Utilization of Biomass (*Eucalyptus Lanceolata*) as an Adsorbent - Removal of Methylene Blue from Wastewater

Inamullah Mian[1,3]*, Sultan Alam[1], Noor Rehman[2]*, Hidayat Ullah[2]

[1]Department of Chemistry, University of Malakand (18800) Khyber Pakhtunkhwa, Pakistan.
[2]Department of Chemistry, Shaheed Banazir Bhutto University (18000) Sheringal, Dir (Upper) Khyber Pakhtunkhwa, Pakistan.
[3]Key Laboratory of Coal Clean Conversion and Chemical Process Autonomous Region, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830000, Xinjiang, China.

*Corresponding author: Inamullah Mian, email: u.inam63@gmail.com; Noor Rehman, noorrehman@sbbu.edu.pk

Abstract. Investigation relevant to the influence of activated carbon (AC) supports biomass of *Eucalyptus Lanceolata* as an adsorbent was not reported previously. The recent work synthesized a series of studies to know various experimental parameters equilibration time and temperature of the adsorbent for the elimination of dye. Physical structure characterization measured that the surface area of activated carbon increased from 399 to 475 $m^2.g^{-1}$ revealed that the raw biomass had more compact surface than those of activated carbon. FTIR bands were found in the region between 3406.29 cm^{-1} and 3414.0 cm^{-1} indicates (-OH) stretching group which leads to hydrogen bonding. Adsorption of Methylene blue was studied on raw and activated carbon. The average activation energy of the activated carbon was 33.67 $kJ.mol^{-1}$, slightly lower than those of raw carbon, which was 49.14 $kJ.mol^{-1}$. Intraparticle diffusion, Elovich and Bhangam models were applied to evaluate kinetics studies at 20, 30 and 40 ºC. Thermodynamic parameters, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta E^{\neq}$ were calculated from the adsorption of kinetics. Results indicate that adsorption is a spontaneous process. The negative value of entropy determined that the acid molecules take an oriented position on the surface of the adsorbent. The results show that all the models were best fitted for adsorption.
Keywords: Activated carbon; adsorption; adsorbent; FTIR; adsorbate.

Resumen. Una investigación relevante y no reportada previamente respecto a la influencia del carbón activado (CA) apoya que la biomasa de *Eucalyptus Lanceolata* es un adsorbente. El reciente trabajo sintetizó una serie de estudios para conocer diversos parámetros experimentales de tiempo de equilibrio y temperatura del adsorbente para la eliminación del colorante. La caracterización de la estructura física determinó que el aumento del área superficial del carbón activado de 399 a 475 $m^2.g^{-1}$ revela que la biomasa cruda tenía una superficie más compacta que las del carbón activado. Se encontraron bandas FTIR en la región entre 3406.29 cm^{-1} y 3414.0 cm^{-1} indicando el estiramiento del grupo (-OH) que conduce al enlace de hidrógeno. Se estudió la adsorción de azul de metileno en carbón crudo y activado. La energía de activación media del carbón activado fue de 33,67 $kJ.mol^{-1}$, ligeramente inferior a la del carbón bruto, que fue de 49,14 $kJ.mol^{-1}$. Se aplicaron modelos de difusión intrapartícula, Elovich y Bhangam para evaluar estudios cinéticos a 20, 30 y 40 ºC. Los parámetros termodinámicos, $\Delta H^{\neq}$, $\Delta S^{\neq}$ y $\Delta E^{\neq}$ se calcularon a partir de la cinética de adsorción. Los resultados indican que la adsorción es un proceso espontáneo. El valor negativo de la entropía determinó que las moléculas de ácido

toman una posición orientada en la superficie del adsorbente. Los resultados muestran que todos los modelos se ajustaron mejor para la adsorción.
Palabras clave: Carbón activado; adsorción; adsorbente; FTIR; adsorbato.

Introduction

Among the sustainable energy sources, organic solid waste is believed to be a viable alternative to fossil fuels due to its capacity to support the transportation, power, and chemical industries as a main source of inexhaustible, concentrated non-fossil carbon that is accessible on earth [1]. Organic solid waste is a significant renewable energy source and accounts for approximately 10 % of global energy consumption [2], because of its rich reserves, low sulfur and nitrogen contents, "carbon neutral" and so on [3]. However, the properties of biomass, such as high water and oxygen content, low bulk density and heating value, hinder its broad utilization as fuel by conventional technologies [4].

There are various organic materials which were hazardous to human health as well as to the ecosystem. Aromatic compounds exist in the effluents which originate from paint, oil, pharmaceutical, plastics, paper, and tissue industries [5]. Dye compound was used in a large quantity for the coloring of different materials, which were further divided into colorants substances such as dyes and pigments. Dyes are soluble in water while pigments are insoluble [6].

Activated carbon is commonly used for the elimination of contaminants from wastewater [7]. It determined exceptional adsorption ability such as high Surface area, pore structure and the properties of chemicals available on the surface. The structures of carbon absorbents are mostly microporous, mesoporous and macroporous. The equipment used for the preparation of carbon is well-ordered which would offer the application not only in the field adsorption and separation of macromolecules which cannot enter into the micropores but is also used in electrical double-layer capacitors, gas separation, catalysis, water and air purification and energy storage [8-10].

Methylene blue is a cationic dye, largely used for acrylic, nylon, silk and fabric dyeing in the textile industries. In the universe, approximately 11 ~ 16 % of the recycled dye is discharged in the waste of textile [11]. Methylene Blue causes eye burns leading to severe damage to the eyes of humans and animals. It causes short periods of inhalation problems and ingestion causes burning of the alimentary tract and may cause nausea, mental confusion, and vomiting [12].

