



Adsorption of Acid Dye by Activated Carbon from Agricultural Solid Waste *Leucaena Leucocephala* Seed Shell Waste: Kinetics, Equilibrium and Isotherm Study

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Abstract

Activated carbons from *Leucaena leucocephala* Seed Shell left over were generated accompanied by 10% phosphoric acid solution in the N₂ atmosphere by chemical activation and their characteristics were investigated. SEM, FTIR and XRD analysis were used to analyse the characteristics of the triggered preparations. Isothermal models, namely the Freundlich and Langmuir representations, were the equilibrium studies carried out. The equilibrium adsorption result was better suited to the isotherm model of Langmuir and its maximum monolayer adsorption potential for acid blue was 70.67 mg/g. Adsorption kinetics studies have shown that the best fit is provided by the pseudo second-order dynamic model. An intraparticle dispersion model demonstrated that the dissemination of the intraparticle was not a step of rate control. Studies of thermodynamics have shown that the sorption mechanism is spontaneous and exothermic in nature. The findings suggest that the seed shells of *Leucaena leucocephala* may be used as a possible adsorbent for Acid blue1 adsorption.



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Introduction

Activated carbon is among the finest extensively acknowledged adsorbents on account of its high adsorptive limit for that reason, it has been usually exploited as adsorbent^{1,2} and in catalysis^{3,4} or

Separating Techniques^{5,6}. Thus, the significance for activated carbon is escalating. In spite of, Activated carbon is pricey which confine its substantial choice application. from this day forward, minimal effort woodland and rural squanders are viewed as

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promising adsorbents for adsorption applications. In addition, they are less expensive and promptly reachable materials. Lately, a ton of examination has been accounted for on enacted carbons from farming squanders, for example⁷, sago squander⁸, pine saw dust⁹, sugar stick dust¹⁰, coir substance¹¹, oil palm squander¹², coconut shell squander¹³, tropical wood¹⁴, saw dust¹⁵, pinus pinaster bark¹⁶, corncob¹⁷, eucalyptus bark¹⁸, pistachio shells¹⁹, babool wood²⁰, *Feronia limonia*²¹, *Leucaena leucocephala* seed shell²², *Pongamia pinnata*²³, *Jatropha curcas*²⁴. There were also few reports on adsorbents employed in water purification^{25,26}, Poison Removal²⁷ Heavy metals Removal²⁸. This examination uncovers that the enacted carbon arranged from *Leucaena leucocephala* seed shell squander as a farming adsorbent and the adsorption of corrosive blue1 was researched.

Materials and Methods

From the town of Tirupur, *Leucaena leucocephala* seed shell left over is gathered and dried and broken into little pieces. The pieces were then impregnated for 2 hours with a 10% phosphoric acid solution and immersed for 24 hours in a same solution. The excess solution was decanted and dried in the air. In the muffle furnace, the material was then carbonized at 120-130°C. The dried material was powdered and triggered for a period of 60 minutes in the muffle furnace at 800 C. The sample was then washed with a high volume of water to extract residual acid, and the dried and powdered sample was placed in sealed flasks. Scanning Electron Microscopy SEM characterised the prepared activated carbon morphological sample. FTIR analysis determined the character of functional groups.

Dye Adsorption Measurements

Of all the reagents used, the AR grade was (E-merk). Different Acid Blue1 dye solution concentrations were prepared with distilled water. Batch mode adsorption experiments were conducted in a thermostated water bath with the addition of 50 mg of adsorbent and 50 mL of dye solution shaker with certain concentrations, varying pH and temperatures. The samples were extracted at fixed time intervals from the shaker and the solutions were isolated by centrifugation from the adsorbent. Before and after adsorption, the dye concentrations in the solutions were measured using the Elico UV

visible spectrophotometer. Using a 0.1N NaOH or HCl solution, the pH of the solution for the dye was changed. The adsorption experiments were performed at various temperatures. The adsorbed dye quantity q (mg/g) and the efficiency of adsorption is determined as follows:

$$q = \frac{C_0 - C_e}{m} \times V \quad \dots(1)$$

$$\text{Adsorption Efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad \dots(2)$$

where,

C_0 = original dye concentration (mg/L)

C_e = equilibrium concentration (mg/L)

V = volume of solution (ml)

m = mass of adsorbent (g)

