

## Kinetics and Thermodynamics Evaluation of Activated Carbon Derived from Peanuts Shell as a Sorbent Material

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### Abstract

Studies on resource assessment of raw materials shows that many agricultural waste raw materials are available to be used as adsorbent material. We were investigated the adsorption factors such as initial concentration (25 to 125 mg/l), pH (2 to 12), temperature (30 to 60°C) adsorbent dose (0.50 to 1.50 gm/l) and particle size (0.05 to 0.5 mm), by using a batch adsorption technique to obtain information on treating effluents from the dye industry. The results showed that Peel Peanuts Activated Carbon (PPAC) was effective, for which the removal reached 99% methylene blue at 30°C. Adsorption of methylene blue was highly pH-dependent (6-8) and adsorption increases with initial MB concentration. Also temperature and smaller adsorbate particle were found to increase the percentage removal of MB, for which the removal reached 99.9% methylene blue at 60°C. Adsorption of MB on PPAC will fit the Langmuir model, corroborating the assumption of that the adsorbate molecules could be adsorbed in one layer thick on the surface of the adsorbent material. A comparison of kinetic models at different conditions showed that the pseudo second-order kinetic model correlate the experimental data well. The thermodynamic parameter shows that the adsorption process is endothermic. This is in accordance with increasing adsorption rate with increasing temperature.

**Keywords:** Kinetic models; Activated carbon; Peanuts shell; Thermodynamic parameters

### Introduction

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate (solid) phase. In principle adsorption can occur at any solid fluid interface. Examples include Gas-solid interface and Liquid-solid interface [1,2] studied the equilibrium conditions of adsorption of a basic dye on hardwood sawdust, they found that the adsorption of astrazone-blue (basic blue FRR 69) on beech-wood conform with both Langmuir and Fuendlich isotherms. The temperature of adsorption had the greatest effect on decreasing the contact time. A 44.4% reduction in contact time was obtained by raising the temperature from 25 to 80°C [3,4] tested the ability of maize cobe, (an agricultural waste), to adsorb dyestuffs. The author studied the adsorption of two basic dyestuffs (astrazone-blue and maxilon-red) and two acid dyestuffs (telon-blue and erionyl-red) onto maize cobe. He reported that, while high adsorption was observed in the case of basic dyes (160 and 94.5 mg of astrazone blue and maxilone-red per gm maize cobe, respectively), low adsorption was observed for acidic dyes (47.7 and 41.4 mg of erionyl-red and telon-blue per gm of the same adsorbent, respectively). Further studies [5,6] stated the rate of adsorption increases by increasing the rate of agitation and decreases by increasing the particle size. These reports studied adsorption equilibria of some basic dyestuffs namely, basic blue and basic red 22 onto maize cobe, in terms of the coast of maize cobe. McKay et al. [7] studied the adsorption of four dyestuffs onto bagassepith (by-product of the sugar industry remaining after the extraction of juice), for the adsorption of two basic dyes namely, basic-blue 69 and basic-red 22 and two acid dyes including acid-blue 3 and acid-red 114. Gupta et al. [8] studied the removal of omega chrome dye red (ME) from aqueous solutions by using mixed adsorbents fly ash and coal in different proportions, they presented a comparative studies of the adsorption capacities and coast of the activated carbon, fly ash, coal and fly ash-coal mixture (1:1) showing that the mixture of fly ash and coal (1:1) may substitute the activated carbon. El-Saiid et al. [9,10] studied the factors that affecting the removal of basic dyes namely

rosaniline (basic violet 14) and methylene blue (basic blue 9) from industrial wastewater using the Egyptian bagasse (a waste by-product of the sugar industry) as adsorbent, they stated that bagasse is a suitable adsorbent and methylene blue has much higher affinity for bagasse than rosaniline. Rashed et al. [11,12] reported that carbon soot (by-product result from partial oxidation of natural gas, Talkha fertilizer and chemical plant, SEMADCO-Egypt, now named as El-Delta for Fertilizer Production) is a promising material for different industrial applications as a substitute for commercial powdered activated carbon. Sarkar and Poddar [13] studied the adsorption of methyl violet (C.I. basic violet) from aqueous solutions onto coal, fly ash under varying reaction condition. They reported that the process is endothermic and diffusion controlled and follow first order kinetics. The equilibrium data conform to the Langmuir adsorption model. Al-Sarawy et al. [14] studied the removal of some commercial soluble organic dyes (drymarine violet, cibacrone yellow, reactive yellow, brokion rabin, reactive green) from their solutions at room temperature by using powdered activated carbon (PAC) and carbon soot as adsorbents in a comparative study. Benfield et al. [15] studied the adsorption of various organic compounds onto activated carbon. Their result helps to explain the effect of such characteristics as functionality, molecular weight, polarity, and solubility on adsorption. Low and Lee [16] studied the removal of some organic dyes by using hexane extracted spent bleaching earth (a waste material from the palm oil industry)

