International Journal of Advanced Multidisciplinary Research
ISSN: 2393-8870
www.ijarm.com
DOI: 10.22192/ijamr Volume 4, Issue 1 -2017

Research Article

DOI: http://dx.doi.org/10.22192/ijamr.2017.04.01.007

Adsorption of methylene blue onto phosphoric acid activated carbon prepared from leaves of *Memsops elengi*

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Keywords

Activated carbon,
Phosphoric acid activation,
Isotherms,
Kinetics,
Methylene Blue dye,
Desorption.

Abstract

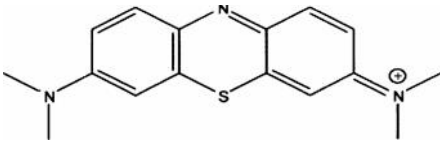
In this study, leaves of *Memsops elengi* were used as a precursor to prepare activated carbon using phosphoric acid as a chemical activation agent. The prepared activated carbon characteristics as an adsorbent were investigated. The results indicate that the prepared activated carbon has a highly porous structure and a specific surface area of 362 m^2/g. Batch mode adsorption experiments were carried out for adsorption studies. Influence of the parameters such as Dose of the adsorbent, agitation time, initial dye concentration of the solution and temperature on adsorption were studied. Kinetics of the system was studied with linearised forms of Lagergren, Ho and Webber Morris models. Equilibrium data were fitted with Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich isotherms. The order of best describing isotherms was given based on R^2 value. The obtained results show that leaves of *memsops* elengi is a good low cost precursor for the production of activated carbon.

1. Introduction

Fresh water is a renewable resource, yet the world's supply of groundwater is steadily decreasing, with depletion occurring most prominently in Asia, South America and North America, although it is still unclear how much natural renewal balances this usage, and whether ecosystems are threatened [1]. When water is contaminated it causes illness and disease. Poor water quality continues to pose a major threat to human health. The treatment of coloured effluents have been investigated by various physico-chemical methods and purely chemical methods like coagulation, flocculation, adsorption, ion exchange, reverse osmosis and electrochemical coagulation in treating the textile dye.

Several studies demonstrated the feasibility of chemical coagulation and precipitation for colour removal. Rebhun *et al.*,(1970) found adsorption on the activated carbon resulted in complete removal of the colour[2].The most widely used adsorbents are activated carbon because of their high surface area due to the presence of micro and meso pores. A number of studies have also been performed using activated carbon prepared from agricultural wastes for the removal of dyes from aqueous solution. Methylene blue dye (MB dye) is used as model adsorbate for adsorption of organic substance because of its known strong adsorption to activated carbon [3,4].

Structure of MB dye



In this present study, leaves of *Memsops elengi* have been used to prepare activated carbon. *Mimusops elengi* is a medium-sized evergreen tree found in tropical forests in South Asia, Southeast Asia and northern Australia. Hence, it is used to prepare carbon using phosphoric acid and to remove pollutants from aqueous solution.

Table 1 Data Processing Tools.

S. No.	Parameters		Formula
1.	**Mass balance relationships**	% of Removal	$(C_i- C_t)100/C_i$
		Quantity adsorbed at equilibrium, q_e	$(C_i- C_e)$ V/W
		Quantity adsorbed at the time t, q_t	$(C_i- C_t)$ V/ W
2.	**Kinetic Models and SSE**	Pseudo First order kinetics (Legergren equation) [5]	$\log (q_e-q_t)=\log q_e - k_1 /2.303 \times t$
		Pseudo Second order kinetics (Ho equation)[6]	$t/q_t=1/ k_2.q_e^2 +1/q_e t$
		The initial adsorption rate h [6]	$h = k_2q_e^2$
		Intra particle diffusion (Weber–Morris equation)[7]	$q_t = k_pt^{1/2} + C$
		Sumoferror squares	$SSE = \sqrt{\sum[(q_e)_{exp}-(q_e)_{cal}]^2}/ N$
3.	**Isotherms**	Langmuir [8]	$C_e/Q_e = 1/Q_0b + C_e/Q_0$
		Separation factor	$R_L = 1 / (1+ bC_0)$
		Freundlich [8]	$\log Q_e = \log K_f + 1/n \log C_e$
		Tempkin [9]	$q_e = RT/b_T \ln a_T + RT/b_T \ln C_e$
		Dubinin – Raduskevich,[8]	$\ln q_e = \ln q_D - B\varepsilon^2$
		Polanyi potential	$\varepsilon = RT \ln (1+1/C_e)$
		Mean free energy of adsorption	$E = 1/ (2B)^{½}$

Table 2 Nomenclature.