C = remaining dye concentration (mg/L)

q = quantity of dye adsorbed (mg/g)

m = mass of adsorbent (g)

C = remaining dye concentration (mg/L)

q = amount of dye adsorbed (mg/g)

Results and Discussion

SEM Analysis

Scanning electron microscope (SEM) image of the carbon sample prepared in figure 1. The SEM images clearly showed that the sample's outer surfaces were rough and Pores of various sizes and shapes were included, such as the honeycomb structure. There were tiny elongated pores on the surface, which are consistent with the well-developed porosity. The micrographs showed that the cavities on the carbon sample surfaces resulted from the evaporation of H_3PO_4 at moderate temperatures during activation, creating an empty room. The molecules of the chemical impregnating agent diffuse through the texture of the lignocellulosic material during impregnation.

Chemical Surface Characterization

Surface functional groups contained by activated carbon contribute considerably to its adsorption capability, such as ion exchangers, adsorbents, catalysts, and catalyst supports. The Fourier Transform Infrared Spectroscopy (FTIR) spectrum of the precursor and LSAC is presented in figure 2.

At 2800-3000 cm^{-1} , the precursor had a peak that was ascribed to the C-H, but the LSAC spectrum was reduced. noteworthy differences happened in the 1400-1700 cm^{-1} cm bands. For the spectrum of the precursor, the band at 1616 cm^{-1} is allocated

to C=O. Changes in the FT-IR spectrum of LSAC have provided signs of the creation of structures comprising many carbon-carbon bonds, as well as the elimination of the originally present oxygen and hydrogen atoms.

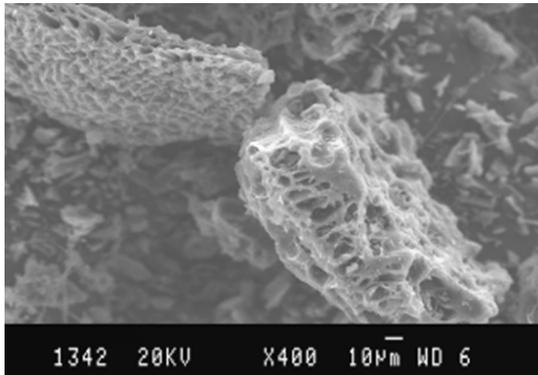


Fig. 1: SEM image for LSAC

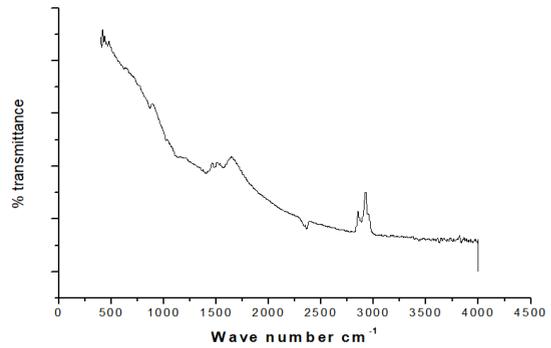


Fig. 2: FTIR Spectroscopy for LSAC

XRD Analysis

Figure 3 confirms that the activated carbon material derived from *Leuceana leucocephala* is

characterised by a large amorphous phase content in the carbon surface structure.

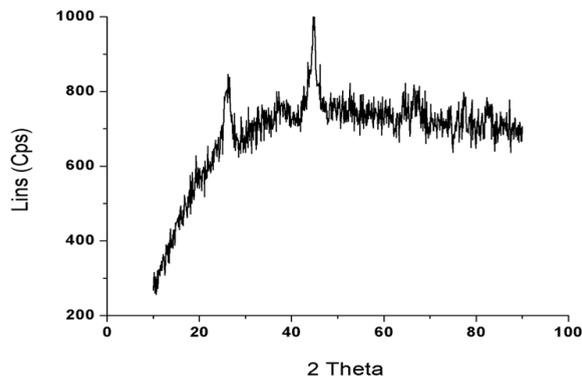


Fig. 3: XRD pattern for LSAC

Adsorption Kinetics

For Acid blue 1 at pH 6.5 up to 240 min, the kinetic of adsorption was studied by varying the initial dye concentration to facilitate investigating the behaviour of acid blue1 adsorption method on LSAC, three kinetic models were applied to adsorption kinetic data. Lagergren offers a basic kinetic study of adsorption, pseudo first-order kinetics and its incorporated shape.²⁹

$$\log (q_e - q_t) = \log q_e - \frac{k_L}{2.303} t \quad \dots(3)$$

where k_L is the pseudo first order rate constant.

