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Study of Methylene Blue Removal by a biosorbent prepared with Apple peels

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Abstract

This work investigates the removal of the methylene blue by adsorption using dried apple peels. For this purpose, various experimental parameters were studied: pH [3-10], adsorbent dose [0.25- 3 g/L], solution temperature [10-40°C] and initial concentration of methylene blue [10- 345 mg/L]. Adsorption data were modeled using Langmuir, Freundlich and Temkin adsorption isotherms. The results indicated that the equilibrium data was well represented by Langmuir isotherm with R^2= 0.99. The maximum adsorption capacity is 107.52 mg/g.The Kinetics of methylene blue adsorption using apple peels is described by the pseudo-second order model. In addition, the thermodynamic parameters such as ΔH°, ΔS° and ΔG° were determined, and the dye adsorption process is exothermic.

1. Introduction

Everything in our world is colored, our clothing, our food, our cosmetics and pharmaceutics etc.These dyes are increasingly synthetic due to their facility of synthesis, their timeliness of production and their variety of colors in comparison with natural dyes [1]. To this end, textile industry produces huge amounts of waste water loaded with dyes. These dyes can be classified as anionic dyes, cationic dyes and no ionic dyes. Cationic dyes are the most toxic ones [2]. They have harmful effects on the environment such as: eutrophication, under-oxidation, resistance to organic biodegradation, bioaccumulation, mutagenicity and carcinogenicity [1].
In this regard, the treatment of waste water containing dyes has become a necessity.
A wide variety of physical, chemical and biological techniques has been introduced for the treatment of these effluents. These techniques are: coagulation-flocculation, membrane filtration, adsorption, oxidation and reduction [1].
Adsorption is relatively an easy technique to implement. Activated carbon is the most used adsorbent due to its high adsorption capacity [3]. But this later is very expensive, so research for other effective and cheaper adsorbents turns out interesting. Many adsorbents are widely used for adsorption of dyes such as clays [4], [5], [6]and agricultural waste specially fruit and vegetable peels. Several bioadsorbents were used for removal of textile dyes, for example: orange peel [7], [8], banana peel [9], pomelo peel [10], jack fruit peel [11], potato peel [12], melon peel [13] and cucumber peel [14].
Apple peels are produced in large amount in the worldwide as biowaste from food processing industries and offer abundant functional groups which can be exploited for water treatment.
The purpose of this work is the evaluation of adsorption capacity of a new adsorbent prepared from apple peels without any chemical treatment, by removal ofmethylene blue, which is most commonly used in dyeing in the textile industry, in biology and as an antiseptic in pharmacy.
Various experimental parameters were studied: pH, adsorbent dosage,initial dye concentration and temperature. Kinetics, adsorption isotherms and thermodynamic parametersof the adsorption of MB on dried apple peel were also studied.

2. Materials and methods

2.1. Adsorbent Preparation

Apples (Golden Delicious) were purchased from the local market. They were peeled and peelsdevoid of pulp were dried at a temperature of 60 °C for 24 h. Driedapple peels (DAP) were ground and sieved in order to obtain particles size inferior to 250 µm. The adsorbent is stored in closed container at room temperature.

2.2. Adsorbate

Methylene blue (MB) is a cationic dye of the thiazine class. It has the formula of $C_{16}H_{18}N_3SCl$, a molecular weight of 319.85 mol/g and its solubility in water exceeds 100 mg/L [15]. A stock solution (1 g/L) was prepared. To prepare various solutions at desired concentrations from the stock solution, distilled water was used for the necessary dilutions. Concentration of solutions was analyzed by measuring the absorbance values with a spectrophotometer at 664 nm.

2.3. Adsorbent characterization

2.3.1. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy of the adsorbent was done by using an FTIR spectrophotometer in therange from 600 to 4000cm^{-1}, in order to determine the functional groups present in the DAP surface.