Marketable dyes are typically a mixture of a large number of complexes and their molecular structure and properties have not been reported so far. Dyes are also very common in chemical composition. In short basic dyes are considered one of the more challenging classes of dyes which are considered toxic colourants. As a consequence, enhanced and cost-effective technologies are required to remove them from textile effluents [13,14].

Methylene blue dye (MB), is a basic dye that has been mostly used in the textiles and printing industry, and it has been found a non-biodegradable dye. Numerous techniques such as chemical or physical have been used for a wide range of wastewater contaminated processes, which include coagulation/flocculation, ozonation, oxidation, ion exchange, irradiation, precipitation, and adsorption [15,16]. Several critical reviews on current treatment technologies were reported [17]. But most of these techniques are costly, required several tools and have limitations. It has been reported that the adsorption onto activated carbon, has proven to be the most efficient and reliable method for the removal of many pollutants, including different dyes [16]. While commercial activated carbon is a very effective adsorbent, its high cost needs the search for substitutes of low-cost adsorbents [18]. Several low-cost adsorbents have been used for eliminating dyes [19], such as orange peel, peat, pith [18], giant duckweed, cellulose, banana pith and other agricultural wastes [19]. While *Eucalyptus Lanceolata* is generally found in different areas in Malakand, Pakistan as well as in other countries.

However, there are no reports of obtaining activated carbon from *Eucalyptus Lanceolata*. Therefore, the basic purpose of the recent research is to prepare efficient adsorbent which can eradicate the toxic substances from an aqueous media and compared the kinetics, adsorption, and thermodynamic properties of raw and activated carbon. Moreover, Intraparticle diffusion, Elovich and Bhangam models were applied to evaluate kinetics studies at different temperatures. Thermodynamic parameters, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta E^{\neq}$ were investigated from the adsorption kinetics.

Experimental

Preparation of carbon used as an adsorbent

The source materials used were the stem of Eucalyptus lenceolata, which were constantly heated in the absence of oxygen for about 8 h in an oven, with an outlet for the release of water molecules. Carbon attained almost half of the sample mass, which was cooled in a room temperature and crushed with the help of a pestle and separated with US standards mesh 150-180 μm. The carbon was leached with standard 0.2 N nitric acid and hydrochloric acid solutions in 1:1 and allowed for 24 h at 25 °C with regular mixing. The sample was filtered and washed with distilled water until it becomes neutral. The carbon was further activated with organic solvent n-hexane for 24 h at 25 °C with mechanical stirring to remove the organic content. The carbon was filtered and was air-dried in an oven at 80 ± 2 °C. The activated carbon was allowed to cool in the presence of an inert atmosphere.

Methylene blue is used as an adsorbate

Methylene blue is used as an adsorbate supplied by BioM Laboratories, Cerritos USA (Chemical Division Malaysia). Dyes stock solution was prepared from which the different solutions were prepared in double distilled water. The chemical structure and trade name of the dye is given in Scheme 1.

Chemical Name:	Methylene blue (C.I. 52015)
Molecular Formula:	$C_{16}H_{18}N_3SCl.xH_2o$
Molecular Weight:	319.85 g.mol^{-1}
λ_{max}	663-67 nm
Water solubility:	Soluble in water
Melting point	100-110 °C (with decomposition)
Boiling point	Decomposes
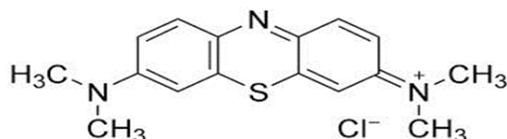
Scheme 1. Chemical structure of methylene blue.

Characterization

The surface area of the carbon was calculated through BET-N$_2$. The test was designed manometrically at 195 °C and pore size analyzer (Model: Quanta chrome NOVA 2200). For the identification of elemental analysis used, Energy dispersive spectrum (INCA 200 Oxford Instruments). SEM of the sample was obtained through aluminum discs (1 cm x 0.25 cm) and by using SEM-Model-JSM-5910, Japan JEOL. Fourier transmission infrared spectrum of the carbon was achieved, using 8201PC Shimadzu Fourier Transform Infrared Spectrophotometer along with FTCOM-1 computer organize disc part.

Adsorption studies
Equilibrium time

0.1 g of carbon was taken in reagent bottles and activated with 10 cm^3 of the basic dye solution. Two altered initial concentrations of the dye were prepared for the sample and added 1:10 carbon to adsorbate in reagent bottles which were homogenized in a thermostated water bath at 25 °C for several periods such as 0.5, 1, 2, 4, 6 and 8 h [20]. Fig. 1 shows the standard curve of absorbance. Moreover, it indicates that the equilibrium was reached up to 4 h and then become plateau. It was concluded from the equilibration study that 4 h is the optimum time to cover the surface. Moreover, the sample was filtered, and the filtrate was examined due to a change in the concentration of dye through spectrophotometer. The quantity of adsorbed dye (D_Φ *Mol.g^{-1})* was calculated.