C_i,C_t and C_e	Initial Concentration, at the time 't' and at equilibrium respectively
q_e and q_t	Quantity adsorbed at the time 't' and at equilibrium respectively
V	Volume of the MB dye solution in liter (L)
W	Mass of the adsorbent in gram (g)
Q_e	Amount of solute adsorbed per unit weight of adsorbent (mg/g)
C_e	Equilibrium concentration of solute in the bulk solution (mg/L)
Q_0	Adsorption efficiency
b	Adsorption energy
R_L	Separation factor
C_0	Initial concentration of the MB dye solution
K_f and n	The constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively

b_T	Tempkin constant related to heat of sorption (J/mg)
a_T	Equilibrium binding constant
q_m	Constant related to adsorption capacity (mg/g)
B and A	Isotherm constants
q_D	Theoretical saturation capacity (mg/g)
B	Constant related to the mean free energy
ε	Polanyi potential
E	Mean free energy of adsorption
R	Gas Constant
T	Temperature (K)
k_1	Rate constant of adsorption (l/min)
k_2	Second-order constants
t	Time in minutes
h	Initial adsorption rate (mg/g min)
k_p	Intra-particle diffusion rate constant
C	Thickness of the boundary film
N	Number of data points
K_c	Equilibrium constant

2. Experimental

2.1Preparation of activated carbon

20 g of the crushed and ground *Memsops elengi* leaf powder were soaked in 100 ml H_3PO_4 solution (40 and 60% concentration) to get the required impregnation ratios of leaf powder of *Memsops elengi* : H_3PO_4 of 1:1, 1:2 and 1:4. Impregnation ratio is defined as the ratio of the weight of precursor, that is, weight of dried crushed and ground *Memsops elengi* leaf powder to the weight of H_3PO_4. The liquid/solid mixture was stirred continuously at ambient temperature for 2 h and left to soak for 12 h to allow penetration of the H_3PO_4 into the leaf powder of *Memsops elengi* [10]. After the stipulated soaking time, the slurry was oven dried at 110°C for 24 h, so as to achieve adsorption of the H_3PO_4 on to the leaf powder of *Memsops elengi*. The activation temperature and time for this work was fixed at the lowest possible value [11,12]. The samples were cooled and washed with cold deionized water until phosphate ions were no longer detected by the lead nitrate test. The product was finally air dried at 105°C for 3 h, after which it was ground and characterized. The sample showing maximum % removal of MB dye was chosen for further adsorption study. The carbon was designated as Phosphoric Acid Treated *Memsops elengi* Activated Carbon (PTMAC).

2.2 Adsorption studies

Adsorption experiments were carried out by batch mode technique because of its simplicity. 50 mg of adsorbent was taken in 250 mL iodine flask and 50 mL of the dye solution was poured into the flask. Then the content of the flask was agitated using rotary shaker with 180 rpm for 180 min duration. Then1mL of aliquot was taken from sample and concentration of MB dye was estimated spectrophotometrically, the absorbance at 680 nm on UV spectrophotometer. The samples were withdrawn from the shaker at predetermined time intervals, the supernatant solution was separated by centrifugation at 180 rpm for 15 minutes and the remaining MB dye was analyzed. The percentage removal of the MB dye from the solution was calculated by the mass balance relationship.

3. Results and Discussion

3.1 Effect of contact time

The effect of contact time on the percentage removal was studied by taking 20 mg/L, 60 mg/L, 100 mg/L, 140 mg/L and 180 mg/L solutions as initial concentrations. The adsorption process was characterized by a rapid uptake of the adsorbate at the initial stages. The rate of percentage removal was found to decrease afterwards as the contact time increases and become constant after attaining equilibrium stage in all the cases.

