



Carbon – Science and Technology

ISSN 0974 – 0546

<http://www.applied-science-innovations.com>

RESEARCH ARTICLE

Received:01/05/2015, Accepted:25/08/2015

Adsorption of Reactive Blue 171 from Aqueous Solution using Low Cost Activated Carbon Prepared from Agricultural Solid Waste: *Albizia amara*

K. Anitha^(*A), P. S. Syed Shabudeen^(B), S. Karthikeyan^(C), N.Aruna devi^(D)

(A) Department of Chemistry, A. P. A. College for Women, Palani, TN, India.

(B) Department of Chemistry, Kumaraguru College of Technology, Coimbatore, TN, India.

(C) Department of Chemistry, Chikkanna Government Arts College, Tirupur, TN, India.

(D) Department of Chemistry, P.S.G.R. Krishnammal College For Women, Coimbatore, TN, India.

Abstract: The adsorption of Reactive Blue 171 (Reactive Dye) from aqueous solution using activated carbon prepared from *Albizia amara* pod shell waste as an adsorbent have been carried out. The experimental adsorption data fitted reasonably well to Langmuir and Freundlich adsorption isotherms. Kinetic parameters as a function of Initial dye concentration have been calculated and the kinetic data were substituted in Pseudo First Order, Elovich and Pseudo Second order equations. A probable explanation is offered to account for the results of kinetic study. The thermodynamic parameter enthalpy change (ΔH) suggests the exothermic nature of absorption of Reactive Blue 171 onto activated *Albizia amara* pod shell waste carbon.

Keywords: Activated *Albizia amara* pod shell waste carbon, adsorption, Reactive Blue 171.

1. INTRODUCTION: Environmental threats posed by reactive dyes to the quality of water is alarming throughout the world. Especially in Tamil Nadu, number of dyeing factories located in and around Erode and Tirupur region let out harmful dyes into the water bodies at an alarming rate. This leads to a serious environmental concern in this zone of Southern India. Adsorption of dyes using activated carbon is an effective method adapted in the treatment of hazardous dye wastes. But using a commercially available activated carbon for this purpose is economically unviable. The reason being that the regeneration and reactivation processes to be followed in case of a commercially available activated carbon are unteanable. The gradual loss of activated carbon during regeneration can materially affect the economic viability of the process [1]. The use of highly structured and robust activated carbons based on expensive, starting materials is unjustified [2]. Therefore, other sources of materials for activated carbons are explored. Cellulosic and lignocelluloses wastes have long been recognized as starting materials for the preparation of activated carbon [3, 4]. Agricultural by-products and waste materials are used for the production of activated carbons [5] such as palm ash and chitosan/oil palm ash [6, 7], pomelo (*Citrus grandis*) peel [8], sunflower seed hull [9], oil palm trunk fibre [10], durian peel [11] and rice straw-derived char [12], biomass fly ash [13], dried biomass of Baker's yeast [14], water-hyacinth [15] *Jatropha Curcas* stem [16], Cashew nut sheath [17] for the removal of dyes from its aqueous solutions. The chemical and physical factors that play an important role in the adsorption of solutes by activated carbons are: molecular structure of the solute, surface chemistry of the activated carbon and solution chemistry. Typical water treatment conditions at neutral pH values, for enhanced uptake of solutes from the solution, the electrostatic forces between the carbon surface and solute macromolecules should be maximized. In order to increase the extent of solute adsorption, the affinity of carbon surface

toward solute molecules must be enhanced. From a physical interactive perspective, it is important to have a good compatibility between the size distributions of activated carbon pores and solution. Comparison of size information available for commercial activated carbon pores and solute molecules in natural waters suggest that some fractions of solute will not be able to access finer carbon pores [18, 19]. Therefore, they will be prevented from fully employing the large surface area (and pore volume) available for absorption. In the present investigation, the adsorption of Reactive Blue 171 on to Activated carbon prepared from *Albizia amara* pod shell waste by carbonization with phosphoric acid has been achieved. The kinetic and equilibrium adsorption data obtained were utilized to characterize the sample prepared.

2. EXPERIMENTAL TECHNIQUE

2.1 Preparation Of Adsorbent: *Albizia amara* pod shell waste is collected from local area of Erode district, Tamil Nadu, India. The dried waste material mixed with excess phosphoric acid, charring of the material occurred immediately accompanied by the evolution of heat and fumes. When the reaction subsided, the mixture was left in an air oven maintained at 80-90 °C for a period of 24 hours. At the end of 24 hours the product was washed with large volume of water to remove free acid and soaked with excess of 10 percent sodium bicarbonate solution for a period of 6 hrs. After 6 hrs, the liquid portion is decanted off and the material was dried at 110 °C and finally activated at 800 °C for 20 minutes [20]. The batch adsorption studies were performed at 30 °C. 100 mg of adsorbent is mixed with known initial concentration (Viz. 20 ppm, 40 ppm and 60 ppm) of Reactive Blue 171 solution and agitated. The adsorbent and the adsorbate were separated by filtration and the filtrate was analyzed for residual Reactive Blue 171 concentration spectrophotometrically using Double beam UV spectro photometer (Elico model BL198).

