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REMOVAL OF METHYLENE BLUE BY ADSORPTION ONTO *RETAMA RAETAM* PLANT: KINETICS AND EQUILIBRIUM STUDY

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Abstract. The feasibility of using medicinal plants species *Retama raetam* as a low cost and an eco-friendly adsorbent for the adsorption of cationic dye methylene blue from simulated aqueous solution has been investigated. Adsorption kinetics of methylene blue onto *Retama raetam* plants was studied in a batch system. The effects of pH and contact time were examined. The methylene blue maximum adsorption occurred at pH 8 and the lowest adsorption occurred at pH 2. The apparent equilibrium was reached after 120 min. Optimal experimental conditions were determined. Adsorption modelling parameters for Freundlich and Langmuir isotherms were determined and, based on R^2, various error distribution functions were evaluated as well. Adsorption isotherm was best described by non linear Freundlich isotherm model. Thermodynamic studies show that adsorption was spontaneous and exothermic. For determining the best-fit-kinetic adsorption model, the experimental data were analyzed by using pseudo-first-order, pseudo-second-order, pseudo-third-order, Esquivel, and Elovich models. Linear regressive and non-linear regressive method was used to obtain the relative parameters. The statistical functions were estimated to find the suitable method that fit better the experimental data. Both methods were appropriate for obtaining the parameters. The linear pseudo-second-order (type 9 and type 10) models were the best to fit the equilibrium data. The present work showed that plant *Retama raetam* can be used as a low cost adsorbent for the removal of methylene blue from water.

Keywords: *Retama raetam*, methylene blue, removal, modelling, adsorption.

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Introduction

The textile industry is one of industrial waste water source. This contaminated water is very toxic for the humans and animals [1]. Methylene blue is used in colouring paper, dyeing cottons, wools, silk, leather and coating for paper stock. Although methylene blue is not strongly hazardous, it can cause some harmful effects, such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in human organisms [2].

Chemical coagulation–flocculation [3], different types of oxidation processes [4], biological process [5], membrane-based separation processes [6] and adsorption [7] were the treatments used in the purification of waters. The most efficient method used for the quickly removal of dyes from the aqueous solution is the physical adsorption [8]. Biosorbents, such as wood sawdust [9], waste-biomass [10], delonix regia [11], agricultural solid waste [12], are able to remove efficiently the colour from water.

Retama raetam plants can be used as biosorbent. This species belonging to the *Fabaceae* family has a very productive vertical and horizontal root system, which can reach 20 m. This, in turn, increases substantially the stabilization of the soil. Moreover, the *Retama* species contributes to the biofertilisation of poor grounds, because of their aptitude to associate with fixing nitrogen bacteria *Rhizobia*. Therefore, the genus of *Retama* is included in a re-vegetation program for degraded areas in semi-arid Mediterranean environments [13].

Retama raetam is a common plant in the North African and East Mediterranean region. In Algeria, it is located in Sahara and Atlas regions and is used in folk medicine under the common name "R'tam" to reduce the blood glucose and skin inflammations, while in Lebanon it is used as folk herbal medicine against joint aches and in Morocco against skin diseases. Previous pharmacological studies on the plant have revealed its various medicinal properties: antibacterial, antifungal, antihypertensive, antioxidant, antiviral, diuretic, hypoglycaemic, hepatoprotective, nephroprotective and cytotoxic effects. *Retama* species have been reported to contain flavonoids and alkaloids [14].

However, there are no reported studies on the adsorption of cationic dyes by *Retama raetam*. This work aims to understand the potential of *Retama raetam* for removal of methylene blue dye from simulated aqueous solution in batch mode. The adsorption efficiency of methylene blue was investigated in order to optimize the experimental parameters. The statistical functions were used to estimate the error deviations between experimental and theoretically predicted adsorption values, including linear and non-linear method. The optimization procedure required a defined error function in order to evaluate the fit of equation to the experimental data.

Experimental

Materials

Methylene blue (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. *Retama raetam* plants were collected in Mostaganem region (Algeria), washed several times with deionized water to remove the color and dried at 105°C for 5 h in a convection oven. The residual organics and lipids were respectively removed by methanol and petroleum ether. After this procedure, *Retama raetam* was washed again with distilled water.