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as adsorbent, they showed that this adsorbent show better adsorption affinity for basic dyes than acid dyes. Experimental data showed that both of the boundary layer and intraparticle diffusion effect play an important role in the rate of dye removal. Safarik et al. [17] used the magnetic charcoal (prepared by entrapment of fine charcoal particles into the structure of magnetic iron oxide) as adsorbent. This adsorbent can efficiently adsorb a variety of organic compounds. Banerjee et al. [18] studied the adsorption kinetics of o-xylene by fly ash, o-xylene is an organic compound found in industrial wastewater, they demonstrated that an intraparticle diffusion mechanism plays a significant role in the adsorption of o-xylene by flash, and it is apparent that the adsorption rate is controlled by the diffusion process.

The aims of the present study are determine the optimum conditions for the removal of methylene blue from simulated wastewater by adsorption technique using Peel Peanuts Activated Carbon (PPAC), study the best isotherm model fit the obtained data and investigate the kinetics and thermodynamics of the adsorption study.

## Materials and Methods

### Preparation of peel peanuts

The Peel Peanuts were thoroughly washed with tap water to remove dirt and grime then rinsed a few times with distilled water and air dried. The clean Peel Peanuts were carbonized in a muffle furnace at 600°C for 3 h. The obtained carbon was lightly ground in a mortar and sieved using test sieve shaker [19].

### Adsorbent activation

Chemical activation using H<sub>2</sub>SO<sub>4</sub> at moderate temperatures produces a high surface area and high degree of micro-porosity. The materials were in a 1:1 wt ratio with 98% H<sub>2</sub>SO<sub>4</sub> soaked for 24 h at room temperature. The samples were placed in an oven and heated to 120 ± °C where they were held for 24 h. After this, the samples were allowed to cool to room temperature and washed with distilled water and soaked in 1% NaHCO<sub>3</sub> solution to remove any remaining acid. The samples were then washed again with distilled water until pH reached to about 6. The activated carbon dried at 105°C for 5 h and sieved to different particle size [19].

### Batch adsorption studies

Batch experiments with PPAC were conducted to investigate the initial adsorbent particle size (0.05 to 0.5 mm), adsorbent dose (0.25 to 1.5 gm), 50 ml volume of dye concentration (25, to 125 mg L<sup>-1</sup>), pH (2 to 11), and temperature (30 to 60°C) on MB adsorption. All reagents used were of AR grade (Sigma-Aldrich, Germany). MB stock solution were prepared by dissolving a known amount of the dye in distilled water and diluted to the required initial concentration. 50 ml of MB solution of known concentration (c<sub>0</sub>) was taken in a 100 ml conical flask with the required amount of adsorbent and was shaking for different time intervals in a shaker at different pH values and different temperatures. Then, the solution was filtered through a filter paper. UV-visible spectrophotometer (model PHTOMECH 301-D<sup>+</sup>, λ<sub>max</sub>: up to 1200, made in German) was employed to determine the remaining concentrations of MB in the filtrate. All adsorption experiments were performed in triplicate, and the mean values were used in data analysis. Blank experiments, performed without the addition of adsorbent, confirmed that the sorption of dye on the walls of flasks was negligible. The Details of the dye used were in Table 1, and the structure in Figure 1.

## Adsorption Isotherms Study

The main factors that play the key role for the dye-adsorbent interactions are charge and structure of dye, adsorbent surface properties, hydrophobic and hydrophilic nature, hydrogen bonding, electrostatic interaction, Steric effect, and van der Waal forces etc. [20]. Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and that remained in solution at equilibrium at fixed temperature. Freundlich, Langmuir and BET isotherms are the earliest and simplest known relationships describing the adsorption equation [21,22].

