

Removal of Methylene Blue Dye Using Saw Palmetto Fruit (Serenoa repens) Waste

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The feasibility of saw palmetto fruit (*Serenoa repens*) waste as a low-cost bio-sorbent for treating methylene blue dye from synthetic textile effluent was evaluated. Two different types *viz.*, untreated and alkaline treated saw palmetto fruit waste was tested to immobilize methylene blue dye from the synthetic effluent solution. Out of these two, the only alkaline treated saw palmetto fruit waste, the sorption of dye increased with time and after reaching equilibrium, back diffusion of the sorbed dye was observed. Equilibrium sorption and kinetic studies were performed with alkaline treated saw palmetto fruit waste and the parameters affecting the sorption process such as initial dye concentration, adsorbent dose, equilibrium time and temperature were analyzed. The kinetic data generated obeyed pseudo-second-order kinetics. The investigated removal capacity of the saw palmetto fruit waste for the methylene blue dye was comparable with the available sorbents.

Keywords: Saw palmetto, Methylene blue, Adsorption.

INTRODUCTION

Dyes are chemical compounds which impart colour to the substrate to which it is being applied. Out of the total production of dyes, 15 % of the dye stuff appear in the effluents issuing from the dye manufacturing industries [1]. The presence of dyes in aqueous streams results in lowering of light penetration which subsequently reduces the photosynthetic activity of algae and harms the aesthetic quality of water surface.

The degradation of dyes in an aquatic environment releases toxic substances which are carcinogenic even at low concentrations. Human contact of these toxic dyes may lead to skin allergies, contact dermatitis, eye infections and respiratory diseases [2]. The presence of dyes in the water affects the quality of water bodies leading to damage to the aquatic environment. It has an adverse effect on the impact of groundwater quality.

Many conventional techniques like oxidation or ozonation [3], electrocoagulation [4,5] biochemical degradation [6] and adsorption [7] have been applied to treat dye effluent streams.

Methylene blue (MB), blue-coloured cationic thiazine dye, is the most commonly used basic aniline dye in various

chemical industrial products. It is a carcinogenic dye which has harmful effects like vomiting, cyanosis, convulsions, burns in eyes of humans and animals, Alzheimers, acute hemolysis, *etc.* The removal of methylene blue from industrial effluents is crucial in order to avoid these harmful effects.

Many low-cost adsorbents based on agriculture and industrial waste have been reported to reduce the contamination of methylene blue in industrial effluents [8,9]. Even though activated carbons from different biomass are well-known adsorbents for the dye immobilization, its high cost of production has restricted its use, particularly in developing countries. Investigation of low-cost adsorbents for the methylene blue dye removal is still in search.

Saw palmetto (*Serenoa repens*) extract from saw palmetto fruit is mainly used in the treatment of benign prostatic hyperplasia, urinary and reproductive system problems. The fruit waste mainly consists of pectin, hemicelluloses and lignin material which are rich in carboxyl and hydroxyl groups. These functional groups are normally responsible for holding the dyes on its surface [10]. The aim of the present study is to investigate the saw palmetto fruit waste (SPW) as a low-cost adsorbent for the removal of methylene blue from aqueous solution.

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EXPERIMENTAL

Methylene blue was procured from Loba-Chemie, Mumbai, India. Stock solutions of required concentrations were prepared using demineralized water and further, the test solutions were prepared by diluting the stock solution as required.

Pretreatment: Saw palmetto fruit waste used in this study was procured from Sami Labs Limited, Bangalore, India. The saw palmetto fruit waste was first washed repeatedly with demineralized water to remove the impurities present and then dried in sunlight. The dried adsorbent powder was then sieved through sieves of different pore size. The dried adsorbent of 70 Mesh was used as untreated saw palmetto fruit waste.

Alkaline treatment: Saw palmetto waste of 70 Mesh was soaked in 1 N NaOH for 48 h and then the sorbent was filtered and washed with demineralized water until the pH of the supernatant remains constant. The treated adsorbent was dried at 80 °C in the oven for 24h until it is completely free of moisture.

Characterization of adsorbent: SEM-EDAX ESEM, (model-Quanta 200) was used to analyze the surface morphology of the saw palmetto fruit waste. The functional groups responsible for sorption were determined using FTIR (Bruker).

Equilibrium studies: Untreated and alkaline treated saw palmetto fruit waste of 0.5g was equilibrated with 100 mL of methylene blue of different concentrations for 48 h. Uniform mixing of samples was ensured by keeping the samples in an orbital shaker at 150 rpm. After reaching equilibrium, the supernatant liquid was separated from the adsorbent and then the final concentration of the dye in the solution was analyzed using UV- spectrophotometer at 652 nm.