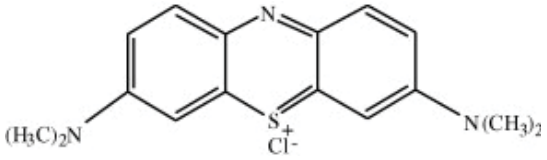

Figure 1. Structure of methylene blue [15].

Methods

The *Retama raetam* was characterized by pH measurement of the pH_{PZC} (point of zero charge). The pH_{PZC} of an adsorbent is a very important characteristic that determines the pH, at which the adsorbent surface has net electrical neutrality [16].

The pH_{PZC} of *Retama raetam* was measured by pH drift method: 0.1 mg of *Retama raetam* is added to 100 mL of water with varying pH from 2 to 12 and stirred for 24 h. Final pH of the solution is plotted against initial pH of the solution and shown in Figure 2 [17]. The value of pH_{PZC} for *Retama raetam* was determined as pH 6.

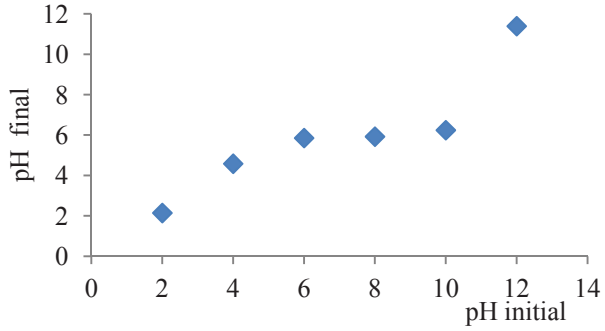

Figure 2. Point of zero charge (pH_{PZC}) of the *Retama raetam* used for the adsorption experiments.

Adsorption isotherms are important for the description of how adsorbates interact with an adsorbent being also critical in optimizing the use of adsorbent. Thus, the correlation of equilibrium data using either a theoretical or empirical equation is essential for interpretation of the adsorption data and prediction, as well. Several mathematical models can be used to describe experimental data of adsorption isotherms. Two famous isotherm equations, the Langmuir and Freundlich, were employed for further interpretation of the obtained adsorption data.

Adsorption kinetics of methylene blue onto *Retama raetam* was studied in a batch system. The effects of pH and equilibrium time were examined. The adsorption parameters were optimized. In each experiment pre weighed amount of adsorbent (0.04 g) was added to 200 mL of dye solution (20 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. The methylene blue concentration in solution was determined at λ_{max} = 665 nm by using UV-1700 PHARMA SPEC SHIMADZU spectrophotometer. The adsorbed amount of methylene blue per mass unit of adsorbent at time t, q (mg/g), (Eq.(1)) and the dye removal efficiency (R, %) (Eq.(2)) were calculated as:

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

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

where C_0 is the initial concentration of methylene blue (mg/L), C is the dye concentration at time t, V is the solution volume (L) and M is the adsorbent mass (g) [18].

The effect of pH was evaluated by mixing 0.2 g of adsorbent with 1 L of methylene blue simulated aqueous solution of 20 mg/L. The pH value of solution was varied from 2 to 13, by adding 0.1M NaOH or 0.1M HCl solutions. The suspension was shaken for 24h at 25°C.

Kinetic experiments were performed by mixing 200 mL of dye solution (20 mg/L) with 0.04 g of adsorbent for different time (5, 10, 30, 60, 90, 120, 150, and 180 min). The initial pH for each dye solution was set at 8. Methylene blue concentration in the supernatants was determined and the adsorbed amount of methylene blue was calculated.

Results and discussion

For studying the effect of every parameter, it is necessary to fix the values of other ones. The elimination of pollutant from simulated aqueous solution by adsorption is extremely influenced by the medium of solution, which affects the nature of the adsorbent surface charge, the ionization extent, the aqueous adsorbate species speciation and the adsorption rate. The adsorptive process through functional groups dissociation on the adsorbate and adsorbent were affected by a pH change [19]. The adsorption of methylene blue augments with increasing the pH of the solution. According to the data presented in Figure 3, the best value of adsorption capacity, q_e = 9.938 mg/g, was recorded at pH 8. From this study, it is obvious that in the basic medium, the negatively charged species tend to dominate leading to a more negatively charged surface. In this case, the adsorbent surface is negatively charged. The methylene blue adsorption increases due to the enhancement of electrostatic attractions between the negative charge of *Retama raetam* particles and the positive charge of methylene blue species.