### Langmuir isotherm

The Langmuir equation is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and is expressed by:

$$q_e = (q_{\max} K_L C_e) / (1 + K_L C_e) \quad (1)$$

The linearize form of the above equation after rearrangement is given by:

$$C_e/q_e = 1/q_{\max} K_L + C_e/q_{\max} \quad (2)$$

The experimental data is then fitted into the above equation for linearization by plotting C<sub>e</sub>/q<sub>e</sub> against C<sub>e</sub>.

### Freundlich isotherm

The Freundlich model named after Freundlich (1926) is an empirical equation used to estimate the adsorption intensity of the sorbent towards the adsorbate and is given by:

$$q_e = K_F C_e^{1/n} \quad (3)$$

Also, the value of n indicates the affinity of the adsorbate towards the adsorbent. The above equation is conveniently used in linear form as:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (4)$$

<b>Molecular Weight</b>	<b>319.85222 [g/mol]</b>
Molecular Formula	C <sub>16</sub> H <sub>18</sub> ClN <sub>3</sub> S
λ <sub>max</sub>	670 nm
Odor	Slight odor
Melting point	105°C (decomposes)
Commercial name	Methylene Blue, thiazine
Covalently-Bonded Unit Count	2
H-Bond Donor	0
H-Bond Acceptor	3
Water solutions	deep blue
Solubility in water	43,600 mg/L at 25°C
pKa	Less than 1

Table 1: Properties of Methylene Blue (MB).

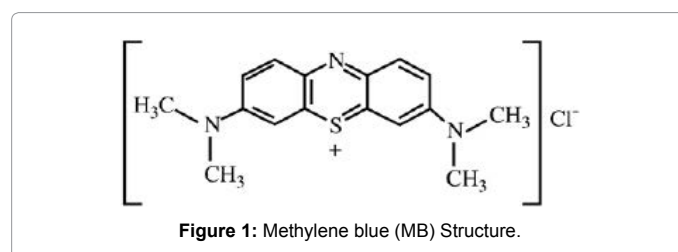


Figure 1: Methylene blue (MB) Structure.

A plot of  $\ln C_e$  against  $\ln q_e$  yielding a straight line indicates the conformation of the Freundlich adsorption isotherm. The constants  $1/n$  and  $\ln K_f$  can be determined from the slope and intercept, respectively.

### BET isotherm

The BET (Brunauer, Emmeth and Teller) derived an adsorption isotherm based on the assumption that the adsorbate molecules could be adsorbed in more than one layer thick on the surface of the adsorbent. Their equation, like Langmuir equation, assumes that the adsorbent surface is composed of uniform, localized sites and that the adsorption at one site does not affect adsorption at neighboring sites. Moreover, it was assumed that the energy of adsorption holds the first monolayer but that the condensation energy of the adsorbate is responsible for adsorption of successive layers. The equation, known as the BET equation, is commonly written as follow:

$$x/m = A c X_m / (c_s - c) [1 + (A-1) c/c_s] \quad (5)$$

Rearranging the BET equation yields:

$$C/(C_s - C)x/m = 1/AX_m + (A-1)(C/C_s)/AX_m \quad (6)$$

Thus, plotting  $C/(C_s - C)$  against  $C/C_s$  will give rise to straight lines with slope  $(A-1)/AX_m$  and intercept  $1/AX_m$  for adsorption processes that conform BET equation [23].

### Adsorption Dynamics Study

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. Kinetics of (MB) adsorption on the PPAC was analyzed using pseudo first-order, pseudo second-order, Elovich, and intraparticle diffusion kinetic models [24].

#### The pseudo first-order model

The pseudo first-order equation (Lagergren, 1898) is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (7)$$

At  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ , the integrated form of Equation (7) becomes:

$$(\log q_e - \log q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (8)$$

where  $k_1$  and  $q_e$  can be determined from the slope and intercept of the plot.

#### The pseudo second-order model

The pseudo second-order kinetic rate equation is expressed as (Ho et al.):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

At  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ , the integrated form of Equation (9) becomes:

$$\frac{t}{(q_e - q_t)} = \frac{t}{q_e} + kt \quad (10)$$

Equation (4) can be rearranged to obtain Equation (11), which has a linear form:

$$\frac{t}{q_t} = \frac{t}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

If the initial adsorption rate,  $h$  (mg/g. min) is:

$$h = k_2 q_e^2 \quad (12)$$

Then Equations (11) and (12) become:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (13)$$

The plot of  $(t/q_t)$  and  $t$  of Equation (11) should give a linear relationship from which  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot, respectively.