The uptake capacity of the saw palmetto fruit waste for methylene blue was obtained as follows:

$$q_e = \frac{(C_o - C_f)V}{W}$$
(1)

where q_e is equilibrium uptake capacity (mg/g) of saw palmetto fruit waste; C_o is the initial concentration of methylene blue

(mg/L); C_f is the equilibrium concentration (mg/L) of methylene blue; V is the volume of solution (L) and w is the weight of the adsorbent used (g).

Adsorption dosage: Methylene blue dye solution of 100 mL of 1000 ppm was equilibrated separately with the alkaline treated saw palmetto fruit waste for different adsorbent dosages ranging from 0.1 to 0.6 g.

Kinetic studies: Batch kinetic studies were performed by adding 0.5 g of adsorbent to 500 mL of dye solution of different concentrations. The stirring speed was maintained at 400 rpm to ensure uniform concentration throughout and the samples were collected at regular intervals of time with the total sampling volume being not more than 4 % of the solution volume.

Temperature studies: Experiments were carried out by equilibrating 100 mL of 1000 ppm methylene blue solution with 0.1 g saw palmetto fruit waste separately at different temperatures ranging from 303 to 343 K.

RESULTS AND DISCUSSION

Pretreatment: The selected adsorbent was given alkaline treatment by washing with demineralized water and soaked in NaOH for 48 h. When the saw palmetto fruit waste was washed with demineralized water, there was no change in the colour of the supernatant solution. But, when it was treated with an alkaline solution, the supernatant solution turned to dark brown colour. The alkaline solution leached the other colour materials from the adsorbent and the alkaline treated sorbent looked light brown in colour compared to other treatments.

Characterization study: The SEM images to study the surface morphology of the alkaline treated saw palmetto fruit waste before and after the adsorption of methylene blue dye were shown in Fig. 1a and 1b, respectively. The surface was rough and irregular with particle cracks and asperities before sorption of methylene blue as seen from Fig. 1a. After sorption

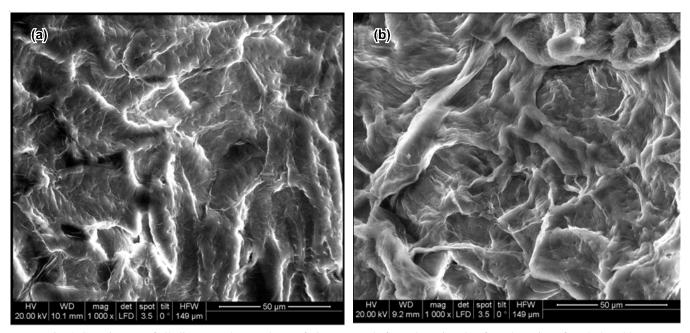


Fig. 1. SEM images of alkaline treated saw palmetto fruit waste (a) before adsorption (b) after adsorption of methylene blue

of methylene blue, the surface was very smooth which might be due to the thin layer of methylene blue on its surface. Also, the increased brightness of the sample after adsorption might be due to the coloured component distribution on the sorbent surface.

FTIR spectra for the alkaline treated saw palmetto fruit waste before and after sorption of methylene blue were shown in Fig. 2. Similar peaks were observed before and after adsorption as seen from Fig. 2. Monosubstituted aromatic rings consisting of C-C, C-O, C-N are predominant functional groups below 1400 cm⁻¹ wavenumber region and C–OH stretching were found at 1021 cm⁻¹. These functional groups might be responsible for holding the methylene blue dye on to the adsorbent surface. Similar observations were mentioned by Al-Anber *et al.* [11] in binding methylene blue on to defatted Jojoba.

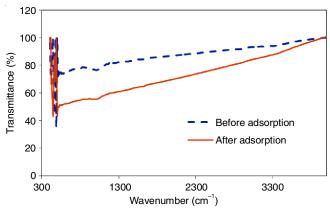


Fig. 2. FTIR for the alkaline treated saw palmetto fruit waste before and after adsorption of methylene blue

Equilibrium studies: Batch equilibrium isotherm studies were performed with different concentrations of methylene blue ranging from 1000 to 4000 ppm. Experiments were performed with two different types of saw palmetto fruit waste. Both untreated and alkaline treated adsorbents were used for adsorption of methylene blue, separately. The equilibrium sorption of methylene blue on to the untreated and alkaline treated saw palmetto fruit waste were shown in Fig. 3. The equilibrium capacity increased with an increase in the initial concentration of dye solution for the sorbents. The maximum saturation capacity was observed to be around 790 mg/g for alkaline treated saw palmetto fruit waste and 280 mg/g for untreated saw palmetto fruit waste. With untreated saw palmetto fruit waste, after equilibrium sorption of methylene blue, back diffusion of the dye was observed. Since the untreated adsorbent was dark in colour, it was not able to hold the dye after reaching saturation capacity. With alkaline treated adsorbent, no back diffusion was observed after reaching equilibrium and the sorbent turned to dark violet in colour.