$$D_\phi = \frac{D_\circ - D_\sigma}{W} V \qquad (1)$$

Where D_o is preliminary concentration and D_σ is the equilibrium concentration of dye (mol dm^{-3}), V represents the volume of dye and the weight of the adsorbent was denoted by W.
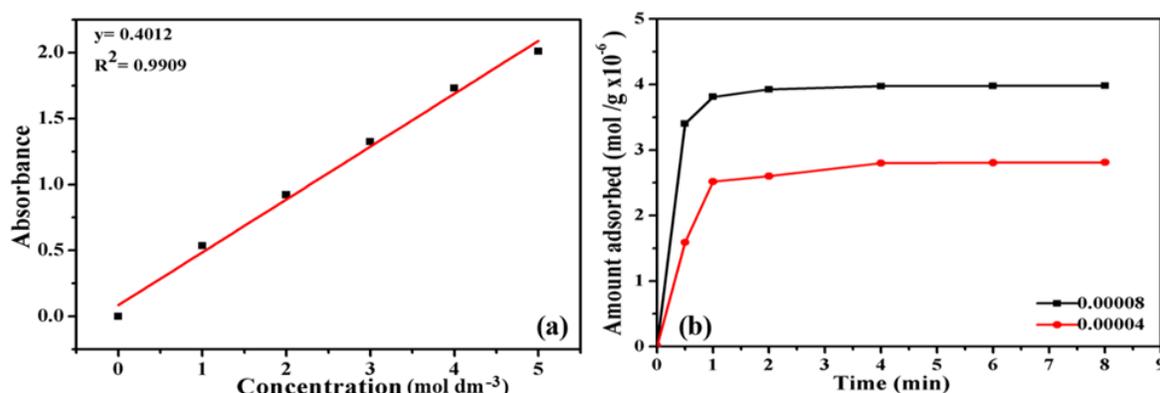
Fig. 1. (a) standard curve **(b)** equilibration curve for the adsorption of methylene blue.

Adsorption kinetic study

The 0.1 g adsorbent was mixed with 10 cm^3 of adsorbate solution. The reaction mixture was shaken at 20 °C, 30 °C and 40 °C for 10-40 mins. Furthermore, changes occur in the concentration were analyzed by the filtered slurry.

Discussion

Raw and activated carbon prepared from the wood of *Eucalyptus Lanceolata* were analyzed through different analytical techniques such as SEM, EDS, and FTIR for the structural composition. However, BET was used to measure the surface area. Adsorption of Methylene blue on the samples was indicated through the batch adsorption procedure at various temperatures. These results were then interpreted by different models.

SEM/EDS

SEM is used to recognize the surface morphologies of the sample. The SEM images indicated that there are various numbers of sizes, as well as shapes and pores, are present on the sample surface which is presented in Fig. 2. Elemental analysis of the raw and activated carbon was examined through EDS which reveals that carbon and oxygen are present in the samples. The ratio of carbon was surplus as compared to oxygen [21]. However, in the raw carbon, a small per cent of calcium is also detected as shown in Table 1.

Table 1. Elemental composition of raw and activated carbon.

Element	Weight % raw carbon	Weight % activated carbon	Atomic % raw carbon	Atomic % Activated carbon
C	77.03	72.29	81.96	77.66
O	22.32	27.71	17.83	22.34
K	0.21	-	0.07	-
Ca	0.45	-	0.14	-
Total	100	100	100	100
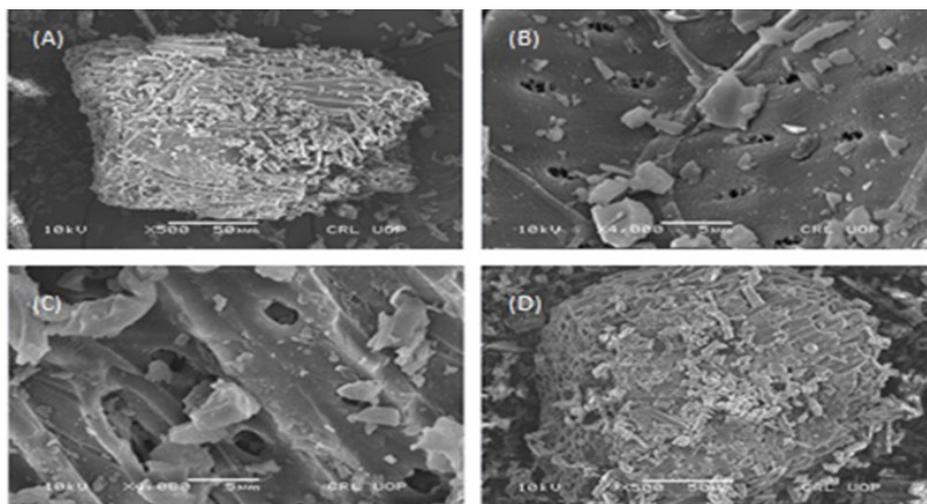
Fig. 2. Scanning electron micrographs of (A) raw carbon with (X500), (B) (X4000), (C) activated carbon with (X500), (D) (X4000).

