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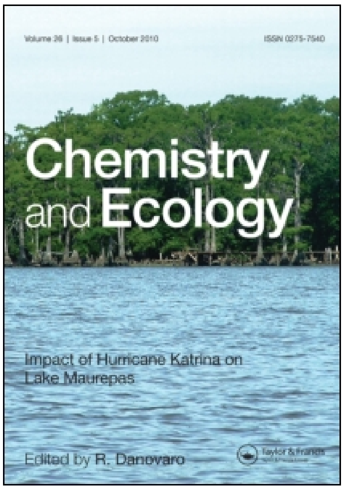

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Adsorption of methylene blue onto activated carbon derived from periwinkle shells: kinetics and equilibrium studies

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Periwinkle shell, an abundant and inexpensive natural resource, was used to prepare activated carbon by physicochemical activation with potassium hydroxide (KOH) and carbon dioxide (CO_2) as the activating agents at 850 °C for 2 h. The adsorption equilibrium and kinetics of methylene blue dye on such carbon were then examined at 25 °C. Adsorption isotherm of the methylene blue (MB) on the activated carbon was determined and correlated with common isotherm equations. The equilibrium data for methylene blue adsorption well fitted to the Langmuir equation, with maximum monolayer adsorption capacity of 500.00 mg/g. Two simplified kinetic models including pseudo-first-order and pseudo-second-order equation were selected to follow the adsorption processes. The adsorption of methylene blue on activated carbon derived from periwinkle shell could best be described by the pseudo-second-order equation. The kinetic parameters of this best-fit model were calculated and discussed.

Keywords: periwinkle shell; adsorption; dye; isotherm; kinetics

1. Introduction

Dyes are widely used by textile industries to colour their products. One of the major problems concerning textile wastewaters is coloured effluent. This wastewater contains a variety of organic compounds and toxic substances, which are harmful to fish and other aquatic organisms [1]. Methylene blue (MB) dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, painful micturition and methemoglobinemia [2,3]. Therefore the treatment of effluent containing such dye is of interest due to its esthetic impacts on receiving waters. Adsorption processes using activated carbons are widely used to remove pollutants from wastewaters. However, commercially available activated carbon is expensive. In the last years, special emphasis on the preparation of activated carbon from several

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agricultural by-products has been given due to the growing interest in low cost activated carbons from renewable and copious sources, especially for application concerning treatment of wastewater. Researchers have studied the production of activated carbon from palm-tree cobs [3], plum kernels [4], cassava peel [5], bagasse [6], jute fiber [7], rice husks [8], olive stones [9], date pits [10], coir pith carbon [11], fruit stones and nutshells [12]. The advantage of using inexpensive natural resource as raw materials for manufacturing activated carbon is that these raw materials are renewable and potentially less expensive to manufacture. The idea of using periwinkle shell (which ordinarily contribute to environmental pollution in some areas) to produce activated carbon rises in this context in the management of dyes. Thus, utilisation of these shells in the removal of dyes will be a great advancement in researches involving chemists. This is because, they will not only help in reducing dangers man are exposed to by having direct contact with such dyes, but also provide solution to littering problems which these shells invariably constitute in some areas. The present study was undertaken to evaluate the efficiency of activated carbon produced from periwinkle shell in the removal of methylene blue dye.

2. Materials and methods

2.1. *Methylene blue*

Methylene blue (MB) was obtained from BDH, it was used as an adsorbate and was not purified prior to use. Double distilled water was employed for preparing all the solutions and reagents. Chemical structure of the dye is shown in Appendix A.