### The Elovich model

The Elovich model equation is generally expressed as:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (14)$$

To simplify the Elovich equation, Chien and Clayton assumed  $\alpha\beta t \gg 1$  and by applying the boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ , Equation (14) becomes:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (15)$$

A plot of  $q_t$  vs.  $\ln(t)$  should yield a linear relationship with a slope of  $(1/\beta)$  and an intercept of  $(1/\beta) \ln(\alpha\beta)$ .

### The intraparticle diffusion model

The intraparticle diffusion model is expressed as (Weber and Morris, 1963)

$$R = k_{id} (t)^a \quad (16)$$

A linearized form is obtained as:

$$\log R = \log k_{id} + a \log(t) \quad (17)$$

If (MB) adsorption fits the intraparticle model, a plot of  $\log R$  vs.  $\log t$  should yield a linear relationship with a slope of  $a$  and an intercept of  $\log k_{id}$ .

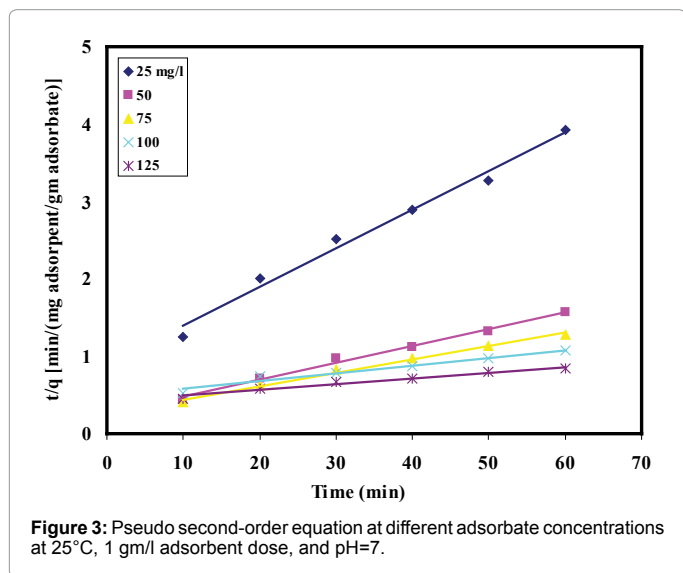
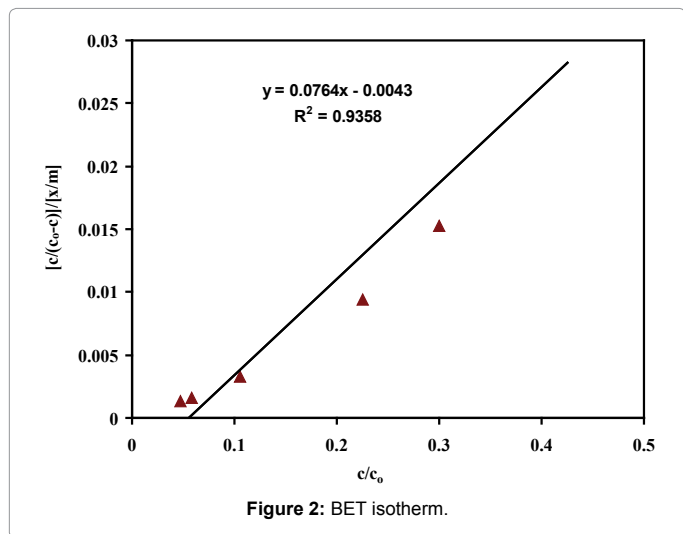
## Results and Discussion

### Adsorption isotherms

The results of this study show that PPAC was effective, in adsorbing MB. The removal reached about 98% at 30°C. Adsorption of MB was highly pH-dependent and the results showed that the optimum pH for the removal was found to be (6-8), at which MB exists mostly as the most easily adsorbed form aqueous solution increases as the initial MB concentration. Also smaller adsorbate particle were found to increase the percentage removal of MB, but the increasing of temperature result no changing in the removal efficiency. The Experimental data were applied in the three isotherms, where results indicate that the adsorption of MB on PPAC fits the BET model (Figure 2) with  $R^2=0.936$ , verifying the assumption that the adsorbate molecules could be adsorbed in more than one layer thick on the surface of the adsorbent.

