ( $D_0$ ), Diffusion Coefficient ( $D_i$ ) for the present study

| S.No. | Parameter   | Value                    |
|-------|---|--------------------------|
| 1.    | $D_i, \text{cm}^2 \text{s}^{-1}$                      |                          |
|       | 30 °C   | $9.249 \times 10^{-7}$   |
|       | 45 °C   | $8.8374 \times 10^{-7}$  |
|       | 60 °C   | $13.3221 \times 10^{-7}$ |
| 2.    | $E_a, \text{kJmol}^{-1}$                              | -9999.02                 |
| 3.    | $D_0, \text{cm}^2 \text{s}^{-1}$                      | $2.66 \times 10^{-6}$    |
| 4.    | $\Delta S^\ddagger, \text{J K}^{-1} \text{mole}^{-1}$ | 34.1757                  |

Table.-4: Thermodynamic parameters for the adsorption of Acid Red 2 on to *Albizia amara pod* shell waste Activated Carbon

| Temp. | $\Delta G$<br>kJ/mole | $\Delta S$<br>J/mole/K | $\Delta H$<br>kJ/mole |
|-------|-----------------------|------------------------|-----------------------|
| 303 K | 0.0033                | -88.853158             | 4.67                  |
| 318 K | 0.0031                |                        |                       |
| 333 K | 0.0030                |                        |                       |

## CONCLUSION

In the present study adsorption of AR 2 on activated *Albizia amara pod* shell waste activated carbon has been investigated. The data obtained through this work supports that the *Albizia amara pod* shell waste activated carbon is an effective low cost adsorbent for the removal of AR 2 from aqueous solution. The adsorption of AR 2 is dependent on the initial concentration and agitation time. Equilibrium of AR 2 adsorption reaches at 100 min. The pseudo first and second order equations provide a best fit description for the sorption of AR 2 on to *Albizia amara pod* shell waste activated carbon, but the pseudo second order correlation coefficient has better correlation value than pseudo first order equation, pseudo second order equation is consider to be the most appropriate due to high correlation coefficient.

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