2.3.2. Point of zero charge (pH_{pzc}) of DAP

pH_{pzc} is one of adsorbent characteristics. It was estimated by introducing 0.5 g of DAP in 50 mL of distilled water at initial pH values of3, 4, 6, 8 and 10 adjusted by adding required amounts of NaOH (0.1 N) or HCl (0.1 N). The mixture was stirred for 24 hours at room temperature, and the final pH was measured [16].

The intersection between the first bisectrix and the curve representing the variation of the final pH with the initial pH gives a pH_{pzc} equal to 5.8.

2.4. Adsorption studies

Adsorption experiments were carried out by introducing a quantity of the adsorbent in 1L of methylene blue solution at initialconcentration and at the desired temperaturemaintained with a thermostated bath. The mixture was stirred on an electromagnetic stirrer at a constant speed(400 rpm). The controlled parameters are: initial concentration of MB, pH, temperatureand adsorbent dose. Samples of the solution were withdrawn at various time intervalsand centrifuged at 2000 rpm for one minute.The supernatant absorbance is measured using the spectrophotometer at 664 nm.The removal percentage (%R) of methylene blue is calculated as follows:

$$\%R = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

C_i (mg/l) is the initial concentration of MB,C_e(mg/L) is the dye concentration at equilibrium.

Adsorption capacity of methylene blue is given by the following formula:

$$q_t = \frac{(C_i - C_t) \times V}{m} \quad (2)$$

q_t (mg/g) is the amount adsorbed at time t (min), C_t(mg/L) is the dye concentration at time t;

V (L)is the volume of dye solution and m (g) is the mass of theadsorbent used.

3. Theory and calculation

3.1. Adsorption isotherms

The study of adsorption isotherm is necessary in order to understand the adsorption mechanism. In the present investigation the experimental data were modeled using Langmuir, Freundlich and Temkin isotherm

3.1.1. Langmuir isotherm

Langmuir theory assumes [17]:

- Adsorbent has a limited adsorption capacity (q_{max})
- Adsorbate forms a monolayer on the adsorbent surface
- Active sites are identical
- Absence of interaction between the adsorbed molecules.

Langmuir isotherm is given by the following equation:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (3)$$

C_e(mg/L) is the concentration of the adsorbate in solution at equilibrium, q_e (mg/g) is the adsorbed amount at equilibrium, q_{max} (mg/g) is the maximum amount adsorbed, K_L(L/mg) is the Langmuir constant.

Its linear form is:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\ K_L} + \frac{C_e}{q_{max}} \quad (4)$$

3.1.2. Freundlich isotherm

Freundlich model [18], is applied in the case of multilayer adsorption. However, this model assumes the existence of interactions between adsorbed molecules. Freundlich isotherm model can be defined by the following equation:

$$q_e = K_F C_e^{1/n} \quad (5)$$

q_e(mg/g) is the adsorbed amount at equilibrium, C_e (mg/L) is the concentration of the adsorbate in the solution at equilibrium, k_F is the Freundlich constant, n is the adsorption intensity.

Its linear form is given by the following equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

3.1.3. Temkin isotherm

Temkin's model is based on the hypothesis that the heat of adsorption due to interactions with the adsorbate decreases linearly with the recovery rate, whiting gas phase adsorption. This is an application of the Gibbs relation to the adsorbents, whose surface is considered homogeneous energy.

Several authors [19], [20] proposed to use this model in the liquid phase.

Temkin equation is given by the following expression:

$$\frac{q_e}{q_{max}} = \frac{RT}{\Delta Q} \ln(K_T \,.\, C_e) \quad (7)$$

q_e (mg/g) is the adsorbed amount at equilibrium, q_{max} (mg/g) is the maximum amount adsorbed, T (K) is the absolute temperature, ΔQ (J/mol) is the variation in adsorption energy K_T (L/mg) is the Temkin constant.

The Temkin equation can be written:

$$q_e = B \ln K_T + B \ln C_e \quad (8)$$

$$B = q_{max} \frac{RT}{\Delta Q} \quad (9)$$

4. Results and discussion

4.1. FTIR characterization of DAP

The FTIR spectrum of dried apple peels before and after methylene blue adsorption is shown in Figure 1.