2.2. *Preparation and characterisation of activated carbon*

Raw material (periwinkle shell) used for preparation of activated carbon was procured locally, washed with deionised water, dried and crushed to the desired mesh size (1–2 mm). The pretreated material was then carbonised at 700 °C under nitrogen atmosphere for 1 h (first pyrolysis). A certain amount of produced char was then soaked with potassium hydroxide (KOH) at impregnation ratio of 1:1 (KOH pellets: char). The mixture was dehydrated in an oven overnight at 105 °C; then pyrolysed in a stainless steel vertical tubular reactor placed in a tube furnace under high purity nitrogen (99.995%) flow of 150 $\mathrm{cm}^3\,\mathrm{min}^{-1}$ (second pyrolysis) to a final temperature of 850 °C and activated for 2 h. Once the final temperature was reached, the gas flow was switched to carbon dioxide and activation was continued for 2 h. The activated product was then cooled to room temperature under nitrogen flow and washed with deionised water to remove the remaining chemical. Subsequently, the sample was transferred to a beaker containing a 250 ml solution of hydrochloric acid (about 0.1 $\mathrm{mol\,l}^{-1}$), stirred for 1 h, and then washed with hot deionised water until the pH of the washing solution reached 6–7. Textural characterisation of the activated carbon (AC) was carried out by N_2 adsorption at 77 K using Autosorb I, supplied by Quantachrome Corporation, USA. The BET (N_2, 77 K) is the most usual standard procedure used when characterising an activated carbon [13].

2.3. *Batch equilibrium studies*

Adsorption isotherms were performed in a set of 43 Erlenmeyer flasks (250 ml) where solutions of dye (200 ml) with different initial concentrations (100–500 $\mathrm{mg\,l}^{-1}$) were placed in these flasks. Equal mass of 0.2 g of particle size (150 μm) activated carbon prepared from periwinkle shell was added to dye solutions and kept in an isothermal shaker (25 ± 1 °C) for 48 h to reach equilibrium of the solid-solution mixture. Similar procedure was followed for another set of Erlenmeyer flask containing the same dye concentration without activated carbon to be used as a blank. The pH was adjusted to 7 by adding either few drops of diluted hydrochloric acid or sodium hydroxide ($0.1\ \mathrm{mol\,l^{-1}}$). The flasks were then removed from the shaker and the final concentration of dye in the solution was analysed. The concentration of methylene blue in the supernatant solution after and before adsorption was determined using a double beam UV spectrophotometer (Shimadzu, Japan) at 668 nm. It was found that the supernatant from the activated carbon did not exhibit any absorbance at this wavelength and also that the calibration curve was very reproducible and linear over the concentration range used in this work.

The samples were filtered prior to analysis in order to minimise interference of the carbon fines with the analysis. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e ($\mathrm{mg\,g^{-1}}$), was calculated by

$$q_e = \frac{(C_o - C_e)V}{W}, \tag{1}$$

where C_o and C_e ($\mathrm{mg\,l^{-1}}$) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (l), and $W$is the mass of dry adsorbent used (g).

2.4. *Batch kinetic studies*

The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of dye were similarly measured. The amount of adsorption at time t, q_t ($\mathrm{mg\ g^{-1}}$) was calculated by:

$$q_t = \frac{(C_o - C_t)V}{W}, \tag{2}$$

where C_o and C_t ($\mathrm{mg\,l^{-1}}$) are the liquid-phase concentrations of dye at initial and any time t, respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g).

2.5. *Desorption and regeneration studies*

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dyes. If the adsorbed dyes can be adsorbed using neutral pH water, then the attachment of the dyes on the adsorbent is weak. If sulphuric acid or alkaline water desorp the dyes, then the adsorption is by ion exchange. If organic acids, like acetic acid desorp the dyes, then the dye is attached to the adsorbent through chemisorption [14]. The effect of various reagents used for desorption studies shows that hydrochloric acid is a better reagent for desorption, because we could get more than 90% removal of adsorbed dyes. Also, the adsorbent exhibits a stable structure towards this reagent. The desorption of dyes by mineral acids indicates that the dyes are adsorbed onto the activated carbon derived from periwinkle shell by physisorption.

3. Results and discussion

3.1. *Textural characteristics of the prepared activated carbon*

The possible functional groups on periwinkle shell are shown in Table 1 which illustrated that the most abundant functional groups included carboxyl and amine, C—O and sulfonyl were second

Table 1. Functional groups in periwinkle shell.