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 Model: The first order kinetic equation [21] may be expressed as

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

where

q_e = The amount of dye adsorbed at equilibrium, mg/g

q_t = The amount of dye adsorbed at equilibrium, mg/g

k_{Lager} = The rate constant for pseudo first order adsorption, l / min.

The values of $\log (q_e - q_t)$ were linearly correlated with t . The plot of $\log (q_e - q_t)$ versus t should give a linear relationship from which k_{Lager} and q_e can be determined from the slope and intercept of the plot, respectively.

Elovich Model: The Elovich or Roginsky-Zeldovich equation is generally expressed as follows [22].

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

where

q_t = the amount of dye adsorbed mg/g, at time t

- α = the initial dye sorption rate, mg/g min
 β = the desorption constant, g/mg, during any one experiment

To simplify the Elovich equation, Chien and Clajton [23] assumed $\alpha\beta t \gg 1$, and on applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the above equation :

$$q_t = \beta \ln(\alpha \beta) + \beta \ln t \quad (3)$$

This the constants can be obtained from the slope and intercept of the linear plot of q_t versus $\ln t$.

The above equation will be used to test the applicability of the Elovich equation to the kinetics of chosen adsorbent adsorbate system.

Pseudo Second Order Model: To describe dye adsorption, the modified pseudo second order kinetic equation is expressed as [24].

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

where

q_e = The amount of dye adsorbed at equilibrium, mg/g

q_t = The amount of dye adsorbed at time t , mg/g

k_2 = The rate constant for pseudo first order adsorption, g/mg.min.

For the boundary conditions $t = 0$ to $t = 1$ and $q_t = 0$ $q_t = q_t$, the integrated form of equation obtained is

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (5)$$

Rearranging the terms in the above equation we get

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{1}{q_e}} \quad (6)$$

which is the integrated rate law for a pseudo second order reaction. This has a linear form is given as below :

$$t / q_t = \frac{t}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

In the limit $(q_t / t) \rightarrow 0$, the initial sorption rate, h , is given by $k_2 q_e^2$, mg/g min. This, a plot t / q_t versus t of the above equation should give a linear relationship with a slope of $1/q_e$ and an intercept of $\frac{1}{k_2 q_e^2}$.

Isotherm Models:

Langmuir Isotherm: The Langmuir model was developed based on the assumption of the formation of a monolayer of the adsorbate species onto the surface of the adsorbent. It has also been assumed that the surface sites are completely energetically homogeneous. But in the true sense, the adsorbent surface is energetically heterogeneous. The study of the Langmuir isotherm is essential in assessing the adsorption

efficiency of the adsorbent. This study is also useful in optimizing the operating conditions for effective adsorption. In this respect, the Langmuir isotherm is important, though the restrictions and the limitations of this model have been well recognized.

The Langmuir and the rearranged Langmuir equations are given below.

$$1/q_e = 1/Q_0 b \cdot 1/C_e + 1/Q_0 \quad (8)$$

$$C_e/q_e = C_e/Q_0 + 1/Q_0 b \quad (9)$$

where,

q_e = The amount of dye removed at equilibrium, mg/g.

C_e = The equilibrium concentration of dye, mg/l.

Q_0 = The Langmuir constant, related to the adsorption capacity, mg/g and

b = The Langmuir constant, related to the energy of adsorption, L/mg.

The essential characteristics of Langmuir isotherm can be expressed in terms of dimension less constant separate ion factor or equilibrium parameter, R_L which is defined by $R_L = 1 / 1 + b C_0$, where C_0 is the initial dye concentration (mg/L) and b is the Langmuir constant (l/mg). The parameter indicates the shape of isotherm as follows;

R_L Value	Type of Isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Freundlich Isotherm: The linear form of Freundlich equation [25] is represented as

$$\log x/m = \log k_f + 1/n \log C_e \quad (10)$$

where 'x' is the amount of Reactive Blue 171 adsorbed in mg. 'm' is the weight of adsorbent (g) C_e is the residual concentration of Reactive Blue 171 at equilibrium in mg.

k_f and $1/n$ are Freundlich constants related to the adsorption capacity and adsorption intensity respectively and are evaluated by least square fitting of the data by plotting $\log x/m$ vs $\log C_e$ with a slope of $1/n$ and intercept of $\log K_f$.