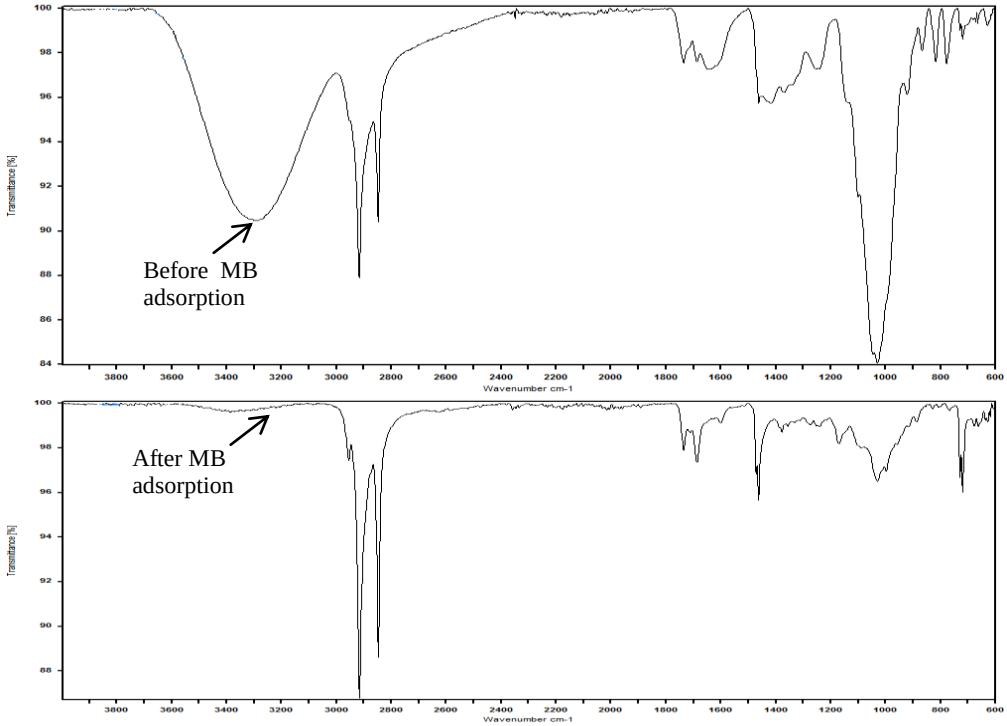


Figure 1: FTIR spectra of DAP before and after MB adsorption

From Table 1 we can see that -OH groups, C=O group of carbonyl, carboxyl groups,C-O-C group andC-O groups disappeared in the FTIR spectra of DAP after adsorption of methylene blue. While C=O groups of esters, asymmetric and symmetric stretching of –C-H in -CH_2 groups, C-O-C group of etherand C=O groups shifted in positions. So we can conclude that MB binding mostly at OH, C-O, C-O-C and C =O groups.

Table 1: FTIR peaks of DAP before and after adsorption of MB

Peaks before adsorption	Peaks after adsorption	Difference	Functional groups
3284.93	disappear	unknown	-OH group
	2955.33	Appear	Stretchingin sym andasym of -CH aliphatic
2916.88	2915.88	-1	–C-H stretching inasym in -CH_2 group
2848.90	2848.24	-0.66	–C-H stretching inasym in -CH_2 group
1736.62	1736.25	-0.37	-C=O of ester group
1687.07	1687.16	+0.9	-C=O group of carbonyl (amide)
1645.25	disappear	unknown	-C=O group of carbonyl
	1472.07	Appear	Stretching of C=C bond in aromatic rings
1461.68	1462.27	+0.59	Stretching of C=C bond in aromatic rings
1417.88	Disappear	unknown	Carboxyl groups
1368.43	1377.20	+8.77	-C-O-C group of ether
1254.18	1239.62	-14.56	-C-O-C group of ether
	1170.32	Appear	-C=S group
1099.85	Disappear	unknown	-C-O group
1047.04	Disappear		-C-O-C group
1029.04	1028.80	-0.24	-C=O groups
866.71	Disappear	Unknown	Deformation of aromatic rings
817.66	disappear	Unknown	Deformation of aromatic rings
777.89	disappear	Unknown	S=O
	677.40		C-Cl