FTIR

The adsorption band that arises at 1735 cm^{-1} can assign to H-O-H bending. According to the literature, the absorption band indicates the bending mode of adsorbed water. All the samples were dried for FTIR analysis but as mentioned in the literature, it is too difficult to remove all the water from the sample. FTIR spectra of raw and activated carbon are given in Fig. 3. A strong band appears in the regions 1032 cm^{-1} indicating the C-O stretching bond was present in the spectrum of both samples, but the changes occur in their transmittance of 83.47 % for activated whereas 91.38 % was associated with raw carbon [22]. C=C group are present at 1595 cm^{-1} with 98.20 % transmittance in raw carbon, but in the case of activated carbon, it was 1598 cm^{-1} with 96.59% transmittance. C–O group was present on 1179.29 cm^{-1}, and 1182.55 cm^{-1} in raw as well as in activated carbon. Whereas the raw and activated carbon display the C=O band in the region of 1732 cm^{-1}. C=C show stretching bonds in the benzene rings band on 1511.12 cm^{-1} with 98.20 % and 1504.59 cm^{-1} with 96.59 % for the raw and activated carbon [23]. C = O represent stretching which indicates the existence of oxygen-containing functional groups, such as carboxyls, phenols and ethers C_6H_5-O-CH_3 or –CH_2-O-CH_3. Sharp bands in the area of 1000-1100 cm^{-1} indicate that mineral matters were present in both spectra.
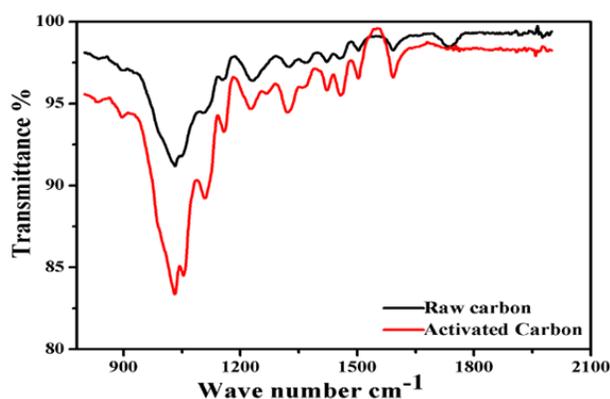
Fig. 3. FTIR spectra of the raw and activated carbon.

The surface area

Brunner Emit and Teller (BET) is a procedure [24] through which the surface area of the sample was calculated. It is built on multilayer adsorption in the presence of an inert atmosphere on the surface of adsorbent, which offers a base to spread microporous surface area of the adsorbent. The process is based on monolayer adsorption Langmuir's theory goes to multilayer adsorption with assumptions: the molecules of N_2 adsorb on the surface of adsorbent in different layers. Whereas the absence of intramolecular attractive forces. Langmuir's model is appropriate for each adsorbed layer. Following is the linear form of BET.

$$\frac{1}{v[(\frac{Po}{P}) - 1]} = \frac{C-1}{v_m c}\left(\frac{p}{po}\right) + \frac{1}{v_m c} \tag{2}$$

p and po are the adsorbate diffusion pressure, a quantity of the adsorbed gas on the surface is denoted by v, whereas v_m is the volume of unilayer N_2 adsorbed and C is used for the constant value which is given below:

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right) \tag{3}$$

E_1 represented the heat of sorption for the first layer, and E_L is used for the upcoming layers.

Equation 2 represented the adsorption isotherm by plotting $v[(\frac{Po}{P}) - 1]$ vs $\emptyset = {}^P/_{P_0}$, which indicated slope and 1 is used for intercept to examine the unilayer adsorbed N_2, v_m as known as constant c by using the following equation.

$$v_m = \frac{1}{A+1} \tag{4}$$

$$c = 1 + \frac{A}{I} \tag{5}$$

The following equation was known as the total specific surface area.

$$S_{BET,total} = \frac{(v_m N_s)}{V} \tag{6}$$

v_m is the molar volume of nitrogen gas, and V represented the Molar volume of adsorbate gas.

$$S_{BET} = \frac{S_{total}}{a} \tag{7}$$

Surface area (S_{BET}) of the activated, as well as raw carbon, were obtained from 1/W [(P_o/P)-1] against P/P° adsorption of N_2 which was increased from 150 to 355m².g⁻¹ for *Eucalyptus lenceolata*. The results show that the surface area increases with treating the carbon samples with chemicals as given in Table 2. During chemical changes the surface became tidy, and the foreign substances were eliminated and developed the surface for the adsorption of dye molecules. Another reason for a high surface area is due to the carbon surface with a non-polarity at high temperature is the fact that these groups are available on the sample surface which leads to a homogeneous [25]. Eisazadeh studied specific surface area and pore structure and its main characteristics in determining its chemical and physical contacts. Due to this fact, most of the chemical reactions occur on the surface. In the same way, the analysis of physical properties such as permeability requires an exact

measurement of specific surface area and the pore structure. One of the most familiar methods for determining the surface area known is BET method [15].

Table 2. BET surface area (m^2/g) of carbon.