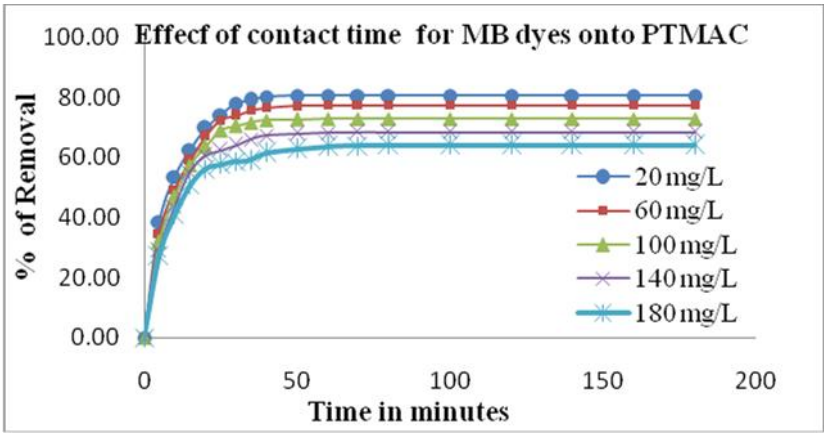


Figure 1 Effect of contact time for MB dye onto PTMAC

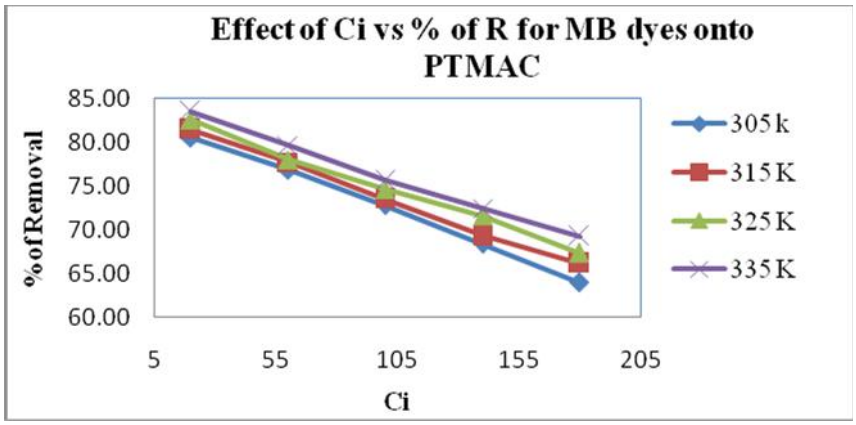


Figure 2 Effect of initial concentration for MB dye onto PTMAC

3.4 Isotherm studies

The equilibrium data obtained from the experiments were processed with different models such as Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich. It is an important step for finding a model that can be applied to design purposes. Inference obtained from each isotherm was discussed in detail one by one[13].

3.4.1 Langmuir and freundlich isotherm

The Langmuir isotherm represents the equilibrium distribution of dye molecules between the solid and liquid phases [14]. The squares of correlation coefficient (R^2) values ranged from 0.990 to 0.998 for the four studied temperatures viz. 305, 315, 325 K and 335 K. These results show the best fitting of the equilibrium data with Langmuir isotherm. The mono layer adsorption capacity Q_0 values (mg/g) for adsorption of MB dye onto PTMAC system ranged from 188.67 to 212.76 mg/g. The adsorption capacity increased with the increase of temperature [15]. The value of R_L in all cases lies between 0 and 1, indicating that the adsorption process was favourable. The Freundlich adsorption capacity constant K_f (mg/g) values ranged from 4.77 to 5.49 mg/g. The magnitude of n reveals the favorability of the adsorption. The values of n are, $0< 1/n<1$ represent favourable adsorption conditions [16].