4.2. Effect of adsorbent dose

To study the effect of DAP dose on the removal of methylene blue in aqueous solution, experiments were conducted using 1L of methylene blue solution at initial concentration of 10 mg/L to which different quantities of DAP were added: 0.25, 0.5, 1, 2 and 3 g. Figure 2 shows the evolution of the adsorption percentage of the MB and of the MB adsorbed quantity (mg/g) as a function of the dose of DAP.

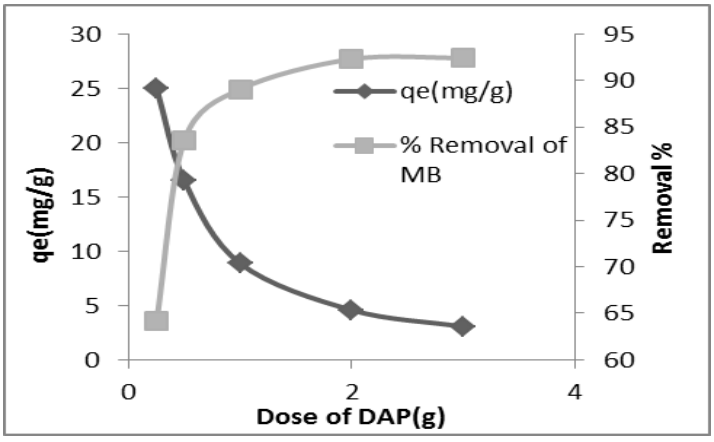


Figure 2: Effect of adsorbent dose on MB adsorption onto DAP
(MB Initial concentration =10 mg/L, T= 20°C, pH=6, time= 6 hours)

The results (Figure 2) indicate that adsorption percentage of MB increases with the increasing of adsorbent dose, it increased from 64% for 0.25g to 92% for 2g. This is due to the number of active sites that increases with increasing of adsorbent dose. While the amount of MB adsorbed (mg/g) decreased from 25.03 mg/g for 0.25g to 4.58 mg/g for 2g. When the mass exceeds 2g, the percentage of MB removed and adsorbed amount does not change significantly.

4.3. Effect of pH

pH is an important factor in adsorption study, because it can influence the adsorption mechanism.For this reason, the behavior of adsorption as a function of pH was studied in a pH range of 3 to 10. Figure 3 shows the effect of pH on methylene blue adsorption.As shown in Figure 3, the adsorption capacity (mg/g) increases in the pH range of 3- 6, then the amount becomes constant within the range of 6-10.

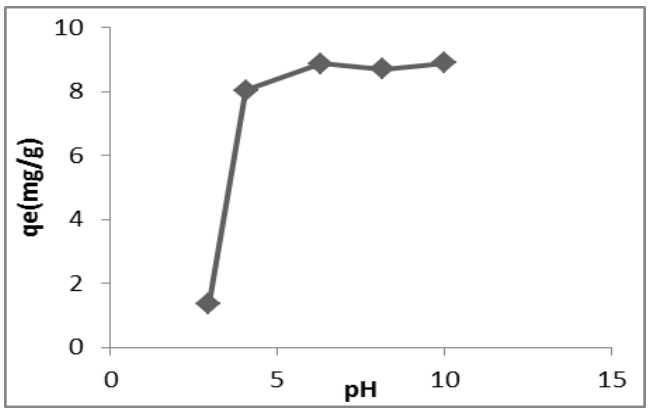
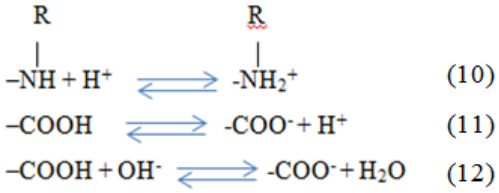