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 a system are the Gibbs free energy change ΔG , the enthalpy change ΔH and the entropy change ΔS . These parameters were determined using the following relations [26].

$$k_L = Q_0 b \quad (11)$$

$$G = -RT \ln k_L \quad (12)$$

$$\log k_L = \Delta S / 2.303 R - \Delta H / 2.303 RT \quad (13)$$

where K_L is the equilibrium constant, CA_e is the solid phase concentration at equilibrium, C_e is the residual concentration at equilibrium. R is the gas constant (J /mole) and T is the temperature in Kelvin.

3. RESULTS AND DISCUSSION

Surface characters of activated carbon: The morphology of the surface of the prepared activated carbon sample by various processes were examined using Scanning Electron Micrographs. These images provide positive reception of the porosity of adsorbents and consequently their ability to adsorb the dye molecules in solution. ALAC has many pores, small cavities and rough areas with micro pores which were clearly found on the surface. This shows that Phosphoric acid treatment created activated carbon with large surface area and porous structure.

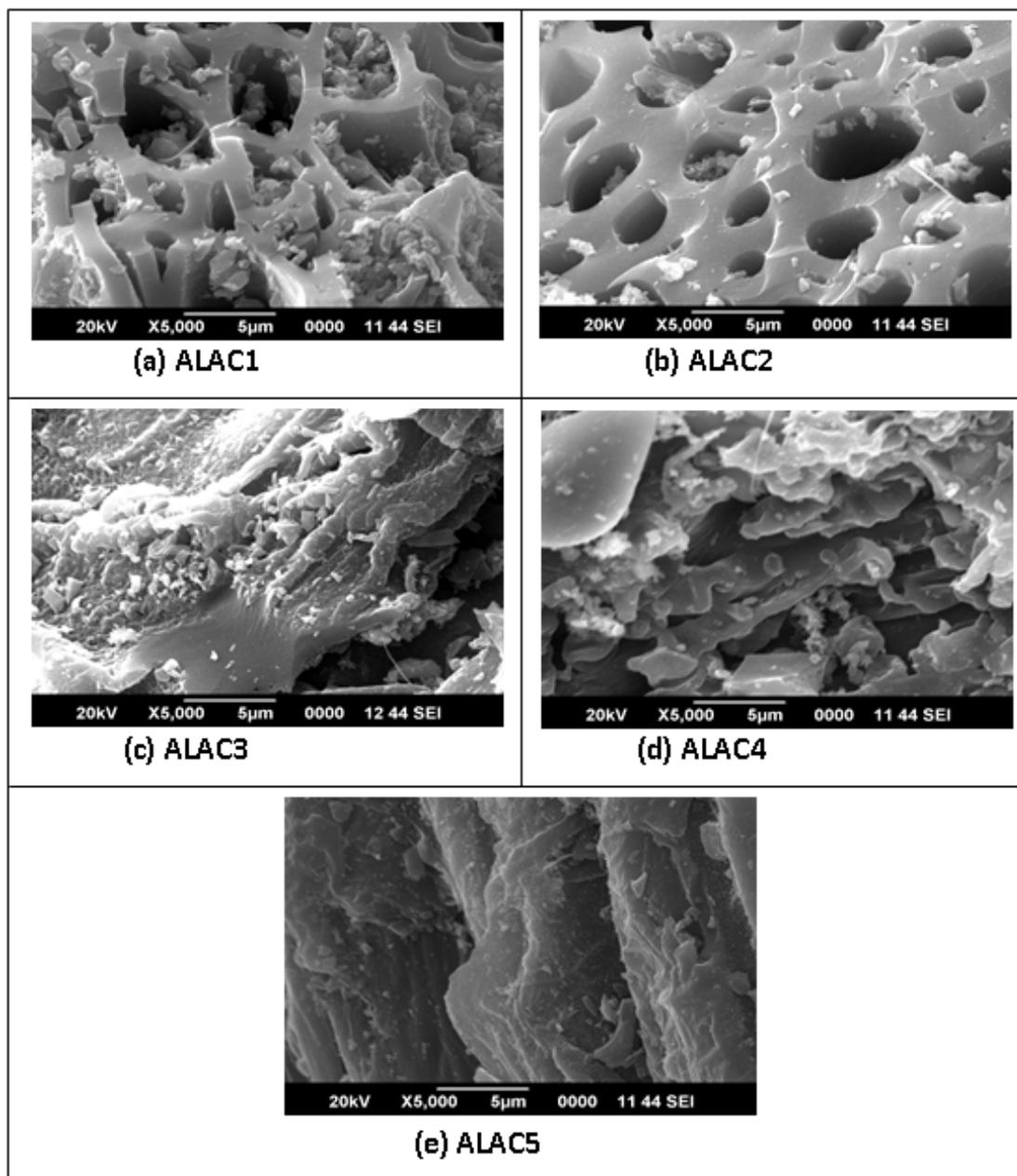


Figure (1): SEM image of *Albizia amara* pod shell waste activated carbons prepared from various processes (a) H_3PO_4 process (b) H_2SO_4 process (c) K_2CO_3 process (d) Na_2SO_4 process (e) $ZnCl_2$ process.