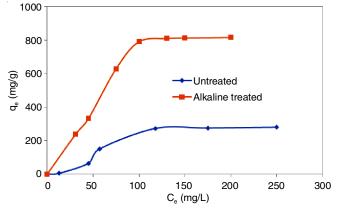


Fig. 3. Equilibrium isotherms for untreated and alkaline treated saw palmetto fruit waste

Equilibrium sorption models like Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm models were used to fit the equilibrium data. The model constants were estimated from the linear plots and shown in Table-1. The equilibrium isotherms generated using these model parameters were compared with the experimental data as shown in Fig. 4.

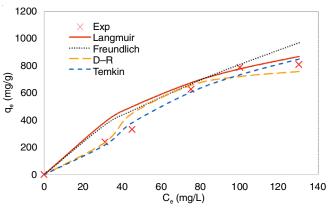


Fig. 4. Equilibrium isotherms for sorption of methylene blue on alkaline treated saw palmetto fruit waste

Langmuir model assumes the adsorbent surface to be homogeneous and the sorption is limited to monolayer sorption of adsorbate [12]. The linearized Langmuir's isotherm model (eqn. 3) was used to fit the equilibrium sorption data.

$$\frac{\mathbf{q}_{e}}{\mathbf{q}_{m}} = \frac{\mathbf{K}_{L}\mathbf{C}_{e}}{1 + \mathbf{K}_{L}\mathbf{C}_{e}} \tag{2}$$

$$\frac{1}{q_{e}} = \frac{1}{q_{m}} + \frac{1}{q_{m}K_{L}C_{e}}$$
(3)

The model constants K_L and q_m were estimated from the slope and intercept of the plot of $1/q_e vs. 1/C_e$.

TABLE-1 EQUILIBRIUM ISOTHERM MODEL CONSTANTS FOR UPTAKE OF METHYLENE BLUE ON ALKALINE TREATED SAW PALMETTO FRUIT WASTE

			DLUE UI	N ALKALI	INE I KEAI	IED SAW PA	ALMETIO	FRUIT WF	ASIE			
Freundlich		Langmuir		Dubinin-Radushkevich			Temkin					
$\begin{array}{c} K_{F}(mg^{1-l/n}\\ L^{l/n}\!/g) \end{array}$	n _F	\mathbb{R}^2	q _m (mg/g)	K _L (L/mg)	\mathbb{R}^2	β (mol ² /kJ ²)	ε (kJ/mol)	q _o (mg/g)	\mathbb{R}^2	b _t (L/mol)	a _t	R ²
35.481	1.469	0.9019	1428.571	0.011	0.9579	0.0002	50	816.39	0.9234	15.49	0.0015	0.9302

Separation factor (R_L), a dimensionless equilibrium parameter of the Langmuir model, indicates the favourability of the sorption process which is given in eqn. 4:

$$R_{\rm L} = \frac{1}{(1 + K_{\rm L}C_{\rm o})} \tag{4}$$

where, C_o represents the different initial concentrations of adsorbate. Depending on the values of R_L , the sorption process may either be unfavourable ($R_L \ge 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). For the different initial concentrations studied, the average value of R_L was found to be 0.0124 which shows the sorption is highly favourable.

Freundlich model assumes that the sorbent surface to be heterogeneous and it deliberates multilayer sorption of adsorbate on the adsorbent surface [13]. The Freundlich model is linearized and expressed as follows:

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

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

where C_e is the equilibrium adsorbate concentration (mg/L); q_e is the equilibrium adsorbate concentration on adsorbent (mg/ g); q_m is the maximum uptake capacity of adsorbent (mg/g); K_F (mg^{1-1/n}L^{1/n}/g) and n are Freundlich constants and b is the Langmuir constant (L/mg).