Figure 3: Effect of pH on MB adsorption onto DAP (MB concentration 10 mg/L, T= 20°C, DAP dose = 1g, time= 6 hours)

Methylene blue is a cationic dye; its adsorption is influenced by the adsorbent surface charge, which is influenced by the solutionpH. According to Uddinet al. [21] and[22], at pH <pH_{pzc}, adsorbent surface is positively charged due to the fixation of H^+ ions (protonation of amine groups(equation (10)). The $pH_{pzc}$of DAP is 5.8, which causes repulsion between MB and adsorption sites at pH<pH_{pzc}. At pH>pH_{pzc}, OH^- ions concentration increases leading to deprotonation of the carboxyl groups (equation (11) and equation (12)), and theadsorbent surface becomes negatively charged. So there is an attraction between MB and adsorbent surface. This explains the increase in the quantities adsorbed in comparisonwith those observed at pH <pH_{pzc} (Figure 3).



4.4. Effect of initial dye concentration

The effect of initialdye concentration was studied by introducing 1g of DAP in 1L of MB solution at different concentrations: 10, 20, 40, 54, 100 and 345 mg/L, at a temperature of 20°C , a pH of 6 and a contact time of 6 hours. Figure 4 represents the adsorption capacity (mg/g) versus the contact time for different initial concentrations.

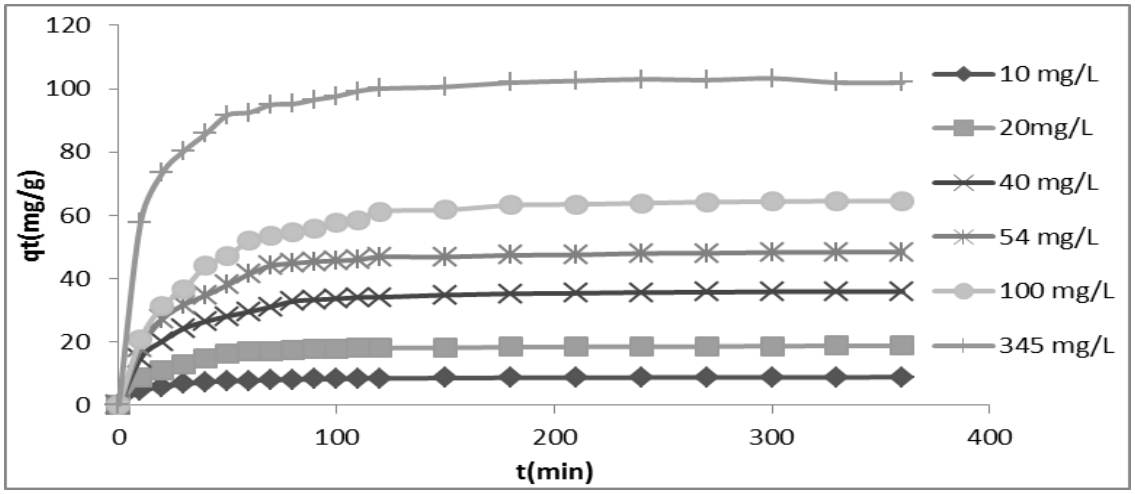


Figure 4: Effect of contact time on MB adsorption onto DAP at different initial concentrations

The results (Figure 4) show that the amount of MB adsorbed (mg/g) increases when the initial concentration increases.The adsorption capacity after 6 hoursis8.89, 48.45 and 103.27 mg/g for the initial dye concentration from 10, 54 and 345 mg/L respectively. This can be interpreted by the increasing of concentration gradient between MB solution and adsorbent surface. More the solution concentration increases more the gradient increases and more adsorption is better.