Effect of Agitation time: The uptake of Reactive Blue 171 from water by activated *Albizia amara* pod shell waste carbon increases from 31.6 to 94.75 % when the agitation time was varied from 10 to 160

minutes and attains equilibrium in 140 minutes at 30 °C and at pH 7.0, when the initial concentration of the Reactive Blue 171 solution used was 20 ppm and the adsorbent dosage was 100 mg. The increase in adsorption of Reactive Blue 171 with increase in agitation time may be attributed to the increased intra particle diffusion occurring at long shaking time (Figure-4). A similar result observed by Rao and Bhole in the removal of Reactive Blue 171 by fly ash and bagasse [27].

The initial concentration of Reactive Blue 171 solution was varied (20, 40 and 60 ppm) and batch adsorption experiments were carried out with 100 mg. of the adsorbent at 30 °C and at pH \approx 7.0. An increased percentage removal of Reactive Blue 171 from 75 to 94.75 % observed with 100 mg. of the adsorbent in agitation time of 160 minutes when the initial concentration of the Reactive Blue 171 solution was varied from 20, 40 and 60 ppm. The higher uptake of Reactive Blue 171 at low concentration may be attributed to the availability of more active centres on the surface of the adsorbent for lesser number of adsorbate species. Reactive Blue 171 adsorption curves are single, smooth and continuous (Figure 2) suggesting the possible monolayer coverage of dye molecules on the surface of the adsorbent. Mise and Rajamanya also reported a similar result in the removal of Cr(VI) using activated carbon from dried stem of Jowar [28].

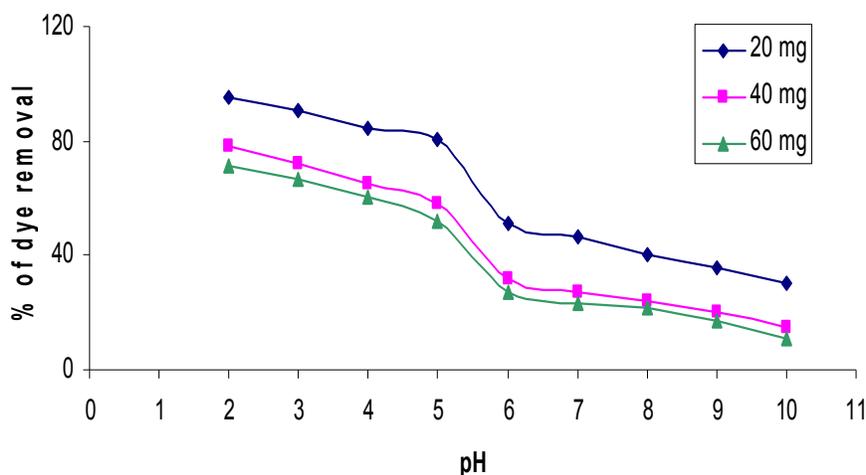


Figure (2) : Effect of pH on dye removal efficiency

Kinetic Modeling:

Pseudo First Order: Figure (3) shows a plot of the Lagergren equation for the results of adsorption of Reactive Blue 171 on to *Albizia amara* in the form of pseudo first order equation. In this case, a linear relationship was obtained between $\ln(q_e - q_t)$ and agitation time over whole sorption period with high correlation coefficient (> 0.998) for all the lines (Table 1). It is clear that a pseudo first order equation may be used to describe the kinetics of sorption of Reactive Blue 171 on to *Albizia amara*. Although the pseudo first order equation does not provide any mechanistic evidence, it has provided suitable for highly heterogeneous systems of which the adsorption of Reactive Blue 171 on to *Albizia amara* undoubtedly such a case.

