USE OF ACTIVATED CARBON FROM SAPINDUS FOR THE ADSORPTION OF METHYLENE BLUE

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ABSTRACT

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Activated carbon was produced from Sapindus fruit residue and ***was*** *used for the adsorption of methylene blue dye from simulated aqueous solution. Adsorption kinetics of methylene blue onto actived carbon were studied in a batch system. The effects of pH and contact time were examined. The goal of the present study was the determination of the optimal experimental conditions. The maximum adsorption of methylene blue occurred at pH 6.0 (4.83 mg/g) and the lowest adsorption occurred at pH 2.0 (4.35 mg/g). 120 min was the time needed for apparent equilibrium. Adsorption modelling was determined by using the Freundlich and Langmuir isotherms. Data were interpreted based on* R^2 *and various error distribution functions. Adsorption isotherm was best described by non linear Freundlich isotherm model. In order to determine the best-fit-adsorption kinetics, the experimental data were analyzed using pseudo-first-order, pseudo-second-order, pseudo-third-order, Esquivel, and Elovich models. The needed relative parameters were determined* ***by*** *linear and non-linear regressive methods. The statistical functions were estimated to find the suitable method which fit the experimental data. Both methods were suitable to obtain the required parameters. The model that best fit the present equilibrium data was the linear Elovich model (type 1 and 2). The present work showed that activated carbon can be used as a low cost adsorbent for the methylene blue removal from aqueous solutions****.***

Keywords: Activated carbon (AC), methylene blue (MB), modelling, linear regression, non-linear regression.

INTRODUCTION

In coloring paper, dyeing cottons, wools, silk, leather and coating for paper stock, methylene blue (MB) is used. The treatment of effluents containing such dyes is of great interest due to its harmful impacts on receiving water (Kushwaha *et al*., 2014). The best efficient method used for the quick removal of dyes from aqueous solutions was physical adsorption (Allen *et al.*, 2005). A slightly better adsorption was shown by aromatic solutes compared to aliphatic solutes, due to the potential to form π-π bonds with the basal planes of activated carbon. No significant influence of solute charge or size was observed (De Ridder, 2012).

Adsorption process was used for the elimination of pollutant from simulated aqueous solution and is extremely influenced by the medium of the solution, which affects the adsorption rate, the nature of the adsorbent surface charge, the aqueous adsorbate species speciation and the ionization extent. Functional dissociation groups on the adsorbate and adsorbent were affected by a pH change during the adsorptive process (Khattria et al. 2009).

In this study, the potential of activated carbon (AC) was evaluated to remove MB dye from simulated aqueous solutions in batch mode.

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MATERIALS AND METHODS

MB (3, 7-bis (Dimethylamino)-phenazathionium chloride tetramethylthionine chloride, $C_{16}H_{18}N_3SCl\cdot 3H_2O$, Mw =373.9 g/mol, Figure 1) used in the present study was purchased from Merck (Germany), being selected from the list of dyes normally used in Algeria.

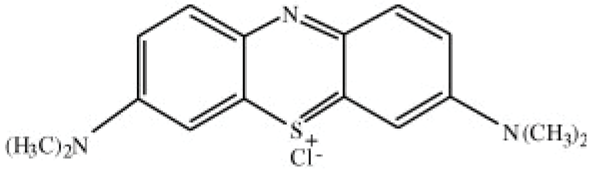

Figure 1. Structure of methylene blue (Al-Degs et al. 2012).

The activated carbon was prepared as reported earlier (Lam 2008). The fruit of Sapindus fruit was collected from Bousmail (Algeria). The fruit of Sapindus was sieved in order to obtain a desirable size fraction (0.5 and 1mm). The sieved residue of Sapindus fruit was then washed with distilled water to remove any residues or impurities. Subsequently, it was dried in an oven for 12 hours at 80°C. After drying, the material was pyrolysized in a fluidized bed furnace at 300, 400 and 500 °C for half an hour. The char produced was then discharged from the first cyclone of the fluidized bed furnace. This fast pyrolysis method produced a variety of char at different temperatures.