4.5. Adsorption isotherms

In order to determine adsorption isotherms, experiments were carried out in the following conditions: MB solution volume is 1L, initial concentrations are 10, 20, 40, 54, 100 and 345 mg/L, DAP dose is 1g, pH is 6, temperature is 20°C, stirring speed is 400 rpm and equilibrium time is 6 hours. Langmuir, Freundlich and Temkin constants and there related correlation coefficients were calculated and reported in Table 2.

The results showed that Langmuir fits better than the Freundlich and temkin equations with a $R^2 = 0.998$.

The best fit of equilibrium data in the Langmuir isotherm expression predicts the monolayer coverage of MB onto DAP, without any interaction dye-dye. The maximum adsorption capacity of MB on DAP in the studied conditions is equal to 107.5 mg/g. It is higher than some adsorbents capacities listed in Table 3.

Table 2: Constants of adsorption isotherms of MB onto DAP

Langmuir			**Freundlich**				**Temkin**		
q_{max} (mg/g)	K_L	R^2	1/n	n	K_F	R^2	A	B	R^2
107.52	0.091	0.998	0.398	2.509	15.258	0.827	1.773	16.92	0.984

Table 3: Comparison of adsorption capacity of DAP with other low-cost adsorbents

Adsorbent	**q_{max} (mg/g)**	**Reference**
Activated banana peel	19.7	[9]
Natural banana peel	18.6	[9]
Pomelo peel	133.0	[10]
Jackfruit peel	285.7	[11]
Potato peels	33.5	[12]
Palm kernel fiber	95.4	[16]
Wood apple shell	95.2	[14]
Tea waste	85.2	[21]
Dried Apple peel	107.5	This study

4.6. Adsorption Kinetics

In order to modelizeadsorption kinetics of MB on DAP, two kinetic models were tested.

4.6.1. Pseudo-first order model

The pseudo-first order model is expressed by the Lagergren equation [23]:

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \quad (13)$$

q_e and q_t are respectively the amounts of dye (mg/g) adsorbed at equilibrium and at time t. K_1 is the rate constant of the pseudo-first order (min^{-1}). After integrating and applying the initial conditions (at t = 0, $q_t = 0$ and $t = t_e$, $q_t = q_e$), the equation takes the form:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2{,}303} t \quad (14)$$

Figure 5 shows the presentation of the pseudo-first order model.

4.6.2. Pseudo-second order model

Adsorption data were also analyzed according to the kinetic model of the pseudo-second-order[24]:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad (15)$$

K_2 is the rate constant of pseudo-second order (g/mg. min). After integrating and applying the conditions (at t = 0, $q_t = 0$ and $t = t_e$, $q_t = q_e$), the equation takes the linear form:

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{1}{q_e} t \quad (16)$$

Figure 6 gives the presentation of the pseudo-second order model.