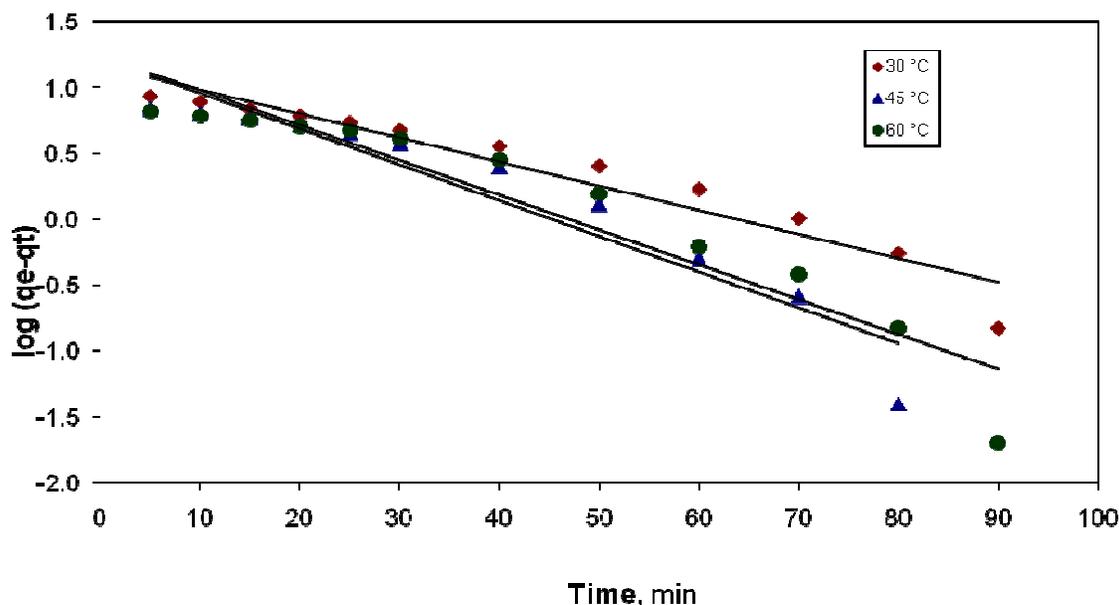


Figure (3): Pseudo-first order kinetic equation describing the Reactive Blue 171 dye adsorption onto ALAC

Elovich Model: The results of the sorption of Reactive Blue 171 onto *Albizia amara* pod has been represented in the form of Elovich Equation in Figure (4) at various Initial dye concentrations (Viz. 20 ppm, 40 ppm, 60 ppm). From the plot a linear relationship between the amount of Reactive Blue 171 adsorbed, q_t and $\ln(t)$ was established. These plots showed different distinct linear regions within individual sets of data. In these cases, it was thus necessary to perform multiple regressions on different ranges of the data. The kinetics could not be approximated using Elovich model.

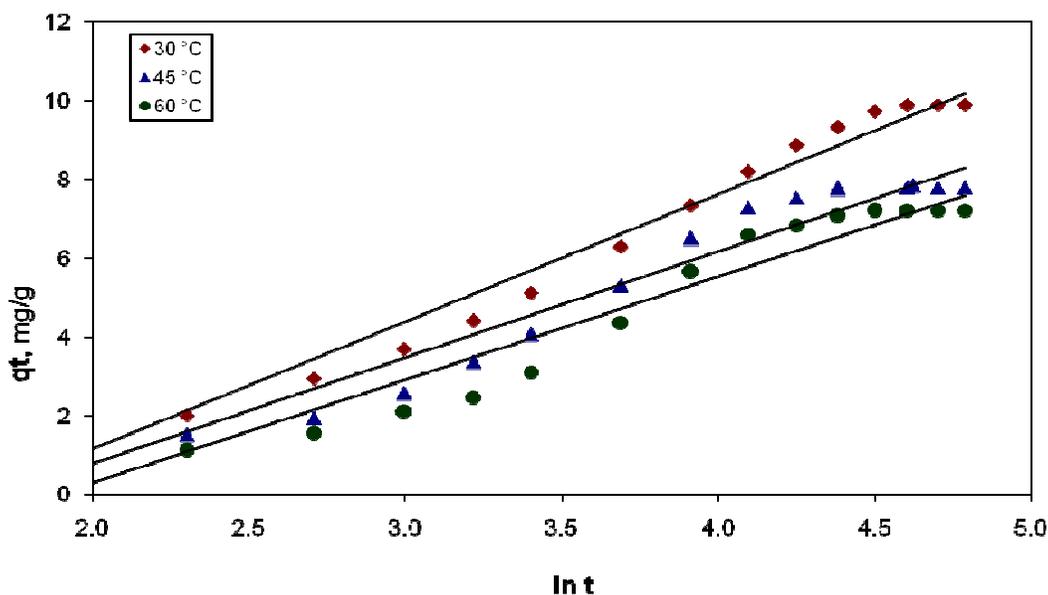


Figure (4): Elovich Plot for the Reactive Blue 171 dye adsorption onto ALAC

Pseudo Second Order Model: The same data are shown as pseudo second order equations in Figure (5). These plots show the data fits had good correlation coefficients (> 0.987) when the pseudo second order equation was employed; it was possible to ascertain from them whether the rate determining process is a chemical reaction. Thus, increasing the initial dye concentration from 20 ppm to 60 ppm the

Reactive Blue 171 sorbed at any contact time increases. This is obvious for higher Initial Concentration values, as a more efficient utilization of the sorptive capacities of the sorbent would be expected due to greater sorption driving force.