Adsorbent	*Eucalyptus lenceolata*	
	Raw	**Activated**
	399 m^2/g	475 m^2/g

Adsorption studies
Equilibration time and adsorption kinetics

Equilibration time for dye adsorption on the surface of carbon was activated for a while of 0.5, 1, 2, 4, 6 and 8 h at room temperature. Fig.1 shows that equilibrium was achieved up to 4h and then it becomes linear. It was decided from the study of equilibration that 4hrs is the optimum period for surface coverage. Due to equilibration time, the range of solution for the adsorption kinetics was prescribed and adsorption of dye was considered at 20, 30 and 40 °C on all the raw and activated samples were shown in Fig. 4 and Tables 3-4. It was detected that adsorption within fifteen minutes was very quick and then reduced due to the extreme diffusion on the surface of the carbon. With rising in adsorption temperature sorption of dyes on adsorbent increases that was the evidence of the endothermic process.
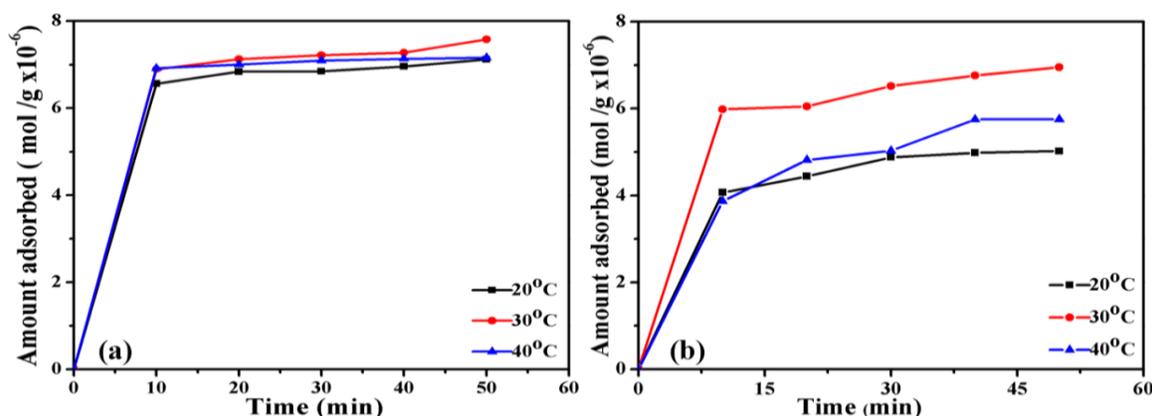
Fig. 4. Adsorption kinetics of methylene blue on the surface of **(a)** raw **(b)** activated carbon.

Linear equations for adsorption kinetic

Calculation of the rate constant by using the first order for the adsorption of Methylene blue on the woody plants *Eucalyptus Lanceolata* [26].

$$\ln D_\sigma = \ln D_o - k_{ad} t \tag{8}$$

D_o is initial and D_σ is the equilibrium concentration of dyes (mol dm^{-3}), whereas rate constant is represented by k_{ad} which were examined from the straight line of $\ln D_\sigma$ vs. t at various temperatures given in Tables 3-4. The values for rate constant increased with increasing experimental temperature. The value of R^2 was (0.8– 0.99) near to 1, indicating best agreement with literature.

The activation energy was calculated through the Arrhenius straight line equation [27].

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad (9)$$

Activation energy is denoted by E_a, k_1 and k_2 represent rate constants, R denoted gas constant and T is used for absolute temperature. The calculated activation energies for adsorbed dyes at different temperatures on the surface of carbon are mentioned in Table 7. The sequence of the adsorbed dye was given in the following order. 33.67, 49.14 were recorded for the activated, as well as for the raw samples. The rate of reaction of Methylene blue on raw carbon is low, whereas the rate of reaction is high for Methylene blue on activated carbon. Different thermodynamic parameters such as $\Delta H\#$ and $\Delta S\#$ were calculated from activation energies given in Table 5 by using the equations [26].

$$\Delta H^{\#} = \Delta E^{\#} - RT \qquad (10)$$

$$\Delta S^{\neq} = R\left[\ln \frac{kh}{k_B T} + \frac{\Delta H^{\neq}}{RT}\right] \qquad (11)$$

Where **k,** k_B, h, was the rate constant, Boltzmann constant and Planck constant respectively. The value of $\Delta H^{\#}$ for the adsorbed dye on a raw and activated carbon was 1.495 to 0.915. The endothermic nature of the sample was known by the positive values of $\Delta H^{\#}$. The negative values of the entropy ($\Delta S^{\#}$) exposed the affinity of the dyes towards carbon which decreases with the increase in adsorption temperature leads that the system is in order.

Elovich model

Linear form of the Elovich model is expressed as [28].

$$q_t = \frac{1}{A}\ln(BA) + \frac{1}{A}\ln(t) \qquad (12)$$

Straight lines were obtained by drawing q_t against ln (t) with the slope of "*1/A*" and intercept "*1/AlnBA*" were shown in Fig. 6. The values of "*A*" reduced from 20 °C to 40 °C which displays that higher temperature is preferred for the adsorption Tables 6-7. The value R^2 is near to 1 determined that Elovich is best fitted for the adsorption of dyes on the surface of the carbon.
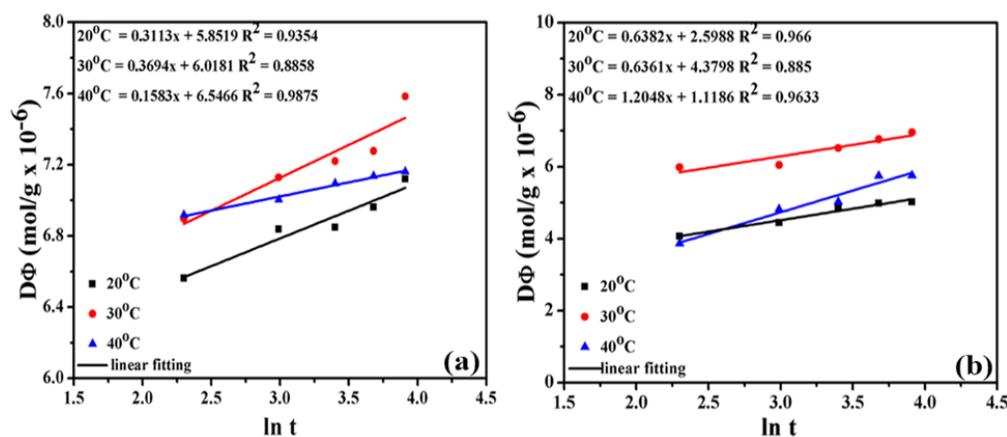
Fig. 5. Elovich graph for adsorption of Methylene blue on the surface of **(a)** raw **(b)** activated carbon.