From the slope and intercept of the linear plot, $\log q_e$ *versus* $\log C_e$, the Freundlich model constants n and K_F were evaluated. The magnitude of n indicates the favourability of sorption. For favourable sorption of adsorbate onto the adsorbent, the values of n should be between 1 and 10. From Table-1, Freundlich constant, $n_f = 1.467$, indicates adsorption to be favourable.

Dubinin-Radushkevich (D-R) model: It is applied to distinguish between physical and chemical adsorption of adsorbate with its mean free energy, ε per molecule of adsorbate [14]. The model isotherms are represented as:

$$\ln q_{\rm e} = \ln q_{\rm m} - \beta \epsilon^2 \tag{7}$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{8}$$

where, q_e = amount of adsorbate in the adsorbent at equilibrium (mg/g); q_s = theoretical isotherm saturation capacity (mg/g); β = Dubinin-Radushkevich isotherm constant (mol²/kJ²) and ϵ is Dubinin-Radushkevich isotherm constant (kJ/mol).

Temkin isotherm model: Temkin isotherm assumes that the heat of sorption of all molecules in the layer would decrease linearly rather than logarithmic [15]. It is generally expressed as follows. The linear form of which is used to determine the model constants.

$$q_e = \frac{RT}{b_t} \ln(a_t C_e)$$
(9)

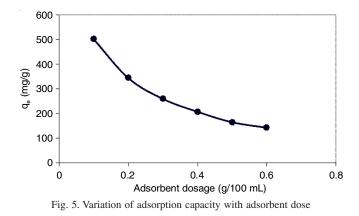
$$q_{e} = \frac{RT}{b_{t}} \ln a_{t} + \frac{RT}{b_{t}} \ln C_{e}$$
(10)

where R is gas constant; T is absolute temperature (K); a_t is Temkin isotherm equilibrium binding constant (L/g); b_t is Temkin isotherm constant and $B = RT/b_t$ represents a constant related to the heat of sorption (J/mol).

From the linear plot of Temkin isotherm, the heat of sorption was found to be 442.02 J/mol which is an indication of the physical adsorption process.

The different equilibrium model isotherms were compared with the experimental data in Fig. 4. Based on the correlation coefficient (R^2) from Table-1, the Langmuir model was observed to fit the experimental data well compared to other isotherm models.

Adsorbent dose rate: In order to find the optimal dosage of alkaline treated saw palmetto fruit waste for the removal of methylene blue, the adsorbent dosage varied from 0.1 to 0.6 g/100 mL for an initial dye concentration of 1000 ppm. It was seen from Fig. 5 that the adsorbent capacity decreased with increase in the adsorbent dose from 0.1 g/100 mL to 0.5 g/100 mL. With the increase in adsorbent amount, more sites are available for adsorption and hence the capacity of the adsorbent decreased for a constant initial concentration of the dye. Beyond 0.5 g/100 mL, no significant decrease in capacity of the adsorbent was observed. So, 0.5 g/100 mL was considered to be the optimal dosage of alkaline treated saw palmetto fruit waste for methylene blue adsorption.



Kinetic studies: This study gave an insight into the rate of adsorption of methylene blue on alkaline treated saw palmetto fruit waste. There was a rapid increase in methylene blue uptake by the saw palmetto fruit waste till 30 min and reached saturation after 60 min for an initial concentration of 1500 ppm (Fig. 6). The sorption capacity remained constant after 60 min indicating the saturation of the sorbent. A maximum uptake capacity of 1355.43 mg/g was observed at the end of 150 min. Lower uptake of 602.62 and 229.78 mg/g was observed for initial concentrations of 670 and 250 ppm, respectively. Since the concentration gradient of methylene blue between the adsorbent and dye solution decreases with a decrease in initial solution concentration, the saturation capacity was observed to decrease with a decrease in the initial concentration of the dye. Equilibrium contact of 60 min was observed to be sufficient for the two phases to reach equilibrium for all the studied concentrations.

The rate constants determine the sorption phenomenon of adsorbate on the active sites of the sorbent and different kinetic models were available for predicting the sorption kinetic behaviour. Pseudo-first-order, pseudo-second-order and

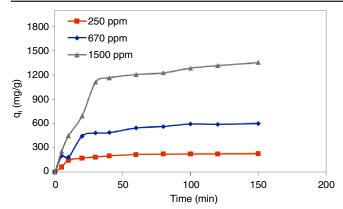


Fig. 6. Kinetic sorption studies for different initial concentration of methylene blue

intra-particle diffusion models were fitted to the kinetic data in order to analyze the sorption kinetics of methylene blue onto saw palmetto fruit waste.