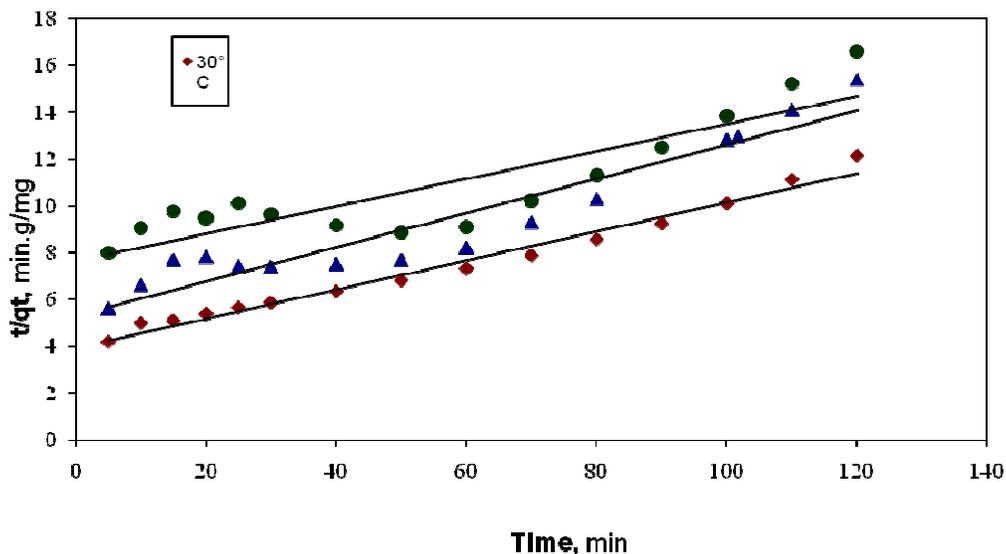


Figure (5): Pseudo second order plot for Reactive Blue 171 dye adsorption onto ALAC

Table 1: Kinetic Model Values for the Adsorption of Reactive Blue 171 onto *Albizia amara* pod Activated Carbon at 30°C, 45°C, 60°C.

Temperature °C	Pseudo First Order Values		Elovich Values			Pseudo Second Order Values			
	$k_{Lager} \times 10^{-2}$	R^2	α	β	R^2	q_e	$k_2 \times 10^{-3}$	h	R^2
30	0.0402	0.9270	0.6268	0.3092	0.9692	16.0942	0.0153	3.9708	0.9811
45	0.0597	0.9078	0.4893	0.3713	0.9431	13.6887	0.0284	5.3200	0.9061
60	0.0582	0.9010	0.3970	0.3818	0.9303	17.0098	0.0264	7.6284	0.7761

Isotherm Modeling: The Langmuir adsorption isotherm obtained in 160 minutes of agitation time is shown in the Figure (6). The values of $R_L < 1$, obtained in this study indicates the applicability of Langmuir adsorption isotherm.

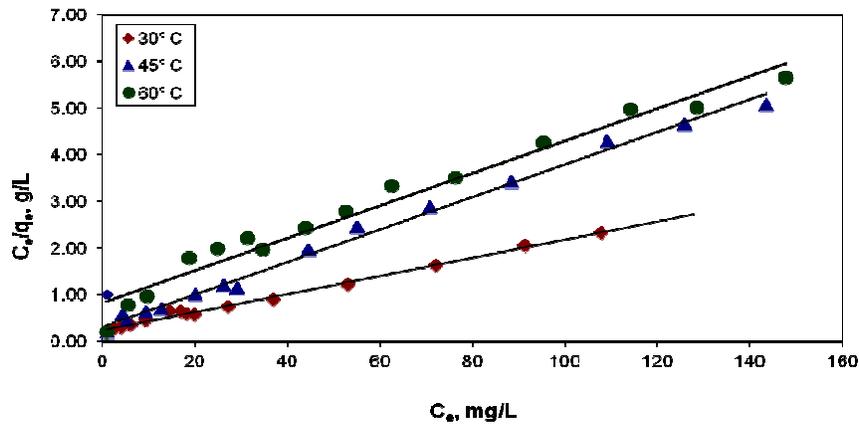


Figure (6) : Langmuir adsorption isotherm for the Reactive Blue 171 dye adsorption onto ALAC.