A plot of $\log (q_e - q_t)$ vs time for acid blue 1 adsorption onto LSAC facilitates computation of the rate constant k_1 and q_e from the slope and intercept of the plot outline (figure 4).

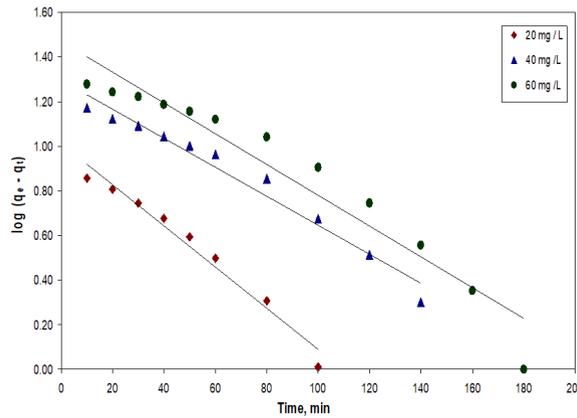


Fig. 4: Effect of pseudo first order plot for the adsorption of acid blue 1 onto LSAC

To illustrate dye adsorption, the tailored pseudo second order kinetic equation³⁰ is articulated as

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

where, k_2 is the pseudo second order rate constant. A plot of t/q_t Vs t for acid blue1 adsorption on LSAC

is revealed in figure 5, which facilitates computation of the rate constant k_2 which is used to estimate the original sorption rate h as follows

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

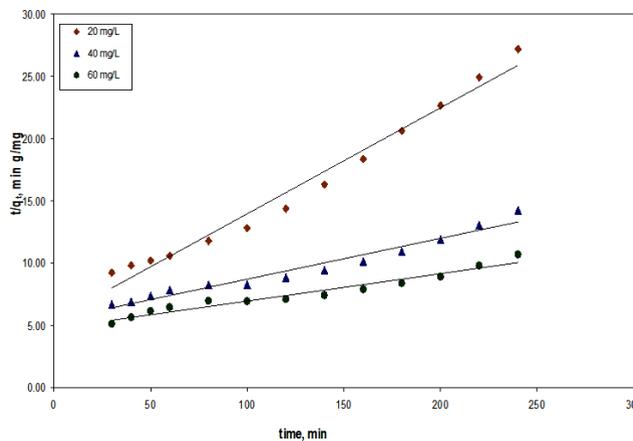


Fig. 5: Effect of pseudo first order plot for the adsorption of acid blue 1 onto LSAC

The solute relocate is typically marked by exterior mass transfer or intra-particle dissemination or both for a solid-liquid adsorption method. To describe the mechanism involved in the adsorption process, the intra-particle diffusion model projected by Weber and Morris³¹ was utilized.

$$q_t = k_{id} t^{0.5} + C \quad \dots(6)$$

where k_{id} ($\text{mg/g min}^{0.5}$) is the rate constant of the intra-particle dissemination representation and C (mg/g) replicates the boundary layer outcome. The k_{id} and C can be established from the slope and intercept of the plot q_t Vs $t_{0.5}$ and is shown in figure 6 for acid blue 1 adsorption. As the dye concentration increased, the constant pseudo first order and second order rate decreased. According to the model of intra particle diffusion, if intra particle

diffusion is concerned in the adsorption method, the plot of uptake should be linear, and if the line passes through the origin, then the rate control step is intra particle diffusion. It is an indicator of boundary layer control when the plot does not move through the

source. This reveals that intra-particle dissemination only is not the rate-limiting stage, but the rate of adsorption also regulated by other kinetic models, all of which can work simultaneously.