Activation of the char was done by using a steam average flowrate of 300 ml/min at temperature of 800°C in a muffle furnace for 1 and 2 hours. The activated carbon was then ground and dried overnight in an oven at 100 °C.

The adsorption parameters were optimized. In each experiment pre-weighed amount of adsorbent (50 mg) was added to 50 mL of dye solution (5 mg/L) taken in a conical flask of 250 mL and 0.1 M NaOH or 0.1 M HCl were added to adjust the pH value. This solution was agitated at 300 rpm and centrifuged. A spectrophotometer UV-1700 PHARMA SPEC SHIMADZU was used for determining the MB concentration in aqueous solution at λ_{max} = 665 nm. The adsorbed amount of MB per mass unit of adsorbent at time t, q (mg/g), (Equation 1) and the dye removal efficiency (R %) (Equation 2) were calculated as follows:

$$q = (C_0 - C)\frac{V}{M} \qquad (1)$$

$$R = \frac{(C_0 - C)}{C_0} \times 100 \qquad (2)$$

Where C_0 is the initial concentration of MB (mg/L), C is the MB concentration at time t, V is the volume of solution (L) and M is the adsorbent mass (g) (Santhi *et al.*, 2009).

By mixing 1 g of the adsorbent with 1 L of the MB simulated aqueous solution of 5 mg/L, the effect of pH was evaluated. The pH value varied from 2 to 12, by adding 0.1M NaOH or 0.1M HCl solutions. The suspension was shaken for 24 h at 25°C. Kinetic experiments were performed by mixing 50 mL of dye solution (5 mg/L) with 50 mg (0.05 g) of adsorbent for different periods (5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 180, 240 and 300 min). The initial pH for each dye solution was set at 6. MB concentration in the supernatants was determined and the adsorbed amount of MB was calculated by equation 1.

RESULTS AND DISCUSSION

Adsorption isotherms are important for the description of how adsorbates will interact with an adsorbent. Thus, the correlation of equilibrium data using either a theoretical or empirical equation is essential for the adsorption data and prediction, as well. For further interpretation of the obtained adsorption data the two famous isotherm equations, the Langmuir and Freundlich isotherm equations, were employed.

The adsorption of MB increased with increasing the pH of the solution. The best value of adsorption capacity, qe = 4.83 mg/g, was recorded at pH 6 (Fig. 2).

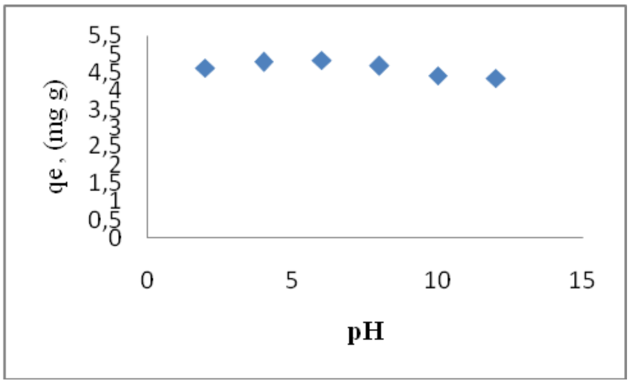

Figure 2. Effect of the initial pH on the AC equilibrium adsorption capacity.

In the basic medium, the negatively charged species of the adsorbent tended to dominate leading to a more negatively charged surface. In this case, the adsorbent surface was negatively charged. The MB adsorption increased due to the enhancement of electrostatic attractions between the negative charge of AC particles and the positive charge of MB species.

In order to determine the best-fit-adsorption isotherms, the experimental data were analyzed using Freundlich and Langmuir equations. Equations of these models (Fadi Al Mardini *et al*., 2009) are presented in Table 1, where q is the equilibrium dye concentration on adsorbent (mg/g), q_m is the monolayer capacity of the adsorbent (mg/g), C is the equilibrium dye concentration in solution (mg/L), K_L is the Langmuir adsorption constant representing the energy constant related to the heat of adsorption, n and K_F are Fruendlich constants related to adsorption intensity of the adsorbent and adsorption.