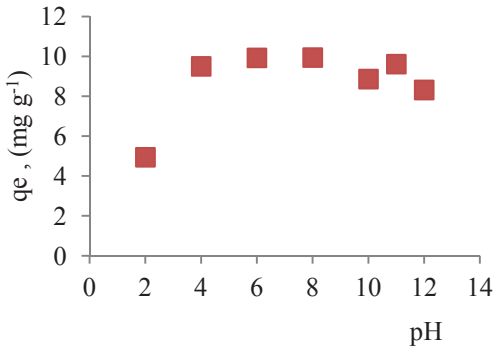

Figure 3. Effect of the initial pH of solution on equilibrium adsorption capacity of *Retama raetam*.

The experimental data for methylene blue adsorption on *Retama raetam* were analyzed with the Freundlich and Langmuir equations. Equations of these models [20] 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 Freundlich constants related to adsorption intensity of the adsorbent and adsorption. A non-linear and linear fitting procedure using Excel and Origin software were used, respectively. The constants of all models were given in Table 2.

Table 1

Adsorption isotherms models and their linear and non linear forms [20].

Applied model	*Non linear form*	*Linear form*
Langmuir	$\frac{q}{q_m} = \frac{K_L C}{1 + K_L C}$	$\frac{C}{q} = \frac{C}{q_m} + \frac{1}{k_L q_m}$
Freundlich	$q = K_F C^{1/n}$	$\ln(q) = \ln(k_F) + n \ln(C)$

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: pentachlorophenol/(M)Al-MCM-41 [21], and toluene/activated carbon [22].

The optimization procedure 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 error deviation between experimental and predicted data. The mathematical equations of these error functions were illustrated in Table 3.

Table 2

Constants for linear and non-linear Langmuir and Freundlich isotherms related to the adsorption of methylene blue onto *Retama raetam*.

Model	*Linear method*	*Non-linear method*
Langmuir model		
q_m	- 142.857 < 0	$3.986 \cdot 10^{+6}$
K_1	- 0.350 < 0	$4.811 \cdot 10^{-44}$
R^2	0.609	0.799
Freundlich model		
k_F	115.353	96.837
n	1.806	0.483
R^2	0.989	0.967

Table 3

Mathematical equations of error functions.

Error functions	*Equations*	*Reference*
ARED	$ARED = \frac{100}{n}\sum_{i=1}^{n}\left\lvert\frac{q_{\exp}-q_{calc}}{q_{\exp}}\right\rvert_i$	[23]
ARE	$ARE = \frac{\sum\left\lvert(q_{calc}-q_{\exp})/q_{\exp}\right\rvert}{n}$	[24]
SAE = EABS	$SAE = EABS = \sum_{i=1}^{n}\left\lvert q_{\exp}-q_{calc}\right\rvert$	[25]
ARS	$ARS = \sqrt{\frac{\sum\left[\left(q_{\exp}-q_{calc}\right)/q_{\exp}\right]^2}{(n-1)}}$	[26]
MPSD	$MPSD = 100\sqrt{\frac{\sum\frac{\left[\left(q_{\exp}-q_{calc}\right)\right]^2}{q_{\exp}}}{n-p}}$	[27]
Δq(%)=100*ARS	$\Delta q(\%) = 100\sqrt{\frac{\sum\left[\left(q_{\exp}-q_{calc}\right)/q_{\exp}\right]^2}{(n-1)}}$	[28]
SSE	$SSE = \sum\left(q_{calc}-q_{\exp}\right)^2$	[29]
MPSED	$MPSED = \sqrt{\frac{\sum\left[\left(q_{\exp}-q_{calc}\right)/q_{\exp}\right]^2}{(n-p)}}$	[20]
HYBRID	$HYBRID = \frac{1}{(n-P)}\sum_{i=1}^{n}\left\lvert\frac{q_{\exp}-q_{calc}}{q_{\exp}}\right\rvert_i$	[30]

where n is the number of experimental data points, q_{calc} is the predicted (calculated) quantity of methylene blue adsorbed onto *Retama raetam*, q_{exp} is the experimental data, p is the number of parameters in each kinetic model, *ARED* is the average relative error deviation (dimensionless parameter), *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), *MPSD* Marquardt's is the percent standard deviation (dimensionless parameter), *MPSED* Marquardt's is the percent standard deviation (dimensionless parameter), *SAE=EABS* is the sum of absolute error (mg/g), *SSE* is the sum of the squares of the errors $(mg/g)^2$, and $\Delta q(\%)$ is the normalized standard deviation (mg/g). The constants of all error analysis are represented in Table 4.