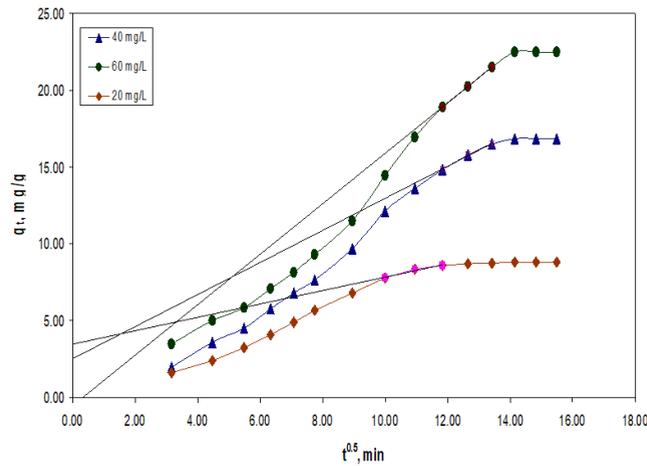


Fig. 6: Effect of pseudo first order plot for the adsorption of acid blue 1 onto LSAC

Table 1: Kinetic factors for the adsorption of acid blue1 on LSAC

Model	Parameters	Concentration (in mg/L)		
		20	40	60
Pseudo first order	K_1	0.0137	0.0096	0.0078
	R_2	0.9301	0.9688	0.9715
Pseudo second order	K_2	0.0323	0.00587	0.0026
	h	3.7786	2.9923	2.5508
	q_e	10.8145	22.5744	31.1593
	R^2	0.9987	0.9911	0.9921
Weber Morris	K_{id}	0.5508	1.1662	1.5793
	R_2	1.000	0.9981	0.9772

Adsorption Isotherms

In this work, the Langmuir and Freundlich models were fitted with adsorption isothermal data of acid blue 1 dye for variation in the most commonly used activated carbon (LSAC) dose. The isothermal fits were compared using the correlation coefficient (R_2) and were listed in the table (1 & 2). The Langmuir model³² assumes that a solid surface carries a small number of sites characterised by equivalent

adsorption energy, irrespective of the degree of coverage and thus implying an equal amount of adsorption energy.

$$\frac{1}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_e} \quad \dots(7)$$

where, Q_o is the highest adsorption capability, b is the Langmuir binding energy coefficient. The b and Q_o can be intended from the intercept and slope of

the linear system of $\log q_e$ against $\log C_e$ as revealed in figure 7.

The Langmuir adsorption isotherm is clearly more fitting to characterise the adsorption equilibrium ($R_2 > 0.99$). Monolayer coverage of acid blue 1 onto LSAC particles with maximum adsorption potential of 66.21, 70.67 and 66.91 mg/g at 30, 45 and 60°C was therefore obtained. Because of the available sites present in the carbon surface, the adsorption potential was increased by 30 and 45°C, then decreased by 60°C because the sites were not available or desorption would take place. As the temperature rose, the K_L values decreased.

The Freundlich isotherm³³ is one of the most usually utilized isotherms for the depiction of multi-site adsorption and is an empirical condition.

The linear form as follows:

$$\log q_e = 1/n \log C_e + \log K_f \quad \dots(8)$$

Where K_f and n are the constants of the Freundlich isotherm indicating the respective adsorption potential and adsorption strength. It is possible to determine K_f and n from the intercept and slope of the linear plot of $\log q_e$ against $\log C_e$. The value of n suggests that acid blue 1 onto LSAC has beneficial adsorption.