Table 1. Adsorption isotherms models and their linear and non linear forms (Fadi Al Mardini et al. 2009)

Applied model	Linear form	Non Linear form
Langmuir 1	$\frac{C}{q}=\frac{C}{q_m}+\frac{1}{k_L q_m}$	$\frac{q}{q_m}=\frac{K_L C}{1+K_L C}$
Langmuir 2	$\frac{1}{q}=\frac{1}{C}\frac{1}{q_m K_L}+\frac{1}{q_m}$	
Langmuir 3	$q=\frac{1}{K_L}\frac{q}{C}+q_m$	
Langmuir 4	$q=-\frac{1}{K_L}\frac{q}{C}+q_m$	
Langmuir 5	$\frac{q}{C}=-K_L q+K_L q_m$	
Langmuir 6	$\frac{1}{C}=K_L q_m\frac{1}{q}-K_L$	
Freundlich	$\ln(q)=\ln(k_F)+n\ln(C)$	$q=K_F C^{1/n}$

Excel and Origin software were used respectively for the non-linear and linear fitting procedure. The constants of all models are given in Table 2.

TABLE 2. Constants for linear and non-linear Langmuir and Freundlich isotherms related to the adsorption of MB onto AC.

Model	Linear method	Non-linear method
Langmuir 1		
q_m	-76.923	161468.291
K_L	-1.625	$1.370*10^{-3}$
R^2	0.643	0.983
Langmuir 2		
q_m	-66.667	
K_L	-1.875	
R^2	0.869	
Langmuir 3		
q_m	-58.740	
K_L	1.949	
R^2	0.363	
Langmuir 4		
q_m	-58.740	
K_L	-1.949	
R^2	0.363	
Langmuir 5		
q_m	-0.008	
K_L	-0.708	
R^2	0.363	
Langmuir 6		
q_m	-0.003	
K_L	-2.733	
R^2	0.869	
Freundlich		
n	1.251	0.911
K_F	301.569	243.527
R^2	0.949	0.989

The coefficient of correlation indicated that Freundlich isotherm fitted the experimental data better than Langmuir isotherm. Good agreement between the experimental isotherms and the Freundlich model was found in the case of systems: Methylene Blue/Cactus (Sakr et al. 2015), pentachlorophenol/(M)Al-MCM-41 (Marouf-Khelifa et al. 2004), and toluene/actived Carbon (Benkhedda et al. 2000).

The optimization procedure has required a defined error function in order to evaluate the fit of equation to the experimental data. The best-fitting equation is determined using the well-known special functions to calculate the deviation error between experimental and predicted data. The mathematical equations of these error functions are illustrated in Table 4.

Table 3. Mathematical equations of error functions.

Error functions	**Equations**	**Reference**
MPSED	$MPSED = \sqrt{\dfrac{\Sigma\left[\left(q_{\exp} - q_{calc}\right)/q_{\exp}\right]^2}{(n-p)}}$	(Ncibi 2008)
ARE	$ARE = \dfrac{\Sigma\left\lvert(q_{calc} - q_{\exp})/q_{\exp}\right\rvert}{n}$	(Han et al. 2009)
ARS	$ARS = \sqrt{\dfrac{\Sigma\left[\left(q_{\exp} - q_{calc}\right)/q_{\exp}\right]^2}{(n-1)}}$	(Han et al. 2009)
HYBRID	$HYBRID = \dfrac{1}{(n-P)}\Sigma_{i=1}^{n}\left\lvert\dfrac{q_{\exp} - q_{calc}}{q_{\exp}}\right\rvert_i$	(Gulipall et al. 2011)

Where n is the number of experimental data points, q_{calc} is the predicted (calculated) quantity of MB adsorbed onto AC, q_{exp} is the experimental data, p is the number of parameters in each kinetic model, ARE is the average relative error (dimensionless parameter), ARS is the average relative standard error (dimensionless parameter), HYBRID is the hybrid fractional error function (dimensionless parameter) and *MPSED* Marquardt's is the percent standard deviation (dimensionless parameter). The constants of all error analysis are presented in Table 4.

Table 4. Error deviation data related to the adsorption of MB onto AC employing the most commonly used functions.