### Adsorption dynamics

**Effect of adsorbate concentrations:** The removal of MB by adsorption on PPAC was found to increase with time and attained a maximum value at 40 min. On changing the initial concentration of MB solution from 25 to 125 mg/l, the amount adsorbed increased at 30°C, pH 7.5 and particle size of 0.05 mm. The experimental results correlate with the theoretically predicted curves. Results obtained show good compliance with the pseudo second-order kinetic model (Figure 3), with values of correlation coefficient,  $r^2 > 0.969$ .



**Effect of temperature:** Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. The experimental data were obtained at pH 7.5, particle size blew 0.05 mm, and initial concentration of 25 mg/l. The increasing adsorption rate of MB on the surface of PPAC may be explained by considering more conversion of the dimer species to monomers. The data obtained for each of the kinetic models from the slopes of plots (Figure 4) show a good compliance with the pseudo second-order equation, with values of correlation coefficient,  $r^2 > 0.9994$ .

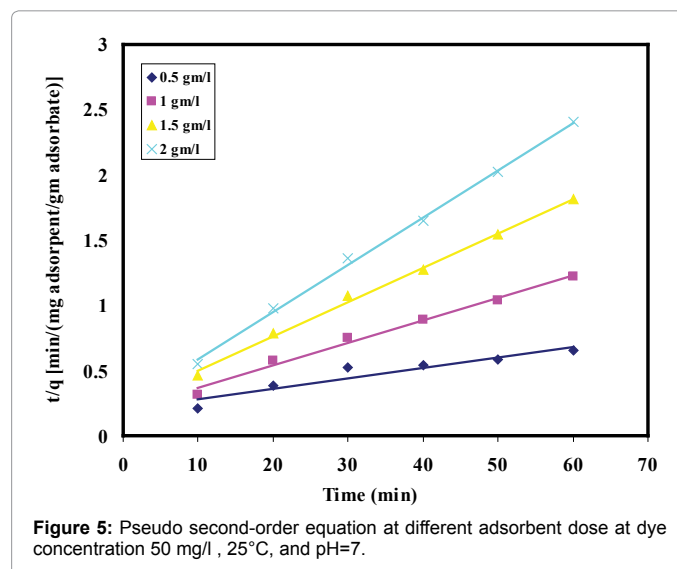
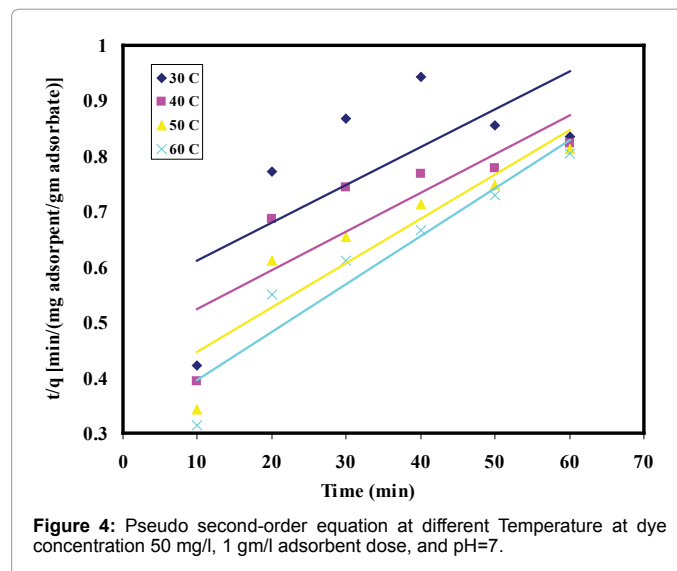
**Effect of adsorbent dose:** MB uptake was studied using different doses of PPAC by using 50 ml of solution at pH 7.5, 30°C, particle size blew 0.05 mm and initial concentration of 25 mg/l. The concentrations used were 0.5, 0.75, 1, 1.25 and 1.5 gm adsorbent/ liter adsorbate, keeping the batch experimental volume the same in all cases. The results indicated that the percent adsorption increased with the increase in PPAC dose. The curves in Figure 5, showed good compliance with

pseudo second-order model with values of correlation coefficient,  $r^2 > 0.985$ .