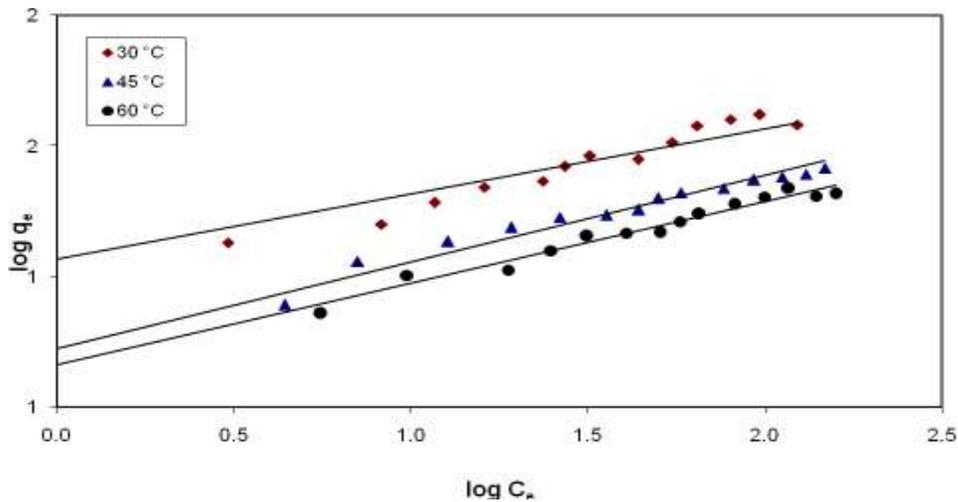


Figure (7): Freundlich Plot for the Reactive Blue 171 dye adsorption onto ALAC

From Table 2, the values of adsorption intensity $1/n \ll 1$ reveals the applicability of this adsorption isotherm. The values of k_f are given in the table 2. The study of temperature effects on the freundlich parameters reveals that decreasing trend in the adsorption capacity with increase in temperature. However, the variation in the adsorption intensity is negligible. These data are useful for practical design purposes

Table 2: Parameters of Langmuir and Freundlich Adsorption Isotherms for Reactive Blue 171 Adsorption Calculated for 160 Minutes of Agitation Time onto Activated *Albizia amara* pod Waste Carbon.

Temp. ° C	Langmuir Isotherm			Freundlich Isotherm		
	b, L / mg	Q ₀ , mg / g	R _L	1/n	n	k _f
30	0.0895	42.3201	0.3584	0.3386	2.9533	13.4311
45	0.0405	46.8527	0.2183	0.3984	2.5100	6.0731
60	0.0584	22.9103	0.1569	0.4311	2.3196	4.6236

Thermodynamic Parameters: ΔH and ΔS were obtained from the slope and intercept of Vant Hoff plot ($1/T$ vs $\ln K_c$). Batch adsorption studies were carried out with Reactive Blue 171 solution at $\text{pH} \approx 6.0$ and by varying the temperature (303 K, 318 K and 333 K). The initial concentration of Reactive Blue 171 solution used was maintained to be 20 ppm with 100 mg of the adsorbent Table 3 gives the value of ΔG , ΔS and ΔH for the adsorption of Reactive Blue 171. The negative values of free energy change (ΔG) indicate the feasibility and spontaneous nature of the adsorption of Reactive Blue 171 species [29]. The negative ΔH values of the process suggest the exothermic nature of adsorption of Reactive Blue 171 on to activated *Albizia amara* pod shell waste carbon. The negative value of ΔS is due to the lower degree of disorderness in the displane meet of adsorbed molecules [30].

Table-3 : Thermodynamic Parameters for the Adsorption of Reactive Blue 171 on to Activated *Albizia amara* Waste Carbon.

Temperature in Kelvin	ΔG , J mole ⁻¹	ΔS , J mole ⁻¹	ΔH , J mole ⁻¹
303	-3355.0	-1.2062	-2.6231
318	-1695.2		
333	-806.7		

4. CONCLUSIONS:

In the present study adsorption of Reactive Blue 171 on activated *Albizia amara* pod shell waste carbon has been investigated. The data obtained through this work supports that the *Albizia amara* waste carbon is an effective low cost adsorbent for the removal of Reactive Blue 171 from aqueous solution. The adsorption of Reactive Blue 171 is dependent on the initial concentration and agitation time. Equilibrium of Reactive Blue 171 adsorption reaches at 160 min.