Error functions	**Linear Freundlich model**	**Non linear Freundlich model**
MPSED	2.066	0.316
HYBRID	2.095	0.255
ARE	1.496	0.182
ARS	1.886	0.288

The isotherm adsorption data are essentially required for designing the adsorption systems. In order to optimize the design of a specific sorbate/sorbent system for the removal of MB from aqueous solution, it was important to establish the most appropriate correlation for the experimental kinetic data.

Applicability of some statistical tools to predict the optimum adsorption isotherms of MB onto AC after linear regression analysis showed that the highest R^2 value and the lowest ARE, ARS, MSPED, and HYBRID values can be suitable and meaningful tools to predict the best-fitting equation models.

The best fitting was determined based on the use of these functions for the calculation of the deviation error between experimental and predicted equilibrium adsorption isotherm data, after linear analysis. Consequently, from Table 3, it seems that the most suitable model for the study of adsorption phenomenon is the non linear Freundlich model. Therefore, based on the mentioned results, the best useful estimation error of the statistical tools pointed out to the non linear Freundlich model, followed by linear Freundlich model, as the best-fitting models.

Figure 3 illustrates the effect of contact time on decolorization (dye adsorption) with AC. The plot (simulated aqueous solution) can be divided in three zones: (i) 0-30 min, which indicated the fast adsorption of MB, suggesting rapid external diffusion and surface adsorption; (ii) 30-60 min, shows a gradual equilibrium, and (iii) 60-300 min, indicates the plateau of the equilibrium state. At the initial stage of the contact the adsorption was rapid, but it gradually slowed down until the equilibrium. At the initial stage the fast adsorption can be attributed to the fact that a large number of surface sites are available for adsorption.

The remaining surface sites are difficult to be occupied after a lapse of time. Adsorption is a complex process which is influenced by several parameters related to adsorbent and to the physicochemical conditions, under which the process is carried out (Dahri et al. 2014).

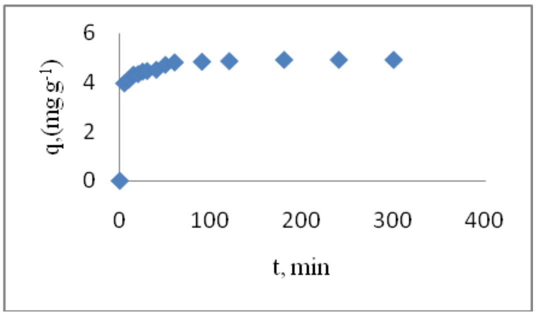

Figure 3. MB adsorption kinetic on AC.

The following equations: Pseudo-first order, Pseudo-second order, Esquivel, Pseudo-third order and Elovich were used for understanding the mechanism of the adsorption process study and were selected to fit the experimental kinetic data. Equations and the constants of these models are presented in Table 6.

Table 5. A linear and non-linear Pseudo-first order, Pseudo-second order, Esquivel, Pseudo-third order and Elovich kinetics isotherms constants related to the adsorption of MB onto AC.

Linear Method	Reference	Non-linear Method	Reference
Pseudo-first order (type 1) $\log(q_e - q) - \log(q_e) = -\frac{k_1 t}{2.303}$ $q_e = 4.901$ $K_1 = 0.037$ $R^2 = 0.727$	(Kumar 2006)	Non-linear Pseudo-first order (type 1) $q = q_e(1 - e^{-k_1 t})$ $q_e = 4.642$ $K_1 = 0.333$ $R^2 = 0.962$	(Kumar 2006)
Pseudo-first order (type 2) $\ln(q_e - q) - \ln(q_e) = -k_1 t$ $q_e = 4.901$ $K_1 = 0.036$ $R^2 = 0.727$	(Tavlieva et al. 2013)		
Pseudo-first order (type 3) $\ln(\frac{C}{C_0}) = k_1 t$ $C_o = 5.000$ $K_1 = 0.019$ $R^2 = -1.000$	(Rao et al. 2011)	Non-linear Pseudo-first order (type 2) $C = C_0 e^{-k_1 t}$ $C_o = 5.000$ $K_1 = 0.230$ $R^2 = 0.894$	(Pereira et al. 2012)
Pseudo-first order (type 4) $\ln\left[1 - \frac{C_0 - C}{C_0 - C_e}\right] = k_1 t$ $C_o = 5.000$ $K_1 = 0.005$ $R^2 = -0.690$	(Rao et al. 2011)		
Pseudo-second order (type 1) $\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ $q_e = 4.950$ $K_2 = 0.080$ $R^2 = 0.999$	(Ho 2006)	Non-linear Pseudo-second order $q = \left[\frac{q_e^2 k_2 t}{1 + k_2 q_e t}\right]$ $q_e = 4.829$ $K_2 = 0.666$	(Kumar 2006) (Kumar 2006)