**Effect of pH:** The removal of MB was studied at different pH in the range 2-12 by PPAC at initial MB concentration of 25 mg/l, and a temperature of 30°C, particle size blew 0.05 mm. The variation in adsorption capacity in this pH range is largely due to the influence of pH on the adsorption characteristics of the PPAC which indicates that the adsorption capacity of the adsorbent is clearly pH dependent. The optimum removal (98%) was observed in the pH range 6-8. Results also showed that the adsorption reaction can be approximated with the pseudo second-order kinetic model (Figure 6), with values of correlation coefficient,  $r^2 > 0.9917$ . The rate constants and values of correlation coefficient are represented in Table 2. Finally the Scanning electron micrographs before and after adsorption are shown in Figures 7 and 8 respectively.

### Thermodynamic parameters

**Determination of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ :** The values of the thermodynamic parameters, enthalpy variation ( $\Delta H$ ) and entropy



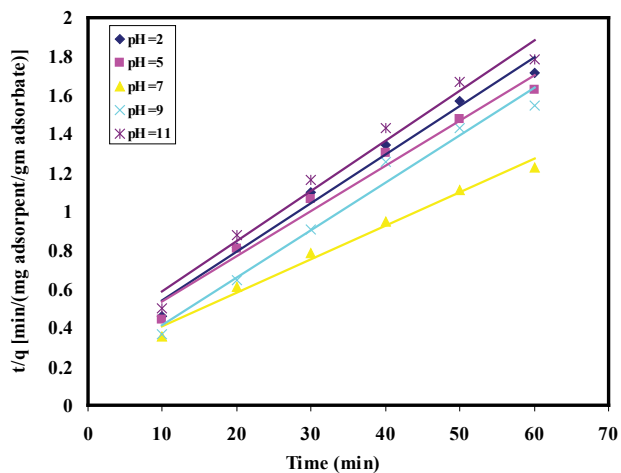


Figure 6: Pseudo second-order equation at different pH values at dye concentration 50 mg/l, 25°C, and 1 gm/l adsorbent dose.

Weight before Carbonization (g)	10
Weight after Carbonization (g)	5.3
Weight after activation, washing and drying (g)	4.7
Yield (%)	47%
Bulk density (g/cm <sup>3</sup> )	0.93
Specific surface area (m <sup>2</sup> /g)	0.145
Total pore volume (cc/g)	0.09
Total micropore volume (cc/g)	0.016

Table 2: Characterization of PPAC.

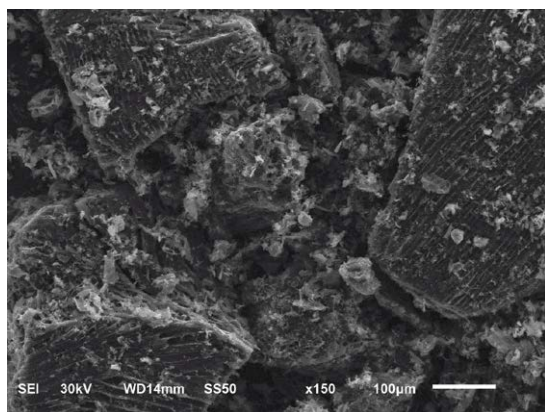


Figure 7: Scanning electron micrographs before adsorption.

variation ( $\Delta S$ ), were calculated from the curve relating the distribution coefficient ( $K_D$ ) as a function of temperature (Figure 9) using the equation:

$$\ln K_D = \left( \frac{\Delta S^\circ}{R} \right) - \left( \frac{\Delta H^\circ}{RT} \right) \quad (18)$$

where  $K_D$  is the distribution coefficient ( $\text{cm}^3 \cdot \text{g}^{-1}$ ), defined as:

$$K_D = \frac{Q}{C_e} \quad (19)$$

where  $Q$  is the amount adsorbed (mg adsorbate/g adsorbent) described by the equation:

$$Q = \frac{V(C - C_e)}{m} \quad (20)$$

where  $C$  and  $C_e$  are the initial and equilibrium concentrations of the solute, respectively ( $\text{mg} \cdot \text{cm}^{-3}$ ). The calculated data for  $K_D$  and  $Q$  are shown in Table 3.

The free energy change ( $\Delta G^\circ$ ) parameter was calculated using equation 21:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (21)$$

From Figure 9 the values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  were determined from the slopes and intercepts of the curves, respectively as well as the calculated values of  $\Delta G^\circ$  and are listed in Table 4. Investigation of the obtained values of the thermodynamic parameters shows that the adsorption process is endothermic. This is in accordance with increasing adsorption equilibrium with increasing temperature.