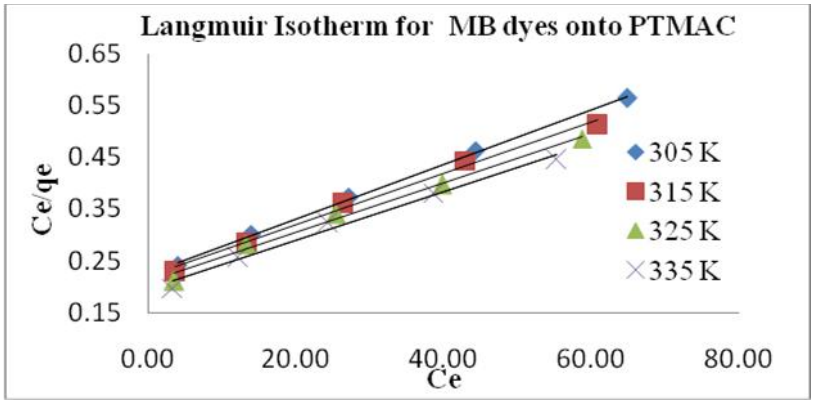


Figure 3 Langmuir isotherm for MB dye onto PTMAC

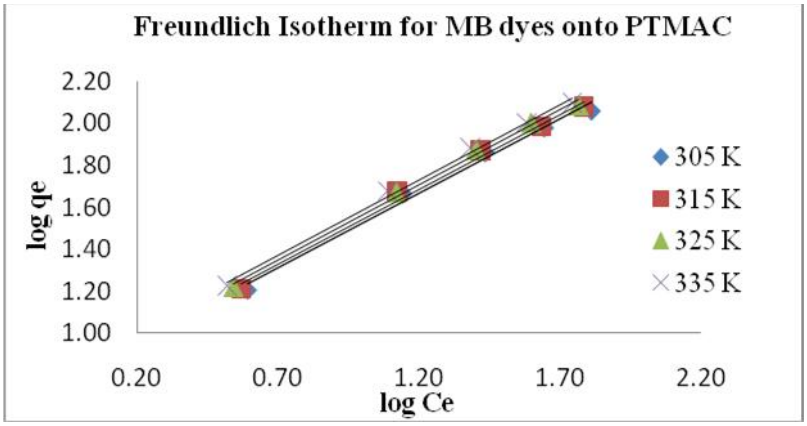


Figure 4 Freundlich isotherm for MB dye onto PTMAC

Table 3Langmuir isotherm results for the adsorption of MB dye onto PTMAC. [MB dye, pH = 7; Dose = 50 mg/ 50 mL]

Temperature (K)	Langmuir Isotherm			Freundlich Isotherm		
	Q_0	b	R^2	n	K_f	R^2
305	188.679	0.0159	0.998	1.3928	4.7753	0.990
315	200.000	0.0167	0.992	1.3680	5.0933	0.993
325	208.333	0.0176	0.990	1.3532	5.3827	0.995
335	212.766	0.0184	0.987	1.3280	5.4954	0.995

3.4.3 Tempkin isotherm

Equilibrium binding constant a_T values (L/g) ranged from 1343.49 to 672.83 and the heat of sorption constant b_T values ranged from 79.56 J/mg to 75.21 J/mg for the three studied temperatures viz. 305, 315, 325 K and 335 K. The lower value of a_T and b_T with respect to adsorption of MB dye adsorption indicates physisorption rather than chemisorption.

Table 4 Tempkin isotherm results for the adsorption of MB dye onto PTMAC. [MB dye, pH = 7; Dose = 50 mg/ 50 mL]

Temperature (K)	b_T	aT	R^2
305	79.5660	1343.49	0.971
315	77.2084	997.52	0.961
325	76.2645	753.29	0.955
335	75.2144	672.83	0.954

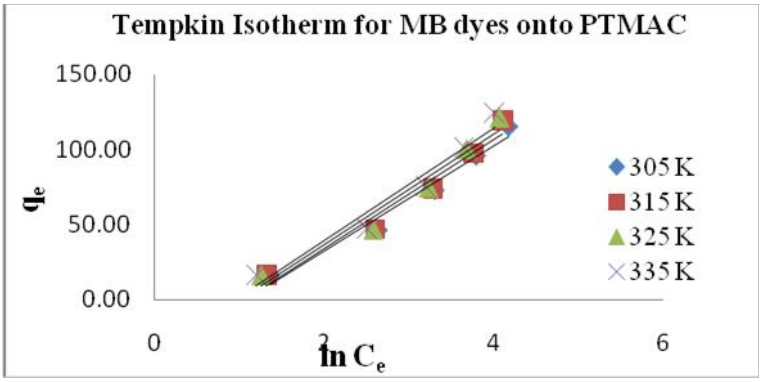


Figure 5 Tempkin Isothermfor MB dye onto PTMAC

3.4.4 D-R Isotherm

'E' is a parameter used in predicting the type of adsorption. An E value less than 8 kJ/ mol is an indication of physisorption. The mono layer adsorption capacity q_D values (mg/g) are ranged from 83.86 to 90.84 mg/g for all the studied temperatures. Further it is noticed that adsorption capacity increased with the increase of temperature. The very low value of E infers the physisorption interaction.