Functional group	Wavenumber from results (cm^{-1})	Relative quantity[a]
Hydroxyl; OH	3200–3600	1
Carboxyl; COOH	3200–3600	1
Amine; NH_2	3200–3600	1
C−O	1000–1200	2
Sulfonyl; S=O	1000–1200	2
Carbonyl; C=O	1600–1750	3
S—O	550	4
Alkyl; C—H	Carboxylic acid; 2900–3000 Alcohol; 3400–3640	5

[a] The quantity in the order from large to small (1 is the most abundant and 5 is the least).

most abundant followed by carbonyl, S−O, and alkyl, respectively. It was found that the BET surface area, total pore volume, average pore diameter and pH point of zero charge (pHpzc) of the activated carbon were 1894 $m^2\ g^{-1}$, 1.107 $cm^3\ g^{-1}$, 2.32 nm and 7.5, respectively. The pH point of zero charge (pHpzc) of activated carbon prepared from periwinkle shell shows that there exists a relationship between pHpzc and adsorption capacity of the adsorbent used. The result shows that cation adsorption will be favourable at pH value higher than pHpzc. While anion adsorption will be favoured at pH values lower than their adsorbent pHpzc [15].

3.2. *Effect of agitation time and concentration of dye on adsorption*

A series of contact time experiments for MB dye have been carried out at different initial concentrations (100–500 $mg\ l^{-1}$) and at temperatures of 25 °C. Figure 1 shows the contact time necessary for MB dye with initial concentrations of 100–300 $mg\ l^{-1}$ to reach equilibrium is 6 h. However,

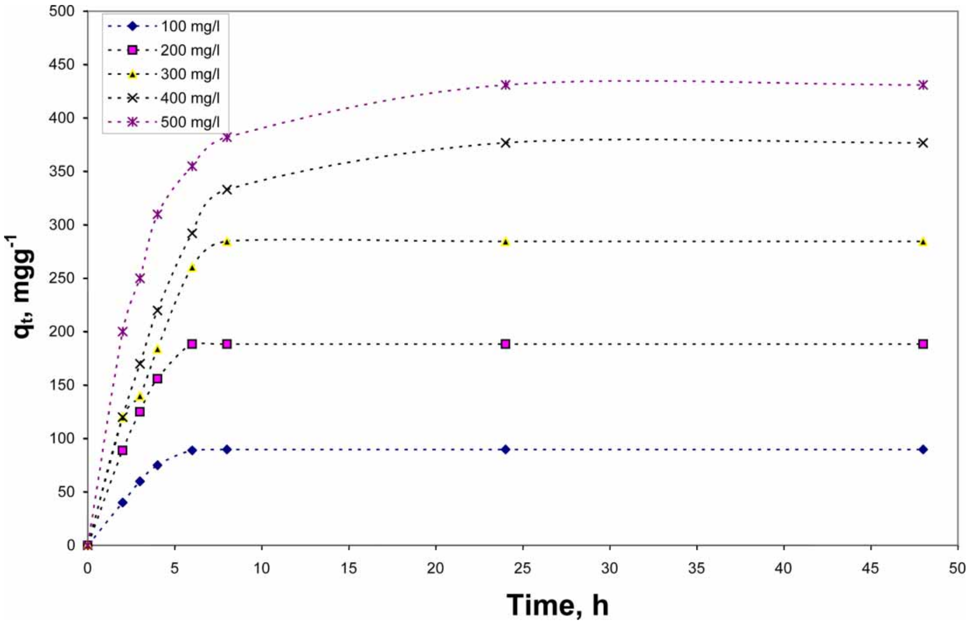

Figure 1. The variation of adsorption capacity with adsorption time at various initial dye concentration at 25 °C (pH 7, W = 0.2 g).

for MB dye with higher initial concentrations (400–500 mg l^{-1}), a longer equilibrium time of 24 h is needed. As can be seen from Figure 1, the amount of the adsorbed dye onto activated carbon increases with time and, at some point in time, reaches a constant value beyond which no more is removed from solution. At this point, the amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the activated carbon. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions.

The adsorption capacity at equilibrium increases from 100 to 430 mg g^{-1} with an increase in the initial dye concentration from 100 to 500 mg l^{-1}. It is evident that the activated carbon prepared from periwinkle shell is efficient to adsorb MB dye from aqueous solution, the process attaining equilibrium gradually. This is due to the fact that activated carbon is composed of porous structures with a large internal surface area (1894 m^2 g^{-1}).