Table 6. Comparison of the parameters for rate equations of methylene blue on the raw carbon.

Kinetic model	Parameter	Adsorption temperatures		
		20 °C	**30 °C**	**40 °C**
Elovich	A_E (g/mg)	3.212	2.707	6.317
	R^2	0.9354	0.8858	0.9875
Intraparticle diffusion	C (mg/g)	6.4936	6.7639	6.8754
	K_{id} (mg/gmin$^{1/2}$)	0.0248	0.0305	0.0124
	R^2	0.9201	0.9336	0.9453
Bangham	A	-0.272	-0.5008	-0.1657
	K_O	3.224	4.606	2.015
	R^2	0.9131	0.7673	0.9826

Table 7. Comparison of the parameters for rate equations of methylene blue on the activated carbon.

Kinetic model	Parameter	Adsorption temperatures		
		20 °C	**30 °C**	**40 °C**
Elovich	A_E (g/mg)	1.566	1.572	0.830
	R^2	0.966	0.885	0.9633
Intraparticle diffusion	C (mg/g)	3.9424	5.6533	3.6323
	K_{id} (mg/gmin$^{1/2}$)	0.049	0.0532	0.0939
	R^2	0.8813	0.9588	0.9078
Bangham	A	-0.1904	-0.4204	-0.4016
	K_O	7.830	7.369	13.587
	R^2	0.9649	0.8644	0.9488

Bangham equation

Linear form of the Bangham equation is written as.

$$\log \log \frac{D_o}{D_o - D_\sigma W} = \log \frac{k_o W}{2.303 V} + \alpha \log t \tag{13}$$

In the solution, D_o is the initial concentration of dye, W represents the weight of adsorbate, the volume of the solution is denoted by V, D_σ is the amount of quantity adsorbed at time t. In the Tables 6-7 the value of k_o and α were calculated from the intercepts and slopes of the linear graph in Fig. 6. With the increase of shaking temperature, the values of α decreases whereas, k_o increased with the increase in temperature of adsorption indicated that the distribution of dye on the pores of carbon is significant leads to a well-controlled process [14,29,30].
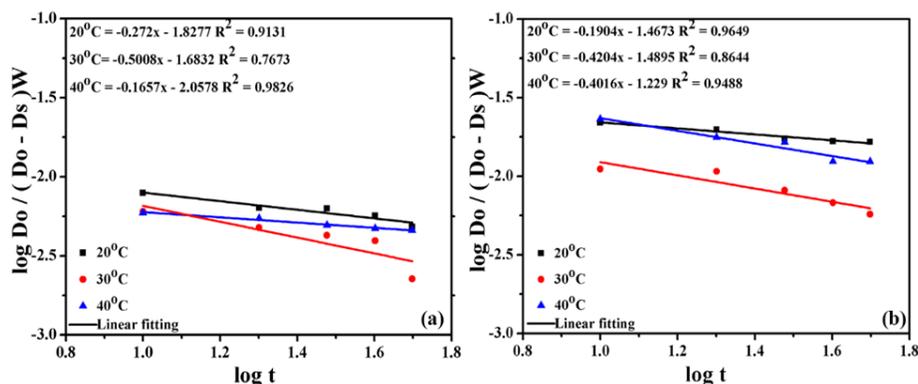
Fig. 6. Bangham plots for adsorption of Methylene blue on the surface of **(a)** raw **(b)** activated carbon.

Parabolic diffusion model or intarparticle difussion

Previous phenomena from the graph between D_Φ vs. $t^{1/2}$ show multi-linearity, which analyzed different phases counting in the adsorption [27]. According to Morris and Weber parabolic diffusion is denoted by the equation:

$$D_\Phi = k_{id}\, t^{1/2} + B \tag{14}$$

The k_{id} value is achieved by a graph of D_Φ against $t^{1/2}$ as revealed in Fig. 7. Moreover, the Intraparticle diffusion coefficient (k_{id}) is specified in Tables 6-7. The k_{id} values for Methylene blue at 40 °C: 0.0939 for activated carbon, and 0.0124 for raw carbon. The correlation coefficient R^2 for the Intraparticle diffusion adsorption is 0.999 which is closer to 1 showing best agreement for the adsorption of dye. This is due to the instant operation of most easily obtainable adsorbing sites on adsorbent the surface.

Equation (1) states a relationship between equilibrium constant and temperature. Fig. 1 indicates a straight line between $\ln K$ against $1/T$. The values of ΔH and ΔS were calculated from the slope and intercept, respectively. The thermodynamic parameters associated with the adsorption of MB onto activated carbon prepared from *Eucalyptus Lanceolata* are listed in Table 5. According to the van't Hoff equation, standard enthalpy and the entropy values in the range of 20-40 °C were obtained as 46.70 kJmol^{-1} and -0.123 kJmol^{-1}K^{-1}, respectively. The positive value of ΔH shows the endothermic nature of the adsorption process. Moreover, it confirmed the endothermic nature of the adsorption process. The negative value of ΔS indicates that the process is spontaneous and adsorption medium interface during the adsorption.
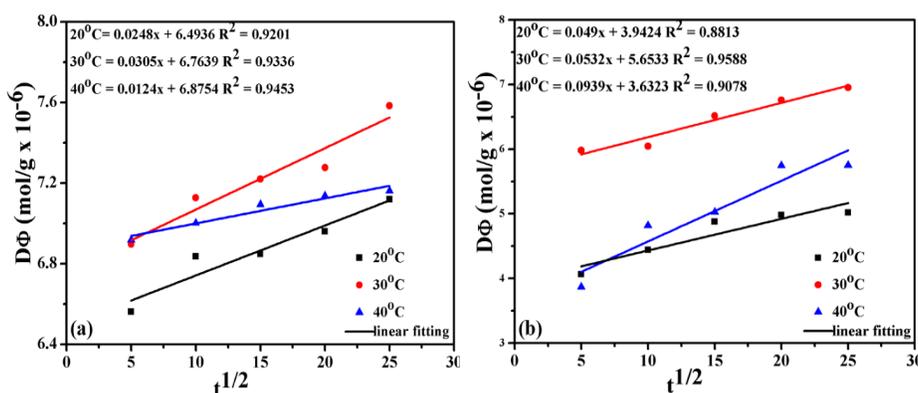
Fig. 7. Intraparticle diffusion for the adsorption of Methylene blue on the surface of **(a)** raw **(b)** activated carbon.