Pseudo first order kinetics: The Lagergren first-order model [16] is given by the following equation:

$$\frac{\mathrm{d}\mathbf{q}_{t}}{\mathrm{d}t} = \mathbf{k}_{1}(\mathbf{q}_{e} - \mathbf{q}_{t}) \tag{11}$$

where, q_e (mg/g) represents equilibrium adsorption capacity, q_t (mg/g) is adsorption capacity at time 't' (min) and k_1 (min⁻¹) is the rate constant.

The linear form of the pseudo-first-order kinetics equation is:

$$\log (q_e - q_t) = \log q_e - k_1 t \tag{12}$$

The graph of log $(q_e - q_i)$ versus t was plotted as shown in Fig. 7 from which k was calculated. The pseudo first order rate constant K₁ increased from 0.0149 to 0.0168 min⁻¹ with increase in initial concentration and then decreased to 0.0124 min⁻¹ for an initial concentration of 1500 ppm. Even though the regression coefficients were good, the predicted capacities were not matching the experimental capacities. Hence pseudo first order model is not a suitable model to predict the kinetic sorption of methylene blue on to saw palmetto fruit waste.

Pseudo Second order kinetics: Ho and McKay [17] proposed the pseudo-second-order relation which is expressed as:

$$\frac{\mathrm{d}\mathbf{q}_{\mathrm{t}}}{\mathrm{d}\mathbf{t}} = \mathbf{k}_{2}(\mathbf{q}_{\mathrm{e}} - \mathbf{q}_{\mathrm{t}})^{2} \tag{13}$$

where, q_e is equilibrium adsorption capacity, q_t is adsorption capacity at time 't' (min) and k_2 (g min/mg) is the rate constant of the second-order sorption process.

The pseudo-second-order relation (eqn. 8) is linearized by applying the boundary conditions and is written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(14)

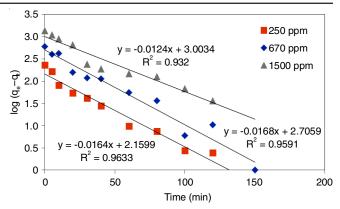


Fig. 7. Linear form of the pseudo-first-order kinetic sorption of methylene blue on alkaline treated saw palmetto fruit waste

The pseudo-second-order rate constant, k_2 and equilibrium uptake capacity, q_e were estimated from the slope and intercept of the plot of t/q_t versus t as shown in Fig. 8.

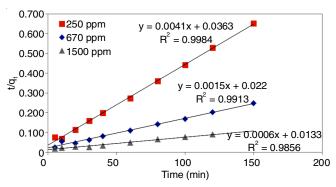


Fig. 8. Linear form of the pseudo-second-order kinetic sorption of methylene blue on alkaline treated saw palmetto fruit waste

From Table-2, it was seen that the regression coefficient of the pseudo-second-order was higher than that of the pseudo-first-order equation and the predicted uptake capacities were comparable to the experimental capacities. The rate constant, k_2 , values decreased from 4.63×10^{-4} to 2.7×10^{-5} g/mg min with increase in initial concentration from 250 to 1500 ppm.

Intraparticle diffusion: The intraparticle diffusion model given by Weber and Morris [18] is expressed as:

$$q_t = k_i t^{0.5} + C$$
 (15)

where k_i (mg/g/min^{1/2}) is the rate constant for intraparticle diffusion. The value of C gives an insight into the thickness of the boundary layer. Large intercept suggests great boundary layer effect. If the linear plot between q_t *versus* $t^{0.5}$ passes through the origin then intraparticle diffusion is said to be the sole rate-limiting step. Otherwise, a complex process may be governing the adsorption process.

	TABLE-2 KINETIC MODEL CONSTANTS FOR ADSORPTION OF METHYLENE BLUE								
Conc. First order kinetics				Second order kinetics			Intra particel diffusion model		
(mg/L)	k ₁ (min ⁻¹)	q _e (mg/g)	\mathbb{R}^2	k ₂ (g/mg min)	q _e (mg/g)	\mathbb{R}^2	k _i (mg/g/min ^{0.5})	С	R ²
250	0.0149	7.050	0.963	0.000463	243.902	0.998	39.99	5.79	0.792
670	0.0168	14.968	0.959	0.000102	666.667	0.991	87.39	19.26	0.912
1500	0.0124	20.154	0.932	0.000027	1666.667	0.986	177.15	34.55	0.984

Multi-linear profiles were observed from the plot of $q_i vs.$ $t^{0.5}$ (Fig. 9). The first linear plots may be due to the external surface adsorption and second linear profile is attributed to the intraparticle diffusion where diffusion is the rate controlling step. The intraparticle diffusion step usually depends on the operating parameters like solute concentration, temperature and particle size is difficult to predict or control. As seen from Table-2, the values of C increased from 5.79 to 34.55 with an increase in initial concentration from 250 to 1500 ppm indicating the boundary layer effects are more significant at higher concentrations. Even the intraparticle diffusion rate constant, k_i , values increased from 39.99 to 177.15 (mg/g/min^{0.5}) with increase in concentration from 250 to 1500 ppm.