3.3. *Adsorption kinetics*

The rate constant of adsorption is determined from the pseudo first-order equation given by Langergren and Svenska [16]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \tag{3}$$

where q_e and q_t are the amounts of MB adsorbed (mg g^{-1}) at equilibrium and at time t(min), respectively, and k_1 the rate constant adsorption (h^{-1}). Values of k_1 were calculated from the plots of $\ln(q_e - q_t)$ versus t for different concentrations of MB. Although the correlation coefficient values at high concentration are higher than 0.90, the experimental q_e values do not agree with the calculated ones, obtained from the linear plots (Table 2). This shows that the adsorption of MB onto activated carbon produced from periwinkle shell is not first-order kinetics.

On the other hand, a pseudo second-order equation based on equilibrium adsorption [17] is expressed as:

$$1/q_t = 1/k_2 q_e^2 + (1/q_t)t, \tag{4}$$

where k_2(g/mg h) is the rate constant of second-order adsorption. If second-order kinetics is applicable, the plot of t/q versus t should show a linear relationship. There is no need to know any parameter beforehand and q_e and k_2 can be determined from the slope and intercept of the plot. Also, this procedure is more likely to predict the behaviour over the whole range of adsorption. The linear plots of t/q versus t (Figure 4) show a good agreement between experimental and calculated q_e values (Table 2).

Table 2. Comparison of the pseudo first- and second-order adsorption rate constants and calculated and experimental q_e values for different initial dye concentration.

		First order kinetic model				Second order kinetic model			
Initial concentration (mg l^{-1})	$q_{e,exp}$ (mgg^{-1})	$k_1(h^{-1})$	$q_{e,cal}$ (mgg^{-1})	R^2	SSE(%)	k_2 $[g(mgh)^{-1}]$	$q_{e,,cal}$ (mgg^{-1})	R^2	SSE(%)
100	89.8	0.8218	137.19	0.95	21.19	0.0124	92.59	0.99	1.40
200	188.4	0.9128	303.17	0.95	51.33	0.0113	192.31	0.99	2.00
300	284.6	0.9893	404.07	0.94	53.43	0.0044	294.12	0.99	4.80
400	376.8	1.0454	503.41	0.93	56.62	0.0012	400.00	0.99	10.40
500	431.1	1.1641	745.68	0.92	140.68	0.00156	454.50	0.99	10.50

The correlation coefficients for the second-order kinetic model are greater than 0.99 indicating the applicability of this kinetic equation and the second-order nature of the adsorption process of MB on activated carbon.

3.4. *Test of kinetic models*

Besides the value of R^2, the applicability of both kinetic models are verified through the sum of error squares (SSE, %). The adsorption kinetics of MB on activated carbon derived from periwinkle shell was tested at different initial concentrations. The validity of each model was determined by the sum or error squares (SSE, %) given by:

$$\mathrm{SSE}(\%) = \sqrt{\frac{\sum (q_{\mathrm{e,exp}} - q_{\mathrm{e,cal}})^2}{N}}, \tag{5}$$

where N is the number of data points. The higher is the value of R^2 and the lower is the value of SSE; the better will be the goodness of fit. Table 2 lists the calculated results. It is found that the adsorption of methylene blue on AC produced from periwinkle shell can be best described by the second-order kinetic model. Similar phenomena processes have been observed in the adsorption of direct dyes on activated carbon prepared from sawdust [18] and adsorption of Congo red dye on activated carbon from coir pith [19].

3.5. *Adsorption isotherms*

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of equilibrium adsorption data by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purposes [20]. Adsorption isotherm study is carried out on two well-known isotherms, Langmuir and Freundlich. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [21]. The Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [21]. The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2.

3.5.1. *Langmuir isotherm*

The linear form of Langmuir's isotherm model is given by the following equation:

$$C_{\mathrm{e}}/q_{\mathrm{e}} = 1/Q_{\mathrm{o}}b + (1/Q_{\mathrm{o}})C_{\mathrm{e}}, \tag{6}$$

where C_{e} is the equilibrium concentration of the adsorbate (MB) (mg/l), $q_{\mathrm{e},}$ the amount of adsorbate adsorbed per unit mass of adsorbate (mg g^{-1}), and Q_{o} and b are Langmuir constants related to monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively. When $C_{\mathrm{e}}/q_{\mathrm{e}}$ was plotted against C_{e}, straight line with slope $1/Q_{\mathrm{o}}$ was obtained (Figure 2), indicating that the adsorption of MB on activated carbon produced from periwinkle shell follows the Langmuir isotherm. The Langmuir constants 'b' and 'Q_{o}' were calculated from this isotherm and their values are given in Table 3.

Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of periwinkle shell carbon surface, i.e. each dye molecule/periwinkle shell carbon adsorption has equal adsorption activation energy. The results also demonstrate the formation of

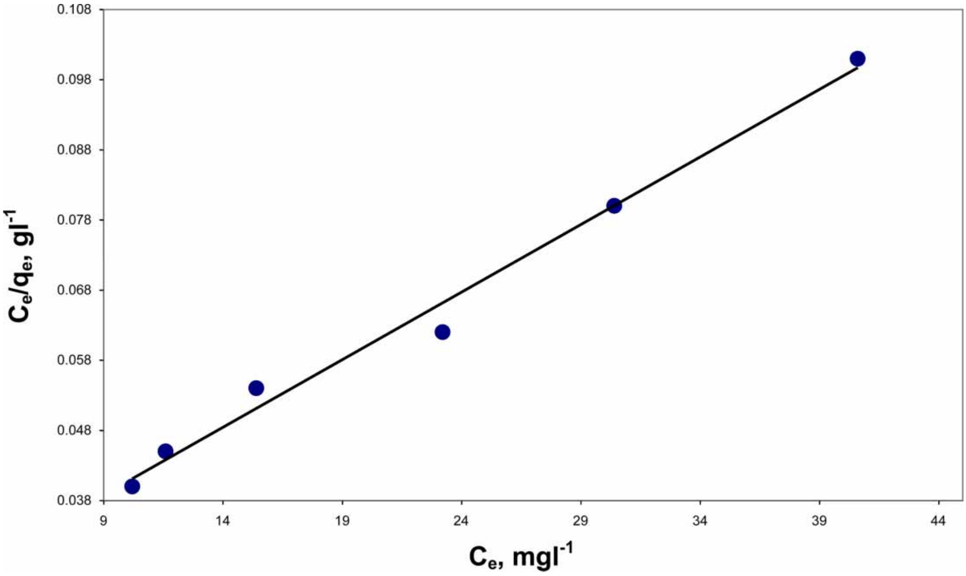

Figure 2. Langmuir adsorption isotherm of methylene blue on activated carbon produced from periwinkle shell at 25 °C.

Table 3. Langmuir and Freundlich isotherm constants for MB at 25 °C.

Langmuir isotherm	
Q_o (mgg^{-1})	500.00 ± 0.07
b (L/mg)	0.101 ± 0.05
R^2	0.9888 ± 0.01
R_L	0.020 ± 0.02
Freundlich isotherm	
$\frac{1}{n}$	0.8506 ± 0.03
K_F [(mgg^{-1})(mg^{-1})$^{1/n}$]	26.63 ± 0.04
R^2	0.9776 ± 0.02

All values are means of triplicates ± SD.

monolayer coverage of dye molecule at the outer surface of periwinkle carbon. Similar observation was reported by the adsorption of acid orange 10 dye onto activated carbon prepared from agricultural waste bagasse [6] and by the adsorption of direct dyes on activated carbon prepared from sawdust [17] and adsorption of Congo red dye on activated carbon from coir pith [18].

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) [19], which is defined by:

$$R_L = 1/(1 + bC_0), \tag{7}$$

where b is the Langmuir constant and C_0 the highest dye concentration (mg l^{-1}). The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Value of R_L was found to be 0.02 and confirmed that the activated carbon is favourable for adsorption of MB dye under conditions used in this study.

3.5.2. *Freundlich isotherm*

The well-known logarithmic form of Freundlich model is given by the following equation:

$$\log q_e = \log K_F + (1/n)\log C_e, \tag{8}$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (MB) and K_F and n are Freundlich constants, n giving an indication of how favourable the adsorption process and K_F (mg g^{-1}(mg^{-1})$^{1/n}$) is the adsorption capacity of the adsorbent. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon adsorbent for a unit equilibrium concentration.

The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [20]. A value for $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption [21]. The plot of log q_e versus log C_e gives straight lines with slope '$1/n$' (Figure 3), which shows that the adsorption of MB also follows the Freundlich isotherm. Accordingly, Freundlich constants (K_F and n) were calculated and recorded in Table 3.