**Determination of mean free energy (E):** The mean free energy of adsorption ( $E$ ) is the free energy change when one mole of ions is transferred to the surface of the membrane from infinity in the solution and it is calculated from:

$$E = -(2K_D R)^{\frac{1}{2}} \quad (22)$$

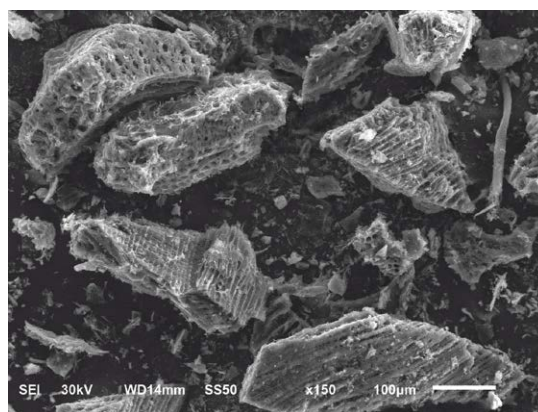


Figure 8: Scanning electron micrographs after adsorption.

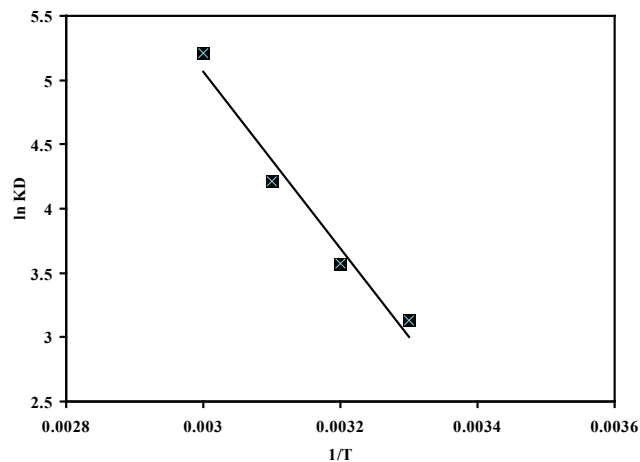


Figure 9: Plot of  $1/T$  versus  $\ln K_D$ .

Parameter		First order		Second order			Elovich model			Intraparticle diffusion		
		$k_1$	$r^2$	$k_2$	$h$	$R^2$	$\beta$	$\alpha$	$r^2$	$k_{id}$	$a$	$r^2$
Concentration (mg/l)	25	0.096	0.893	0.04615	1.12549	0.9858	0.226629	2.436936	0.9716	10.727	0.3877	0.9872
	50	0.138	0.824	0.07551	3.94166	0.9932	1.7191	1.828126	0.9775	28.874	0.2976	0.9861
	75	0.092	0.765	0.05694	3.72439	0.9904	0.081693	8.750758	0.9864	17.049	0.3522	0.9981
	100	0.103	0.701	0.01923	2.09555	0.9629	0.046942	4.544212	0.9716	5.187	0.6257	0.9923
	125	0.111	0.714	0.01661	2.40731	0.971	0.036499	5.373516	0.9709	4.34	0.6608	0.999
Adsorbent dose (mg/l)	0.5	0.105	0.705	0.03657	4.98008	0.8944	0.03862	12.0155	0.8498	2.47	1.2399	0.8888
	1	0.137	0.738	0.07817	5.14138	0.988	0.094429	17.76161	0.9421	1.845	1.5203	0.9567
	1.5	0.126	0.781	0.13581	4.45434	0.9975	0.150231	16.6023	0.9845	1.756	1.5695	0.99
	2	0.13	0.842	0.09734	4.28632	0.9964	0.2465	34.16114	0.9738	1.543	1.6719	0.9787
Temp. (°C)	30	0.122	0.556	0.01155	1.83958	0.4781	0.080762	6.029079	0.7632	2.366	1.2558	0.8308
	40	0.161	0.586	0.01423	2.20312	0.6996	0.076693	7.338248	0.9097	2.345	1.3094	0.95
	50	0.161	0.612	0.02006	2.73224	0.8349	0.086341	11.92138	0.9465	2.019	1.4419	0.9705
	60	0.167	0.633	0.02582	3.24569	0.9052	0.096534	19.90073	0.9773	1.814	1.5369	0.9898
pH	2	0.139	0.574	0.07544	3.48189	0.9821	0.141519	13.1182	0.9404	1.808	1.369	0.9689
	5	0.131	0.593	0.06749	3.32557	0.9749	0.128961	11.69116	0.9142	1.862	1.3669	0.9458
	7	0.153	0.589	0.06426	4.22654	0.9861	0.087207	11.66265	0.9672	2.036	1.4307	0.9871
	9	0.114	0.539	0.12810	6.02409	0.9782	0.139243	9.890058	0.9353	1.4696	1.5677	0.8729
	11	0.124	0.580	0.067503	3.025719	0.9767	0.185663	79.57334	0.8431	1.901	1.3095	0.9685