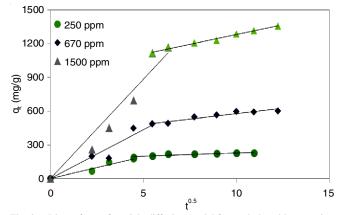


Fig. 9. Linear form of particle diffusion model for methylene blue sorption onto alkaline treated saw palmetto fruit waste

Even though all the tested kinetic models fitted the experimental data with a good regression coefficient ($R^2 > 0.9$), pseudo second-order model only predicted the saturation capacity well compared to the other models.

Temperature studies: Temperature is one of the significant parameters governing the adsorption process. The effect of sorption of methylene blue onto saw palmetto fruit waste spent was investigated at different temperatures. The sorption capacity of methylene blue increased with increasing temperature (not shown). The mobility of the ions increases with an increase in temperature which would have increased the intraparticle diffusion of the dye molecule onto the adsorbent surface. The boundary effects also decreased with increase in temperature which further enhanced the rate of adsorption.

Thermodynamic parameters like a change in free energy (ΔG°) , enthalpy (ΔH°) and entropy (ΔS°) were estimated using the following equations:

$$K_{\rm C} = \frac{C_{\rm se}}{C_{\rm le}} \tag{16}$$

$$\Delta G^{\circ} = -RT \log K_{\rm C} \tag{17}$$

$$\log K_{\rm c} = \frac{\Delta S^{\circ}}{2.303 R} - \frac{\Delta H^{\circ}}{2.303 RT}$$
(18)

where, K_c is the equilibrium constant, C_{se} and C_{le} are the equilibrium concentrations (mg/L) of the adsorbate in the solid and liquid phase, respectively, T is the temperature (Kelvin) and R is gas constant.

Gibbs free energy of change (ΔG°) indicates the spontaneity of the adsorption process. The negative value of ΔG° indicates that significant adsorption has occurred.

To determine the thermodynamic parameters governing the reaction, van't Hoff plot of ln (K) vs. 1/T was plotted (Fig. 10). Δ H° and Δ S° values were estimated from the slope and intercept of the plot. The positive value of Δ H° (10483.95 J/ mol) indicates that the sorption process to be endothermic and the positive value of Δ S° (36.34 J/mol) shows the increase in randomness at the solid-liquid interphase. Since the adsorption is an endothermic process, sorption rate also increased with temperature. The rate of diffusion of the molecules increases with increase in temperature which might be the reason for the increased uptake of adsorbate confirming the process to be endothermic.

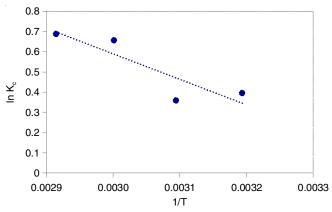


Fig. 10. Effect of temperature on adsorption of methylene blue onto alkaline treated saw palmetto fruit waste

Comparison of the different low-cost sorbent for the removal of methylene blue: Table-3 summarizes the different low-cost adsorbents for the removal of methylene blue from aqueous solution.

Low-cost adsorbents which were examined for methylene blue sorption were either from agriculture or plant waste products. The sorption capacities were varying from the very low value of around 10 to 700 mg/g. Activated carbons provide high surface area due to the presence of pores and hence provide high sorption for methylene blue. In the present study, the alkaline treated saw palmetto fruit waste provides a sorption capacity of 790 mg/g which is quite comparable to the capacities of activated carbon. A high capacity of 1355.43 mg/g was observed with varied operating conditions. In view of all these results, alkaline treated saw palmetto fruit waste can be treated as a low-cost sorbent for methylene blue.