Table 5 D-R isotherm results for the adsorption of MB dye onto PTMAC. [MB dye, pH = 7; Dose = 50 mg/ 50 mL]

Temperature (K)	E (J)	E (KJ)	qd	R^2
305	408.24	0.40	83.86	0.9600
315	500.00	0.50	88.16	0.9600
325	707.10	0.70	89.04	0.9700
335	288.67	0.28	90.84	0.9700

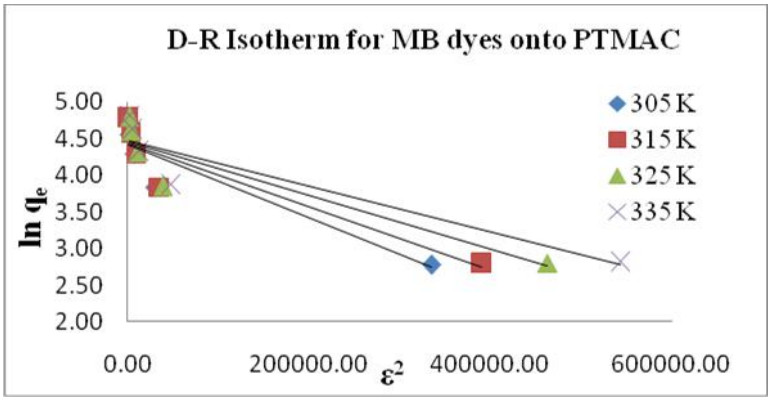


Figure 6 D-R Isotherm for MB dye onto PTMAC

3.5 Kinetic study

Several adsorption kinetic models have been established to understand the adsorption kinetics and rate-limiting step. These include pseudo-first and second-order rate model, Weber and Morris[17] sorption kinetic models.

The first order rate constant, k_1 (min^{-1}) ranged from 0.0854 to 0.1216. The pseudo first order theoretical adsorption capacity ($q_e$cal) values, obtained from the intercept of the linear plots, were compared with the experimental adsorption capacity ($q_e$exp) values. The initial sorption rate h increases directly with the increase of initial MB dye concentration at each temperature for PTMAC, while an inverse relationship exists between the overall sorption rate and initial MB dye concentration for PTMAC.

Between the first order and second order, second order kinetic model seems to best describe the above adsorption system as it has R^2 value which was very close to unity. Moreover, the difference between calculated adsorption capacity (q_e cal) and experimental adsorption capacity (q_e exp) values of second order is little when compared to the first order kinetic model. Statistically it is tested with the tool sum of errors quares(SSE %) [18].

Table 6 Kinetics results for the adsorption of MB dye onto PTMAC. [pH = 7; Dose = 50 mg/ 50 mL; Contact time = 180 min]

Ci	First Order				Second Order				Intra Particle Diffusion		
	qe(Cal)	K1	R^2	MSSE	qe(cal)	K2	R^2	MSSE	Kp	n	h
20	18.7499	0.1204	0.979		16.44	0.0237	0.999		0.58		6.41
60	38.1944	0.0919	0.920		47.61	0.0065	0.999		1.07		14.71
100	83.3681	0.1216	0.994	3.95	74.62	0.0045	0.999	0.65	1.31		25.00
140	84.3335	0.0930	0.992		98.03	0.0031	0.999		2.40		29.41
180	106.4143	0.0854	0.980		119.04	0.0021	0.999		3.16		30.30