In recent work, the values of R^2 obtained from Intraparticle model equation were higher than 0.90, indicating that the Intraparticle model was a rate-limiting step in adsorption. However, if the Intraparticle model is the rate-controlling process, the fitted curve will start from the origin; and if the Intraparticle model occurs independently, there should be two or more fitted lines [31]. In the current research, there was only one fitted line which did not start at the origin Fig. 7. Additionally, the values of R^2 obtained from Bangham model were less than 0.90, suggesting that Intraparticle and Bangham models occurred simultaneously, but the Intraparticle model was the main rate control step; similar results were presented by Youssef et al. [32] and Xu and Liu. [33]. Literature also revealed that the formation of a chemical bond was also a rate control process [34]. The values of this experiment revealed that chemical reaction played an important role during adsorption and was also a rate-limiting step [33].

Table 3. Adsorption kinetics of methylene blue on the surface of raw carbon.

Time (Min)	**Adsorption Temperature = 20 ºC**				**Adsorption Temperature = 30 ºC**				**Adsorption Temperature = 40 ºC**			
	Ab_M	D_σ mol dm^{-3} $\times 10^{-5}$	$D_o- D_\sigma$ mol dm^{-3} $\times 10^{-5}$	D_ϕ mol/g $\times 10^{-6}$	Ab_M	D_σ mol dm^{-3} $\times 10^{-5}$	$D_o- D_\sigma$ mol dm^{-3} $\times 10^{-5}$	D_ϕ mol/g $\times 10^{-6}$	Ab_M	D_σ mol dm^{-3} $\times 10^{-5}$	$D_o- D_\sigma$ mol dm^{-3} $\times 10^{-5}$	D_ϕ mol/g $\times 10^{-6}$
10	1.530	3.934	4.065	4.065	0.785	2.018	5.981	5.981	1.607	4.132	3.867	3.867
20	1.384	3.558	4.441	4.441	0.760	1.954	6.045	6.045	1.238	3.183	4.816	4.816
30	1.214	3.121	4.878	4.878	0.577	1.483	6.516	6.516	1.156	2.972	5.027	5.027
40	1.174	3.018	4.981	4.981	0.482	1.239	6.760	6.760	0.876	2.252	5.747	5.747
50	1.159	2.980	5.019	5.019	0.407	1.046	6.953	6.953	0.875	2.249	5.750	5.750

Initial Concentration of Methylene blue = 8 ×10^{-5}mol dm^{-3}, Adsorbent doze = 0.1 g, Adsorbate volume=10 Cm^{-3}

Table 4. Adsorption kinetics of methylene blue on the surface of activated carbon.

Time (Min)	**Adsorption Temperature = 20 °C**				**Adsorption Temperature = 30 °C**				**Adsorption Temperature = 40 °C**			
	Ab_M	D_σ mol dm^{-3} $\times 10^{-5}$	$D_o- D_\sigma$ mol dm^{-3} $\times 10^{5}$	D_ϕ mol/g $\times 10^{6}$	Ab_M	D_σ mol dm^{-3} $\times 10^{5}$	$D_o- D_\sigma$ mol dm^{-3} $\times 10^{-5}$	D_ϕ mol/g $\times 10^{-6}$	Ab_M	D_σ mol dm^{-3} $\times 1^{-5}$	D_o-D_σ mol dm^{-3} $\times 10^{-5}$	D_ϕ mol/g $\times 10^{-6}$
10	0.559	1.437	6.562	6.562	0.429	1.103	6.896	6.896	0.421	1.082	6.917	6.917
20	0.452	1.162	6.837	6.837	0.339	0.871	7.128	7.128	0.388	0.997	7.002	7.002
30	0.448	1.151	6.848	6.848	0.303	0.779	7.220	7.220	0.352	0.905	7.094	7.094
40	0.404	1.038	6.961	6.961	0.281	0.722	7.277	7.277	0.336	0.863	7.136	7.136
50	0.342	0.879	7.120	7.120	0.162	0.416	7.583	7.583	0.326	0.838	7.161	7.161

Initial Concentration of Methylene blue = 8 ×10^{-5}mol dm^{-3}, Adsorbent doze = 0.1 g, Adsorbate volume=10 Cm^{-3}

Table 5. Thermodynamic constants for adsorption of methylene blue.