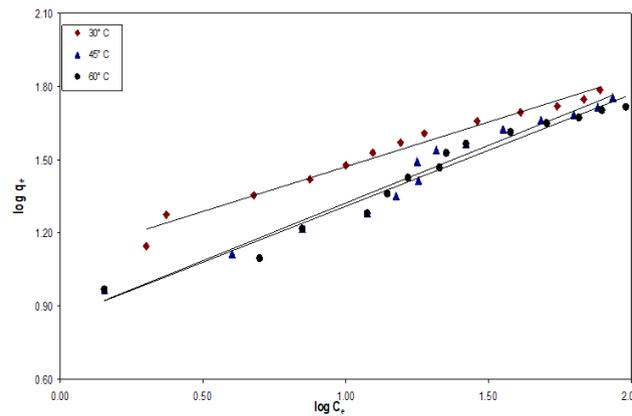


Fig. 7: Effect of langmuir plot for the adsorption of acid blue 1 onto LSAC

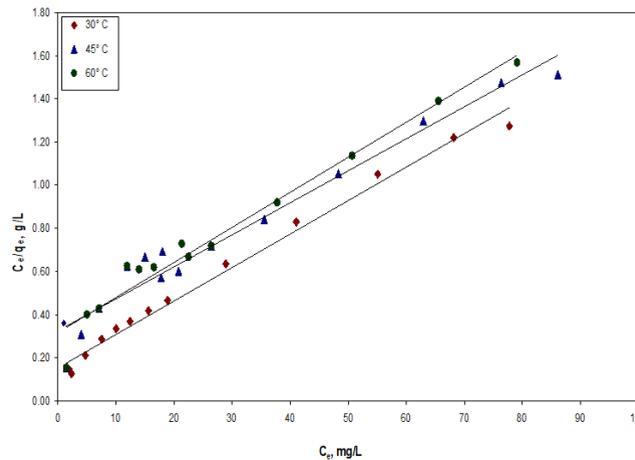


Fig. 8: Effect of Freundlich plot for the adsorption of acid blue 1 onto LSAC

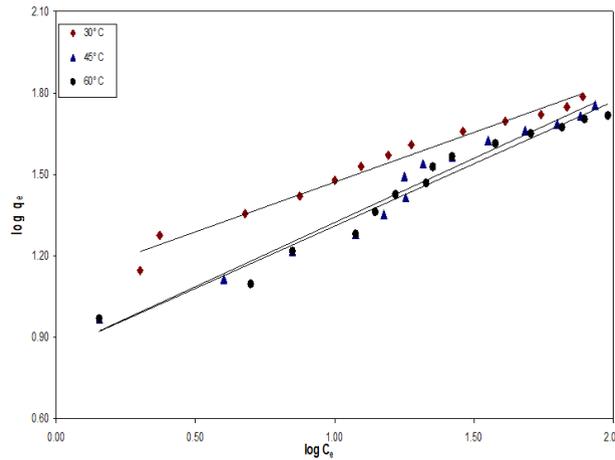


Fig. 9: Effect of Freundlich plot for the adsorption of acid blue1 onto LSAC

Table 2: Isotherm parameters for the adsorption of acid blue1 onto LSAC

Temp- rature	Langmuir Isotherm		Freundlich Isotherm			
	Q ₀ (mg/g)	K _L (L/mg)	R ²	K _f	n	R ²
30°C	66.2177	5.7443	0.9912	7.8161	1.9375	0.9768
45°C	70.6773	4.3305	0.9886	6.0587	1.7965	0.9764
60°C	66.9125	4.1225	0.9911	6.5898	2.102	0.9861

Thermodynamic Parameters for the Adsorption

The thermodynamic factors such as free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) give a depiction of adsorption performance correlated to temperature. Parameter can be calculated from

$$\Delta G = - RT \ln K_L \quad \dots(9)$$

$$\ln K_L = (\Delta S/R) - (\Delta H/RT) \quad \dots(10)$$

R value is the constant (8.314 J/(mol.K), where K_L (L/mol) is from the Langmuir equation, and T (K) is the temperature in Kelvin. As can be observed

from Table 3, at all temperatures measured, the estimations of ΔG were reliably negative, which uncovered that the adsorption cycle was viable and spontaneous process in nature. In addition, the unconditional values of ΔG put forward that the phase of sorption is highly desirable at low temperatures.

The negative value of ΔH was representative of the adsorption process's exothermic existence. In the solid-solute adsorption systems, the negative value of ΔS implied diminished uncertainty, which designated that the increase in entropy produced by the displaced water molecules is lower than that lost by the acid blue 1 molecules.

Table 3: Thermodynamic parameters for the adsorption of acid blue 1 onto LSAC

ΔH (kJ/mol)	ΔS (J/(molK))	ΔG (kJ/mol)		
		303K	318K	333K
-52.9775	-155.0539	-5098.7470	-1280.8649	-4617.6112

Conclusions

In this analysis, the low energy consumption of the *Leucaena leucocephala* seed shell was modified using the H_3PO_4 process. The kinetic adsorption fit the pseudo-second-request model well. The intraparticle dissemination model outcomes show that intraparticle dispersion was not by any means the only advance deciding rate. The Langmuir isotherm model was found to yield the best equilibrium outcome for corrosive blue with a most intense monolayer adsorption of 70.67 mg/g. Investigations of thermodynamics have shown the natural and exothermic presence of the component of sorption process.

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Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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