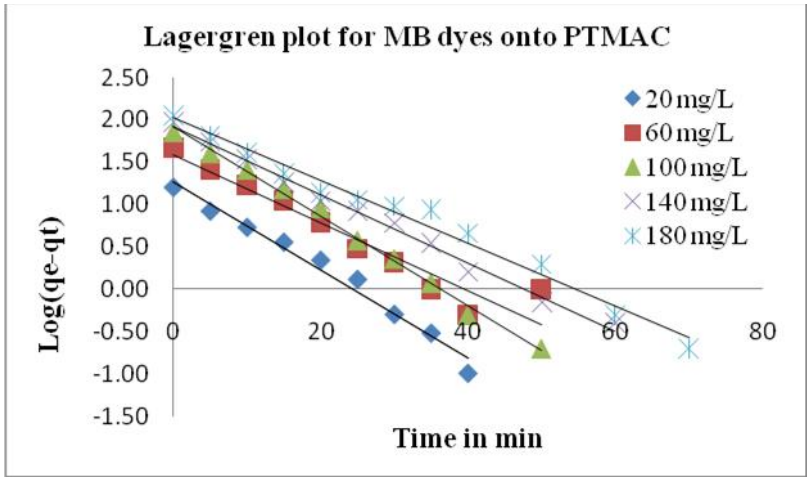


Figure 7 First Order Kinetics for MB dye onto PTMAC

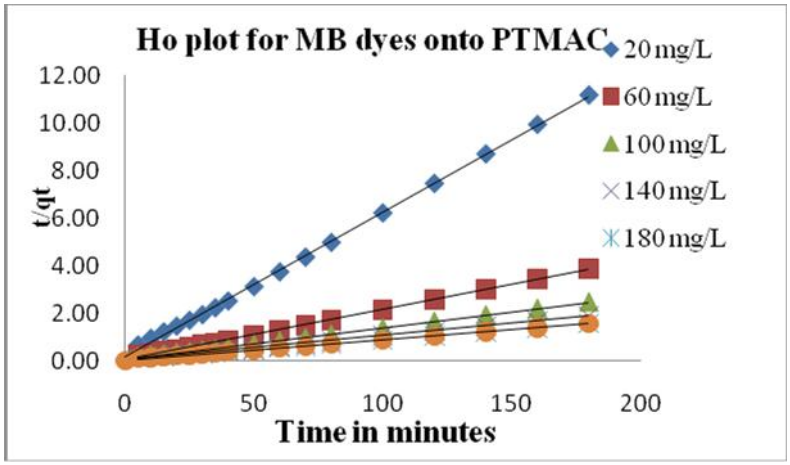


Figure 8 Second Order Kinetics for MB dye onto PTMAC

3.5.1 Intra particle diffusion

The K_p values were found to increase with an increase of MB dye concentration that reveals the rate of adsorption governed by the diffusion of adsorbed MB dye within the pores of the adsorbent. Present results show that pore diffusion limits the overall rate of MB dye adsorption [19].

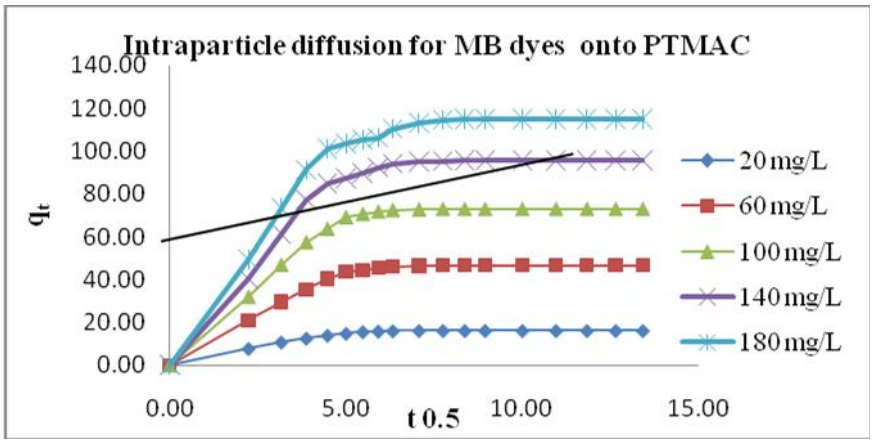


Figure 9 Intra Particle Diffusion for MB dye onto PTMAC

4. Conclusion

In the present study Phosphoric acid activated *Memsops elengi* leaf carbon (PTMAC) was prepared and investigated its potential to abate chosen adsorbate cationic Methylene Blue dye (MB) from aqueous solution. The equilibrium parameter R_L values obtained in Langmuir isotherm study were in between 0 and 1 showing the favourable adsorption process. The values of n were found to be greater than one indicating a favourable adsorption. Theoretically evaluated quantity adsorbed at equilibrium from first order and second order rate equations were compared with the quantity adsorbed at equilibrium in the actual experiments. The statistical tool 'Summation of error square test' revealed that present studied all adsorbent – adsorbate system followed second order kinetics. The variation of k_p values was proportional to the initial adsorbate concentrations which indicates that the intra-particle diffusion limits the rate of the process.

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How to cite this article:
A.Elavarasan, V. Nandhakumar, and M. Rajeswari. (2017). Adsorption of methylene blue onto phosphoric acid activated carbon prepared from leaves of *Memsops elengi*. Int. J. Adv. Multidiscip. Res. 4(1): 50-58.
DOI: http://dx.doi.org/10.22192/ijamr.2017.04.01.007