Conclusion

In this study, saw palmetto fruit waste was used to treat synthetic textile effluents containing methylene blue. Alkaline treated saw palmetto fruit waste resulted in good uptake of methylene blue compared to untreated saw palmetto fruit waste. Back diffusion of methylene blue was observed with untreated saw palmetto fruit waste when the adsorbent was saturated with the adsorbate. The maximum uptake capacity of saw palmetto fruit waste for methylene blue was found to be 790 mg/g and the Langmuir isotherm model better explains the

TABLE-3
COMPARISON OF SORPTION CAPACITIES OF
DIFFERENT ADSORBENTS FOR METHYLENE BLUE

A .1	M	D.f
Adsorbent	Max. capacity	Ref.
Periwinkle shells (AC)	500.00	[8]
Neem leaf	8.76-19.61	[19]
Wheat shells	16.56-21.50	[20]
Sawdust coated with polypyrrole	34.36	[21]
Cherry sawdust	39	[22]
Rice husk	40.58	[23]
Sunflower seed husk	45.25	[24]
Walnut sawdust	59.17	[22]
Pryophyllite	70.42	[25]
Hazelnut shell	76.6	[22]
Calotropis procera leaf powder	192.31	[26]
Palm kernel coat	277.77	[27]
Teak tree bark	333.3	[28]
Spruce wood shavings (AC)	17.91	[29]
Paspalum notatum (AC)	30.4	[30]
Coconut bunch waste (AC)	70.92	[31]
Garlic peel (AC)	82.64	[32]
Coffee husk (AC)	90.1	[33]
Meranti sawdust (AC)	120.48	[34]
Pumpkin seed hull (AC)	141.92	[35]
Palm kernel fiber (AC)	217.95	[36]
Activated carbon	735	[37]
Saw palmetto waste-CT	790	Present study
AC - Activited control CT - Char	ni o al tra a ta d	

AC = Activated carbon; CT = Chemical treated

sorption process. The sorption kinetics of methylene blue over saw palmetto fruit waste follows the pseudo-second-order kinetic model. The uptake of methylene blue by saw palmetto fruit waste was found to be an endothermic and spontaneous process from the thermodynamic study. Finally, alkaline treated saw palmetto fruit waste can be considered as an effective low-cost biosorbent for treating methylene blue dye solutions.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- M. Auta and B.H. Hameed, *Chem. Eng. J.*, **171**, 502 (2011); <u>https://doi.org/10.1016/j.cej.2011.04.017</u>.
- K.Y. Foo and B.H. Hameed, *Bioresour. Technol.*, **104**, 679 (2012); https://doi.org/10.1016/j.biortech.2011.10.005.
- B. Gozmen, B. Kayan, A.M. Gizir and A. Hesenov, *J. Hazard. Mater.*, 168, 129 (2009);
- https://doi.org/10.1016/j.jhazmat.2009.02.011.
- K.S.P. Kalyani, N. Balasubramanian and C. Srinivasakannan, *Chem. Eng.* J., 151, 97 (2009);
- https://doi.org/10.1016/j.cej.2009.01.050. 5. S. Khansorthong and M. Hunsom, *Chem. Eng. J.*, **151**, 228 (2009);
- https://doi.org/10.1016/j.cej.2009.02.038.
 A.N. Kagalkar, U.B. Jagtap, J.P. Jadhav, V.A. Bapat and S.P. Govindwar, *Bioresour. Technol.*, **100**, 4104 (2009);
- https://doi.org/10.1016/j.biortech.2009.03.049. 7. V.K. Gupta and Suhas, *J. Environ. Manage.*, **90**, 2313 (2009);
- https://doi.org/10.1016/j.jenvman.2008.11.017.
 8. O.S. Bello, K.A. Adegoke, A.A. Olaniyan and H. Abdulazeez, *Desalination Water Treat.*, 53, 1292 (2013);
 - https://doi.org/10.1080/19443994.2013.862028.

9.	M. Rafatullah, O. Sulaiman, R. Hashim and A. Ahmad, J. Hazard. Mater.,
	177 , 70 (2010);
	https://doi.org/10.1016/j.jhazmat.2009.12.047.
10	P.S. Plackburn Empiron Sai Trachnol 38 4005 (2004):

- R.S. Blackburn, Environ. Sci. Technol., 38, 4905 (2004); https://doi.org/10.1021/es049972n.
- Z.A. Al-Anber, M.A. Al-Anber, M. Matouq, O. Al-Ayed and N.M. Omari, *Desalination*, **276**, 169 (2011); <u>https://doi.org/10.1016/j.desal.2011.03.043</u>.
- 12. I. Langmuir, J. Am. Chem. Soc., **38**, 2221 (1916); https://doi.org/10.1021/ja02268a002.
- J. Appel, Surf. Sci., 39, 237 (1973); https://doi.org/10.1016/0039-6028(73)90105-2.
- M.M. Dubinin and L.V. Radushkevich, Proc. Acad. Sci. USSR Phys. Chem., 55, 331 (1947).
- 15. C. Aharoni and M. Ungarish, J. Chem. Soc., Faraday Trans., 73, 456 (1977);

https://doi.org/10.1039/f19777300456.