The pseudo first order and pseudo second order equations provide a best fit description for the sorption of Reactive Blue 171 on to Albizia amara relative to Elovich model, but the Pseudo second order correlation coefficient has better correlation coefficient value than pseudo first order equation. Pseudo second order was considered the most appropriate due to high correlation coefficient when compared to pseudo second order equation.

Langmuir and Freundlich adsorption isotherm correlate the equilibrium adsorption data. The adsorption of Reactive Blue 171 onto activated Albizia amara waste carbon is an exothermic reaction based on Enthalpy change values.

REFERENCES:

- [1] S. Karthikeyan and C. Sumithra, J. Environ. Nanotechnol. 3 (2014) 23-29.
- [2] P. Brian, N. O. Kelleheri Marguerite, Callaghan, Martin J Leahy., F. O. Thomas, J. J. Dwyer, and Leahy, J. Chem. Technol. Biotechnol. 77 (2002) 1212-1218.
- [3] J. C. Dean, F. L. Bosqui, K. M. Lanovette, Environ. Sci. Technol. 6 (1972) 518.
- [4] A. F. Mukherjee, "Environmental Pollution and Health Hazards: Causes and Control", (1986).
- [5] K. T. Karthikeyan and K. Jothivenkatachalam, J. Environ. Nanotechnol. 3 (2014) 69-81.
- [6] A. A. Ahmad, B. H. Hameed and N. Aziz, J. Hazard. Mater. 141 (2007) 70-76.

- [7] M. Hasan, A. L. Ahmad, and B. H. Hameed, *Chem. Eng. J.* 136 (2008) 164-172.
- [8] B. H. Hameed, D. K. Mahmoud, A. L. Ahmad, *Colloids Surf. A: Physicochem. Eng. Aspects* 316 (2008) 78-84.
- [9] B. H. Hameed, *J. Hazard. Mater.* 154 (2008) 204-212.
- [10] B. H. Hameed and M. I. El-Khaiary, *J. Hazard. Mater.* 154 (2008) 237-244.
- [11] B. H. Hameed and H. Hakimi, *Biochem. Eng. J.* 39 (2008) 338-343.
- [12] B. H. Hameed and M. I. El-Khaiary, *J. Hazard. Mater.* 153 (2008) 701-708.
- [13] P. Pengthamkeerati, T. Satapanajaru and O. Singchan, *J. Hazard. Mater.* 153 (2008) 1149-1156.
- [14] J. Y. Farah, N. Sh. El-Gendy and L. A. Farahat, *J. Hazard. Mater.* 148 (2007) 402-408.
- [15] M. I. El-Khaiary, *J. Hazard. Mater.* 147 (2007) 28-36.
- [16] K. Sakthivel, I. Arockiaraj, C. Kannan, and S. Karthikeyan, *J. Environ. Nanotechnol.* 2/2 (2013) 66.
- [17] Q. Mortley, W. A. Mellowes, and S. Thomas, *Termochim. Acta.* 129 (1988) 173.
- [18] P. B. Nagarnaik, A. G. Bhole and G. S. Natarajan, *Ind. Journal Environ. Health* 45 (2003) 1-4.
- [19] C. Namasivayam and R. T. Yamuna, *Water, Air and Soil pollution* 113 (1999) 371-384.
- [20] S. Karthikeyan, P. Shanthi, A. Saravanan and K. Saranya, *J. Environ. Nanotechnol.* 3 (2014) 88-100.
- [21] S. Lagergren, *Hand linger* 24 (898) 1 -39.
- [22] K. S. Low, C. K. Lee and A. Y. Ng, *Bioresou. Technol.* 65 (1999) 205-208.
- [23] S. H. Chien and W. R. Clayton, *Soil Sci. Soc. Am. J.* 44 (1980) 265 - 268 .
- [24] Y. S. Ho and G. Mcay, *Adsorp. Sci. Technol.* 18 (2000) 639 –650.
- [25] N. Sumanjit and N. Prasad, *Indian Journal of Chemistry* 40A (2001) 388-391.
- [26] N. Stephen Inbaraj and N. Sulochana, *Indian Journal of Chemical Technology* 9 (2002) 201- 208.
- [27] M. Rao and A. G. Bhole, *Journal of Indian Water Works Association* 97 (2001) 997-1000.
- [28] R. Shashikant, Mise and V. S .Rajamanya, *Indian Journal Environmental Health* 45 (2003) 49-58.
- [29] K. Vinod, T. Gupta, T. Dinesh Mohan, T. Saurabh Sharma, T. Kuk, T. Park, *The Environmentalist* 19 (1999) 129-136.
- [30] A. Krishnamoorthy, Joseph C. Juliet, *Ind. J. Chem.* 43A (2004) 45-50.