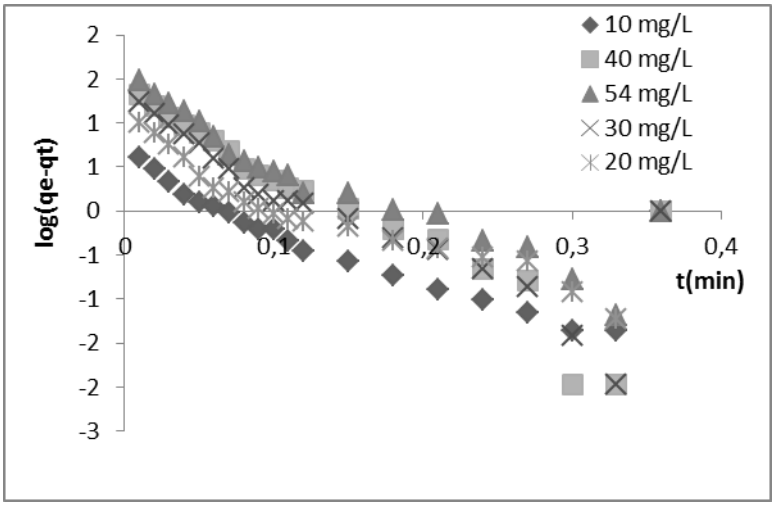


Figure 5: Pseudo-first order model of MB adsorption onto DAP

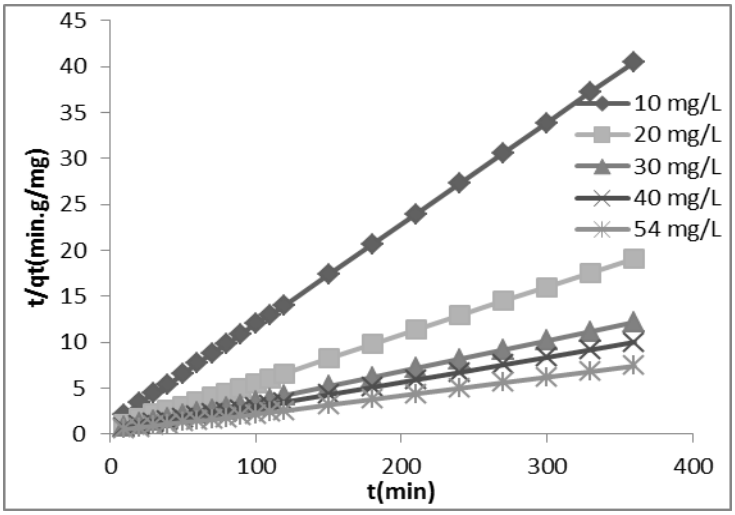


Figure 6: Pseudo-second order model

Results according to Figure 5 and Figure 6, show that the adsorption complies with a pseudo-second order equation. Indeed the R^2in this case is very near to 1 and the calculated q_e values ($q_e$cal), in Table 4, also agree with the q_e experimental ($q_e$exp). These results indicate that the adsorption system studied belongs to the second-order kinetic model.Several works on methylene blue bioadsorption have reported that the pseudo-second order model describes their results [25], [26].

Table 4: Kinetic parameters of MB adsorption on DAP at different initial concentrations

		Pseudo 1st order			**Pseudo 2nd Order**		
C (mg/L)	$q_e$exp (mg/g)	K_1 (min^{-1})	$q_e$cal (mg/g)	R^2	K_2 ($g.mg^{-1}.min^{-1}$)	$q_e$cal (mg/g)	R^2
10	8.90	0.009	1.31	0.6326	0.1055	9.15	1
20	18.84	0.012	1.90	0.8429	0.0699	19.42	0.9997
30	29.52	0.015	2.68	0.7601	0.0511	30.77	0.9995
40	35.88	0.017	3.30	0.7728	0.0432	37.59	0.9996
50	48.45	0.013	3.32	0.8320	0.0375	50.76	0.9993

4.7. Thermodynamic parameters

The influence of temperature on the adsorption was studied in the range of 10 to 40 °C. Figure 7 shows the variation of adsorption capacity (mg/g) of MB on the DAP according to the temperature. As we can see in Figure 7 the adsorption capacity decreased slightly from 9.08 to 8.56 mg/g when the solution temperature increases from 10 to 40°C. Since the adsorption decreased when temperature increased, the system is considered to be exothermic.

Thermodynamic parameters of adsorption were determined from the experimental results obtained at different temperatures using the following equations:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (17)$$

T (K) is solution temperature

$$K_d = \frac{q_e}{C_e} \qquad (18)$$

Where K_d is the distribution coefficient, q_e (mg/g) is the adsorption capacity at equilibrium, C_e(mg/L) is the solution concentration at equilibrium.

The standard enthalpy ΔH° and entropy ΔS° can be determined from the following equation of Van't Hoff:

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (19)$$

Where R is the universal gas constant.