- 16. S. Lagergren, K. Sven. Vetensk. Akad. Handl., 24, 1 (1898).
- Y.S. Ho and G. McKay, *Process Biochem.*, 34, 451 (1999); https://doi.org/10.1016/S0032-9592(98)00112-5.
- W.J. Weber and J.C. Morris, In Proceedings of International Conference on Water Pollution Symposium Pergamon Press, Oxford, pp. 231-266 (1962).
- K.G. Bhattacharyya and A. Sharma, *Dyes Pigments*, 65, 51 (2005); https://doi.org/10.1016/j.dyepig.2004.06.016.
- Y. Bulut and H. Aydin, *Desalination*, **194**, 259 (2006); https://doi.org/10.1016/j.desal.2005.10.032.
- R. Ansari and Z. Mosayebzadeh, J. Iran. Chem. Soc., 7, 339 (2010); https://doi.org/10.1007/BF03246019.
- F. Ferrero, J. Hazard. Mater., 142, 144 (2007); https://doi.org/10.1016/j.jhazmat.2006.07.072.
- V. Vadivelan and K.V. Kumar, J. Colloid Interface Sci., 286, 90 (2005); <u>https://doi.org/10.1016/j.jcis.2005.01.007</u>.
- 24. S.-T. Ong, P.-S. Keng, S.-L. Lee, M.-H. Leong and Y.-T. Hung, *Int. J. Phys. Sci.*, **5**, 1270 (2010).
- A. Gücek, S. Sener, S. Bilgen and M.A. Mazmanci, *J. Colloid Interface Sci.*, **286**, 53 (2005); https://doi.org/10.1016/j.jcis.2005.01.012.
- E.O. Oyelude and U.R. Owusu, J. Appl. Sci. Environ. Sanit., 6, 477 (2011).
- 27. N.A. Oladoja, C.O. Aboluwoye and Y.B. Oladimeji, *Turk. J. Eng. Environ. Sci.*, **32**, 303 (2008).
- 28. S. Patil, S. Renukdas and N. Patil, Int. J. Environ. Sci., 1, 711 (2011).
- P. Janos, S. Coskun, V. Pilarova and J. Rejnek, *Bioresour. Technol.*, 100, 1450 (2009);

https://doi.org/10.1016/j.biortech.2008.06.069.

- 30. K.V. Kumar and K. Porkodi, *J. Hazard. Mater.*, **146**, 214 (2007); https://doi.org/10.1016/j.jhazmat.2006.12.010.
- 31. B.H. Hameed, D.K. Mahmoud and A.L. Ahmad, *J. Hazard. Mater.*, **158**, 65 (2008);
- https://doi.org/10.1016/j.jhazmat.2008.01.034. 32. B.H. Hameed and A.A. Ahmad, *J. Hazard. Mater.*, **164**, 870 (2009); https://doi.org/10.1016/j.jhazmat.2008.08.084.
- L.S. Oliveira, A.S. Franca, T.M. Alves and S.D.F. Rocha, *J. Hazard. Mater.*, 155, 507 (2008);
- <u>https://doi.org/10.1016/j.jhazmat.2007.11.093</u>.
 34. A. Ahmad, M. Rafatullah, O. Sulaiman, M.H. Ibrahim and R. Hashim, *J. Hazard. Mater.*, **170**, 357 (2009);
- https://doi.org/10.1016/j.jhazmat.2009.04.087. 35. B.H. Hameed and M.I. El-Khaiary, *J. Hazard. Mater.*, **155**, 601 (2008);
- https://doi.org/10.1016/j.jhazmat.2007.11.102. 36. A.E. Ofomaja, *Chem. Eng. J.*, **126**, 35 (2007); https://doi.org/10.1016/j.cej.2006.08.022.
- K. Legrouri, E. Khouya, M. Ezzine, H. Hannache, R. Denoyel, R. Pallier and R. Naslain, J. Hazard. Mater., 118, 259 (2005); https://doi.org/10.1016/j.jhazmat.2004.11.004.