Table 3 shows the values of the parameters of the two isotherms and the related correlation coefficients. As seen from Table 3, the Langmuir model yields a somewhat better fit ($R^2 = 0.9888$) than the Freundlich model ($R^2 = 0.9776$). As also illustrated in Table 1, the value of $1/n$ is 0.8506, which indicates favourable adsorption [22].

Table 4 lists the comparison of maximum monolayer adsorption capacity of some dyes on various adsorbents. Compared with some data in the literature, Table 4 shows that the activated carbon studied in this work has very large adsorption capacity. This work has shown that utilisation of activated carbon produced from periwinkle shell will be useful in the treatment of methylene blue dyes from industrial waste effluents; it will also eliminate various ecological problems these waste effluents could cause to aquatic organisms and man.

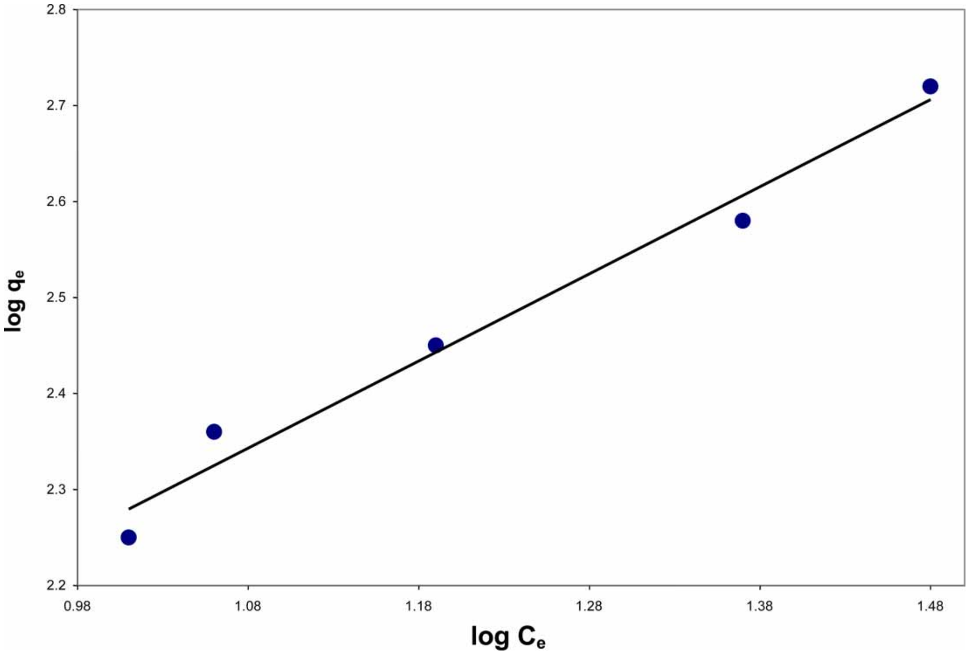

Figure 3. Freundlich adsorption isotherm of methylene blue on activated carbon produced from periwinkle shell at 25 °C.