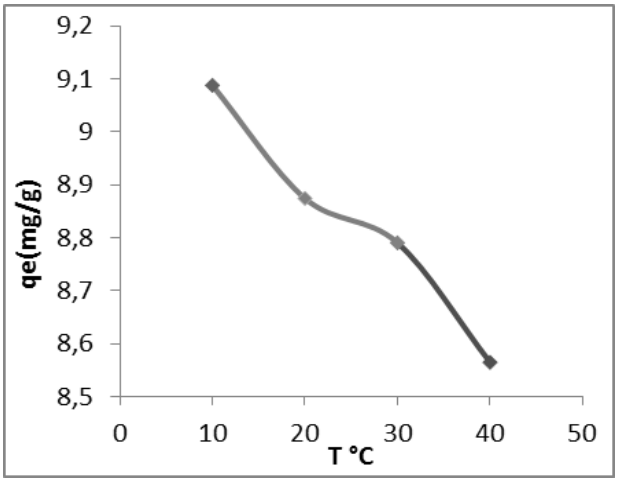


Figure 7: Effect of temperature on MB adsorption onto DAP

ΔH° and ΔS° were obtained from the slope and the intercept of the plot of Ln (K_d) as a function of 1/T respectively (Figure 8). Thermodynamic parameters are summarized in Table 5. The values of Gibbs free energy (ΔG°) of adsorption of MB adsorption on DAP were found to be negative corresponding to a spontaneous process [15]. The negative value of ΔH° confirms that adsorption phenomenon of MB on DAP is exothermic. The negative value of ΔS° indicates that the order of distribution of the dye molecules on the adsorbent is high compared to that in the solution. This also suggests the probability of a thermodynamically favorable adsorption [27].

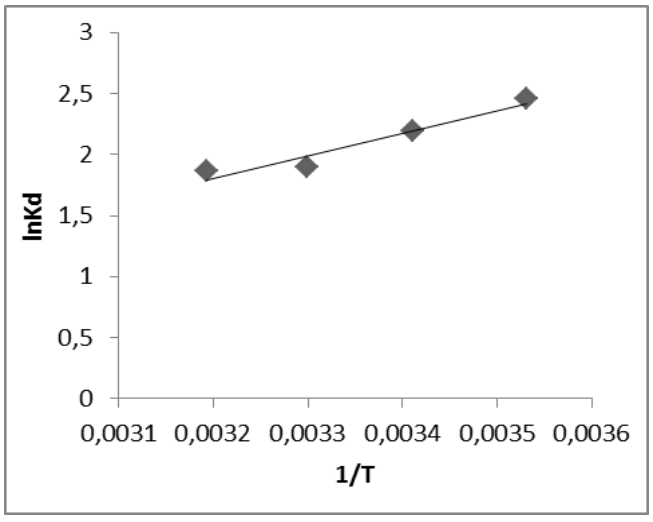


Figure 8: Van'tHoff plot for adsorption of MB on DAP

Table 5: Thermodynamic parameters of MB adsorption on DAP

T°C	q_e(mg/g)	ΔG°(Kcal/mol)	ΔS°(Kcal/K.mol)	ΔH°(Kcal/mol)
10	9.0877	-1.3609	-0.0082	-3.6706
20	8.8981	-1.2794		
30	8.7902	-1.1978		
40	8.5646	-1.1162		

Conclusions

Adsorption of Methylene blue on Dried Apple Peel has been studied. Adsorption experiments were carried out as a function of contact time, dye concentration, adsorbent dosage, temperature and solution pH.

MB adsorption capacity increased with the increasing of initial dye concentration and with the increasing of adsorbent dose until 2g. It increased with the increasing of pH and decreased when the temperature increased.

The adsorption data was well described by the Langmuir isotherm equation with a maximum adsorption capacity of 107.52 mg/g, a satisfying result in comparison with other bioadsorbents, moreover the peels are used without any treatment. The kinetics followed the pseudo-second order model.The thermodynamic parameters obtained show that the adsorption of the MB on DAP is spontaneous and exothermic

The present study concludes that Dried Apple peel could be employed as a low-cost adsorbent for the removal of methylene blue and can be a promising bioadsorbent for the elimination of other pollutants.

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