Sample	**k (min^{-1})**			$\Delta E^{\neq}$ (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})			$\Delta S^{\neq}$ (kJ mol^{-1}K^{-1})		
	20 ºC	**30 ºC**	**40 ºC**		**20 ºC**	**30 ºC**	**40 ºC**	**20 ºC**	**30 ºC**	**40 ºC**
Raw	0.0109	0.0212	0.0065	49.14	46.70	46.62	46.53	-0.157	-0.157	-0.172
Activated	0.0072	0.0175	0.0179	33.67	31.23	31.15	31.06	-0.213	-0.209	-0.213

Conclusion

In a recent paper, sample was examined through SEM, EDS and FTIR to study the structural composition of the *Eucalyptus lenceolata*. BET studies were used to measure the surface area, 399 to 475 m²g⁻¹, confirmed that the surface area increased with the chemical treatment. The adsorption of Methylene blue on each sample was investigated through batch adsorption procedures at various temperatures (20 °C, 30 °C and 40 °C). The spectra of EDS reveal that the sample contains a high content of carbon and oxygen. The region of 3406.29 cm⁻¹ and 3414.0 cm⁻¹ in the FTIR bands are the evidence of (-OH) stretching group which leads to hydrogen bonding. 4 h was the maximum equilibration time for the complete coverage of the surface. The positive value of $\Delta H^{\#}$ indicated that the process was endothermic. Moreover, the negative value of $\Delta S^{\#}$ shows that the system is in order. The results show that the adsorption of dyes on the surface of carbon particles is fit to the linear equations, and it was summarized that it favors a diffusion-controlled process.

Acknowledgments

References

1. Mian, I.,; et al. *Bioresour. Technol.* **2019**, *294*, 122099.
2. Bach, Q.-V.; et al. *Energy Convers. Manag.* **2017**, *141*, 72-78.
3. Kambo, H. S.; Dutta, A. *Energy Convers. Manag.* **2015**, *105*, 746-755.
4. Rai, H. S.; et al. *Crit. Rev. Environ. Sci. Technol.* **2005**, *35*, 219-238.
5. Pholosi, A.; Naidoo, E. B.; Ofomaja, A. E. *Mater. Chem. Phys.* **2019**, *222*, 20-30.
6. Caccin, M.; et al. *J. Radioanal. Nucl. Chem.* **2013**. *297*, 9-18.
7. Ayranci, E.; Duman, O. *J. Hazard. Mater.* **2005**, *124*, 125-132.
8. Shiau, C. Y.; Pan, C. C. *Sep. Sci. Technol.* **2005**, *39*, 1733-1750.
9. Dod, R.,; Banerjee, G.; Saini, S. *Biotechnol. Bioprocess Eng.* **2012**, *17*, 862-874.
10. Rafatullah, M.; et al. *J. Hazard. Mater.* **2010**, *177*, 70-80.
11. Liu, X.; Wang, Y. *Mater. Chem. Phys.* **2019**, *222*, 369-376.
12. Hameed, B.; Ahmad, A.; Latiff, K. *Dyes Pigm.* **2007**, *75*, 143-149.
13. Al-Degs, Y. S.; et al. *Dyes Pigm.* **2008**, *77*, 16-23.
14. Alam, S.; et al. *Bull. Chem. Soc. Ethiop.* **2017**, *31*, 411-422.
15. Crini, G. *Dyes Pigm.* **2008**, *77*, 415-426.
16. Aksu, Z. *Process Biochem.* **2005**, *40*, 997-1026.
17. Robinson, T.; et al. *Bioresource Technol.* **2001**, *77*, 247-255.
18. Pollard, S.; et al. *Sci. Total Environ.* **1992**, *116*, 31-52.
19. Garg, V. K.; et al. *Dyes Pigm.* **2004**, *63*, 243-250.
20. Chiang, Y.-C.; Chiang, P.-C.; Huang, C.-P. *Carbon.* **2001**, *39*, 523-534.
21. Pradhan, B. K.; Sandle, N. *Carbon*. **1999**, *37*, 1323-1332.

22. Cooke, N. E.; Fuller, O. M.; Gaikwad, R. P. *Fuel*. **1986**, *65*, 1254-1260.

23. Qasem, N. A.; El-Shaarawi, M. A. *Sol. Energy.* **2013**, *98*, 523-542.

24. Roosta, M.; et al. *Spectrochim. Acta, Part A*. **2014**, *122*, 223-231.

25. Laidler, K.; Suomen Kemistil. A. **1960**, *33*, 44; Laidler, K. J. in: *Chemical Kinetics*, McGraw Hill, 2nd Edit, New York, **1965**.

26. Sharma, M.; Vyas, R. K.; Singh, K. *Adsorption*. **2013**, *19*, 161-188.

27. Aharoni, C.; Sideman, S.; Hoffer, E. *J. Chem. Technol. Biotechnol.* **1979**, *29*, 404-412.

28. Qadeer, R.; et al. *J. Chem. Soc. Pak.* **1995**, *17*, 82-86.

29. Vadivelan, V.; Kumar, K. V. *J. Colloid Interface Sci.* **2005**, *286*, 90-100.

30. Iqbal, Y.; Khan, M.; Ihsanullah, N. *Int. J. Environ. Stud.* **2005**. *62*, 57.

31. Shahin, M. in: *Water resources and hydrometeorology of the Arab region*, Vol. 59, Springer Science & Business Media, **2007**.

32. Youssef, A.; El-Nabarawy, T.; Samra, S. *Colloids Surf. A.* **2004**, *235*, 153-163.

33. Zengnian, S.; Minghua, Y. *Chin. J. Chem. Eng.* **2010**, *18*, 372-376.

34. Anirudhan, T.; Suchithra, P. *Chem. Eng. J.* **2010**, *156*, 146-156.