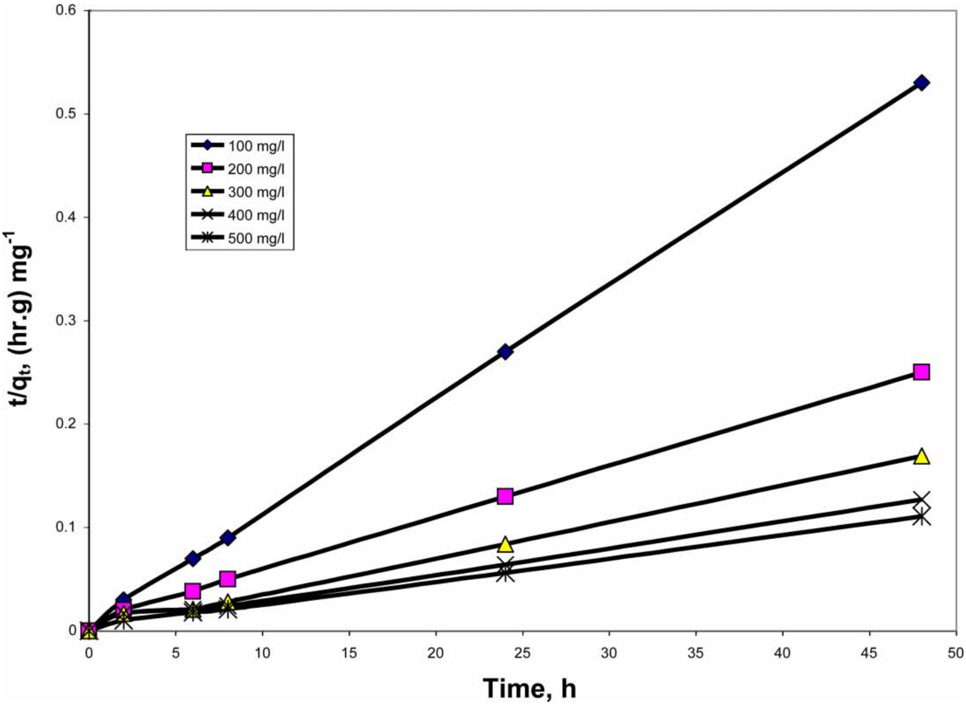

Figure 4. Pseudo-second order kinetics for adsorption of methylene blue adsorption by activated carbon produced from periwinkle shell at 25 °C.

Table 4. Comparison of the maximum monolayer adsorption of some dyes on various adsorbents.

Dyes	Adsorbents	Maximum monolayer adsorption capacity (mg g^{-1})	Temperature (°C)	Reference
Methylene blue	Periwinkle shell based AC	500.00	25 °C	This work
Methylene blue	Bamboo dust AC	143.20	30 °C	[23]
Methylene blue	Coconut shell AC	277.90	30 °C	[23]
Methylene blue	Groundnut shell AC	164.90	30 °C	[23]
Methylene blue	Rice husk AC	343.50	30 °C	[23]
Methylene blue	Straw AC	472.10	25 °C	[6]
Methylene blue	Jute fibre AC	225.64	25 °C	[24]
Basic red 46	Sludge-based AC	188.00	25 °C	[24]
Acid brown 283	Sludge-based AC	20.50	25 °C	[24]
Direct red 89	Sludge-based AC	49.20	25 °C	[24]
Direct black 168	Sludge-based AC	28.90	25 °C	[24]
Basic red 46	Chemviron GW AC	106.00	25 °C	[24]
Acid brown 283	Chemviron GW AC	22.00	25 °C	[24]
Direct red 89	Chemviron GW AC	8.40	25 °C	[24]
Direct black 168	Chemviron GW AC	18.70	25 °C	[24]
Congo red	Coir pith-based AC	6.72	28 °C	[20]

4. Conclusions

The present investigation showed that periwinkle shell can be effectively used as a raw material for the preparation of activated carbon for the removal of methylene blue dye from aqueous solution over a wide range of concentration. Methylene blue is found to adsorb strongly on the surface of activated carbon. Adsorption behaviour is described by a monolayer Langmuir type isotherm. Kinetic data follows pseudo second-order kinetic model. The value of the maximum adsorption capacity, Q_o, ($500.00\,\mathrm{mg\,g^{-1}}$) is comparable with the values for commercial activated carbon reported in earlier studies.

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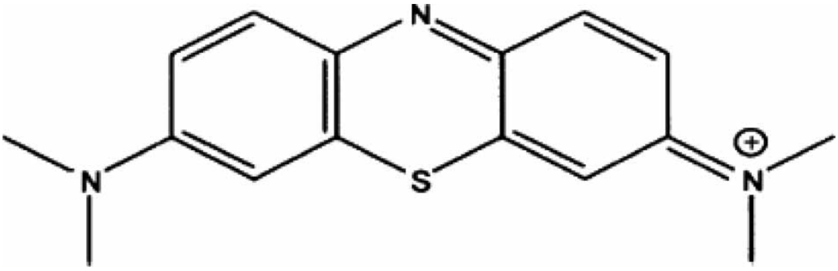
Appendix A. Chemical structure of methylene blue dye



Methylene Blue [3, 9- bis dimethylaminophenazo thionium chloride]
Basic Blue 9, C.I. 52015, $\lambda_{max} = 668\,\text{nm}$.