		$R^2 = 0.989$	
Pseudo-second order (type 2) $\frac{1}{q}=\frac{1}{k_2 q_e^2}\frac{1}{t}+\frac{1}{q_e}$ $q_e = 4.808$ $K_2 = 3.356$ $R^2 = 0.825$	(Ho 2006)		
Pseudo-second order (type 3) $(\frac{1}{q}-\frac{1}{q_e})q_e^2=\frac{1}{k_2}\frac{1}{t}$ $q_e = 4.783$ $K_2 = 0.162$ $R^2 = 0.825$	(Ho 2006)		
Pseudo-second order (type 4) $q = q_e-\left(\frac{1}{k_2 q_e}\right)\frac{q}{t}$ $q_e = 3.044$ $K_2 = 0.074$ $R^2 = 0.670$	(Ho 2006)		
Pseudo-second order (type 5) $(q - q_e)q_e = -\left(\frac{1}{k_2}\right)\frac{q}{t}$ $q_e = 4.800$ $K_2 = 0.155$ $R^2 = 0.802$	(Ho 2006)		
Pseudo-second order (type 6) $\frac{q}{t}=k_2 q_e^2 - k_2 q\, q_e$ $q_e = 4.864$ $K_2 = 0.121$ $R^2 = 0.802$	(Ho 2006)		
Pseudo-second order (type 7) $\frac{1}{q_e - q}-\frac{1}{q_e}=k_2 t$ $q_e = 4.940$ $K_2 = 0.097$ $R^2 = 0.933$	(Kumar 2006)		
Pseudo-second order (type 8) $\frac{1}{t}=k_2 q_e^2\left(\frac{1}{q}\right)-k_2 q_e$ $q_e = 4.849$ $K_2 = 0.128$ $R^2 = 0.825$	(Kumar 2006)		

Pseudo-second order (type 9) $\frac{q_e}{q_e - q} - 1 = k_2 t$ $q_e = 4.940$ $K_2 = 0.483$ $R^2 = 0.933$	(Ho 2006)		
Pseudo-second order (type 10) $\frac{\theta}{1-\theta} = k_2 t$ $q_e = 4.940$ $K_2 = 0.483$ $R^2 = 0.933$	(Ho 2006)		
Pseudo-second order (type 11) $C - \frac{1}{C_0} = k_2 t$ $C_o = 5.000$ $K_2 = -7*10^{-3}$ $R^2 = -0.200$	(Pereira et al. 2012)		
Pseudo-second order (type 12) $\frac{1}{C} - \frac{1}{C_0} = k_2 t$ $C_o = 5.000$ $K_2 = 0.042$ $R^2 = 0.855$	(Ho 2000)		
Pseudo-second order (type 13) $\frac{1}{C_0 - C} = k_2 t + b$ $C_o = 5.000$ $K_2 = 0.000$ $R^2 = 0.539$	(Blanachard et al. 1984)		
Esquivel Model (type 1) $\frac{1}{q} = \left(\frac{K_E}{q_e}\right)\frac{1}{t} + \frac{1}{q_e}$ $q_e = 4.807$ $K_E = 1.308$ $R^2 = 0.825$	(Shilpi et al. 2013)	Non-linear Esquivel Model $q = q_e\left(\frac{t}{t + K_E}\right)$ $q_e = 4.829$ $K_E = 1.502$ $R^2 = 0.989$	(Shilpi et al. 2013)
Esquivel Model (type 2) $(\frac{1}{q} - \frac{1}{q_e})q_e = K_E \frac{1}{t}$ $q_e = 4.783$ $K_E = 1.285$ $R^2 = 0.825$	(Shilpi et al. 2013)		