Table 3: The adsorption kinetic model rate constants for PPAC.

The mean free energies ( $E$ ) were calculated and documented in Tables 5 and 6. The magnitude of  $E$  is useful for estimating the type of sorption reaction, since  $E < 8 \text{ kJ} \cdot \text{mol}^{-1}$ , physical forces such as diffusion processes may affect the sorption mechanism [24]. So, the adsorption of dyes seems to be a complex phenomenon, where diffusion and chemical bonding occur at different temperature ranges, this may support that the monolayer capacity ( $q_{max}$ ) increases with increasing temperature.

## Conclusion

- Adsorption of MB was highly pH-dependent (6-8), at which MB exists mostly as the most easily adsorbed form aqueous solution,
- Adsorption of MB increases as the initial MB concentration,
- Smaller adsorbate particle were found to increase the percentage removal of MB,
- PPAC was effective, for which the removal reached 99% MB at 30°C,
- Adsorption of MB on PPAC fits the Langmuir model, corroborating the assumption of that the adsorbate molecules could be adsorbed in one layer thick on the surface of the adsorbent,

• Investigation of the obtained values of the thermodynamic parameters shows that the adsorption process is endothermic. This is in accordance with increasing adsorption rate with increasing temperature,

• Finally PPAC can be used as effective adsorbent for dyes in industrial wastewater.

## Nomenclature

- A Constant describing the energy of interaction between solute and adsorbent surface;
- C Initial concentration (mg/l);
- $C_e$  Concentration equilibrium (mg/l);
- $C_s$  Saturation concentration of solute (mg/l);
- $K_F$  Freundlich constant;
- N Freundlich constant;
- m Mass of adsorbent (mg);
- $k_1$  Rate constant of pseudo first-order adsorption (l/min);

Temperature (°C)	Q	K <sub>D</sub>
30	47.91024	22.9262268
40	48.63712	35.6868811
50	49.27313	67.7879021
60	49.72742	182.434406

Table 4: Q and K<sub>D</sub> parameters at different temperatures.

ΔH kcal/mol	ΔS kcal/mol. K.	ΔG (kcal/mol)			
		30°C	40°C	50°C	60°C
57.064	0.2133	-7.56	-9.69	-11.8	-13.96

Table 5: Thermodynamic parameters at different temperatures.

Temperature (°C)	K <sub>D</sub>	E, kJ/mol
30	22.9262	-19.525
40	35.6869	-24.359
50	67.7879	-33.57
60	182.434	-55.077

Table 6: Free Energy (E) at different temperatures.

- $k_2$  Rate constant of pseudo second-order adsorption (g/mg.min);
- $K_D$  Distribution coefficient (cm<sup>3</sup>.g<sup>-1</sup>)
- $k_{id}$  Intraparticle diffusion rate constant (min<sup>-1</sup>)
- $K_L$  Constant related to the adsorption/desorption energy (l g<sup>-1</sup>);
- $q_e$  Adsorption capacity at equilibrium,(mg of dye/g adsorbate);
- $q_{max}$  Maximum sorption (mg of dye/g adsorbate);
- $q_t$  Adsorption capacity at time  $t$ , (mg of dye/g adsorbate);
- $R$  Universal gas constant (J/mole. K)
- $R$  Percent (MB) adsorbed;
- $t$  Contact time (min)
- $V$  Volume of the solution
- $x$  Amount of solute adsorbed (mg);
- $X_m$  Amount of solute adsorbed in forming a complete mono layer (mg of dye/g adsorbate);
- $\alpha$  Initial adsorption rate (mg of dye/g adsorbate.min);
- $\beta$  Desorption constant (g/mg) during any experiment.

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