Pseudo-third order $\frac{1}{q^2}=\frac{1}{q_e^2}+k_3t$ $q_e = 4.344$ $K_3 = -6*10^{-5}$ $R^2 = 0.519$	(Ho et al. 2000)		
Elovich (type1) $q = k_5\ln(k_5k_4)+k_5\ln(t)$ $K_4 = 6350477$ $K_5 = 0.252$ $R^2 = 0.932$	(Ho et al. 2002)		
Elovich (type 2) $q = (1/k_5)\ln(k_5k_4)+(1/k_5)\ln(t)$ $K_4 = 403281$ $K_5 = 3.968$ $R^2 = 0.932$	(Tavlieva et al. 2013)		

where k_1 is Pseudo-first order rate constant (min^{-1}), k_2 is Pseudo-second order rate constant (g/(mg min)), k_3 is Pseudo-third order rate constant ($g^2/(mg^2$ min)), K_E is Esquivel rate constant (min), k_4 is Elovich rate constant (mg/(g min)), k_5 is extent of surface coverage and activation energy of the process (g/mg), k_6 extent of surface coverage and activation energy of the process (g/mg), k_7 Elovich rate constant (mg/(g min)), q_e is amount of adsorption at equilibrium (mg/g), and θ dimensionless parameter (=q/q_e).

The constants of all error analysis are represented in Table 6.

Table 6. Error deviation data related to the MB adsorption onto AC employing most commonly used functions.

Error functions	**Linear Elovich model (type 1 and 2)**	**Linear pseudo second order (type 9 and 10)**	**Non-linear esquivel model**	**Non-linear pseudo second order**	**Linear esquivel model (type 2)**
MPSED	0.018	0.040	0.031	0.031	0.047
HYBRID	0.016	0.025	0.029	0.030	0.044
ARE	0.013	0.021	0.025	0.025	0.038
ARS	0.017	0.038	0.029	0.029	0.045

The design of adsorption systems is strongly related to the adsorption kinetic data which are the basic requirements. In order to optimize the design of a specific sorbate/sorbent system to remove MB from aqueous solution, it is important to establish the most appropriate correlation for the experimental kinetic data. Applicability of some statistical tools to predict optimum adsorption kinetic of MB onto AC after linear regression analysis showed that the highest R^2 value and the lowest ARE, ARS, MSPED, and HYBRID values could be suitable and meaningful tools to predict the best-fitting equation models. The best fitting is determined based on the use of these functions to calculate the error deviation between experimental and predicted equilibrium adsorption kinetic data, after linear analysis. The adsorption phenomenon was satisfactorily described by the linear Elovich model (type 1 and 2) (Table 6). Therefore, based on these mentioned results, the best useful error based on such statistical tools should point out the linear Elovich model (type 1 and 2) followed by linear Pseudo-second order (type 9 and 10), non linear Esquivel, non linear Pseudo-second order and linear Esquivel as the best-fitting models.

Activated carbon, produced from the residue of Sapindus fruit, was used for the adsorption of Methylene bleu in simulated aqueous solution. In batch mode, the adsorption was highly dependent on two operating parameters (pH, contact time). The obtained results revealed the following optimal conditions: pH value of 6 and 120 min of contact time, which lead to 98 % MB removal.

Kinetics data correlated well with the linear Elovich model (type 1 and 2), whereas equilibrium study was best described by non-linear Freundlich isotherm model.

The adsorption kinetic of MB onto AC can be better fitted by the linear Elovich model (type 1 and 2), as compared to the linear Pseudo first order, non linear Pseudo first order, the non-linear Pseudo-second-order model, linear Pseudo-second-order model, Pseudo third order, linear Esquivel and non linear Esquivel models. AC is suitable adsorbent for the removal of MB as showed by the entire experimental results.

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