Table 4

Error deviation data related to the adsorption of methylene blue onto *Retama raetam* employing the most commonly used functions.

Error functions	*ARED*	*SAE = EABS*	*MPSED*	*SSE*	*HYBRID*	*ARE*	*ARS*	*Δq(%)= 100*ARS*	*MPSD*
Linear Freundlich model	113.162	1064.355	1.966	313447.05	1.383	1.131	1.865	186.493	1051.57
Non Linear Freundlich model	22.899	277.32	0.285	13850.819	0.28	0.229	0.27	27.028	254.777

The data of adsorption isotherm are essentially required for designing the adsorption systems. In order to optimize the design of a specific sorbate/sorbent system for removal of methylene blue from aqueous solution, it is important to establish the most appropriate correlation for the experimental kinetic data. Applicability of some statistical tools to predict the optimum adsorption isotherms of methylene blue onto *Retama raetam* after linear regression analysis showed that the highest R^2 value and the lowest *ARED, ARE, SAE, ARS, MPSD, Δq, SSE, MSPED* and *HYBRID* values can be suitable and meaningful tools to predict the best-fitting equation models.

The best fitting is determined based on the use of these functions for calculation of the error deviation between experimental and predicted equilibrium adsorption isotherm data, after linear analysis. Hence, according to Table 4, it seems that the linear Freundlich model was the most suitable mode to describe satisfactorily the studied adsorption phenomenon. Therefore, based on the mentioned results, the best useful error estimation statistical tools point out the non linear Freundlich model, followed by linear Freundlich model, as the best-fitting models.

In order to better understand the effect of temperature on the adsorption of methylene blue onto *Retama raetam*, the free energy change (ΔG°, J mol^{-1}), enthalpy change (ΔH°, J mol^{-1}) and entropy change (ΔS°, J K^{-1} mol^{-1}) were determined (such parameters reflect the feasibility and spontaneous nature of the process) using Eqs.(3)-(5).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{3}$$

$$\Delta G^\circ = -RTLn\left(K_c\right) \tag{4}$$

The combination of Eqs.(3) and (4) gives Eq.(5):

$$Ln(K_c) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}\frac{1}{T} \tag{5}$$

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (Kelvin) [31]. Experiments were performed using 20 mg/L dye solutions with 0.2 g of *Retama raetam* for 24 h at various temperatures. The apparent equilibrium constant K_c of the adsorption is defined as Eq.(6) [20]:

$$K_c = \frac{(C_o - C_e)}{C_e}\frac{V}{M} = \frac{q_e}{C_e} \tag{6}$$

The enthalpy and entropy can be obtained from the slope and intercept of the linear plot of lnK_c versus $1/T$. The obtained thermodynamic parameters are given in Table 5.

Table 5

Calculated thermodynamic parameters for adsorption of methylene blue onto *Retama raetam*.

	Temperature (K)					
	293	*303*	*323*	*333*	*343*	*363*
K_c (L/mol)	$5.174\cdot10^5$	$3.204\cdot10^5$	$1.150\cdot10^5$	$0.729\cdot10^5$	$0.435\cdot10^5$	$0.134\cdot10^5$
ΔG° (kJ mol^{-1})	-26.744	-26.117	-24.863	-24.237	-23.610	-22.356
ΔH° (kJ mol^{-1})	$-4.511\cdot10^5$					
ΔS° (J K^{-1} mol^{-1})	-62.687					
R^2	0.989					

A negative enthalpy value of $-4.511 \cdot 10^5$ kJ/mol indicates that adsorption was exothermic. A negative entropy value of -62.687 J/mol and a negatively decreasing Gibbs free energy indicates the increase in the randomness in the solid–liquid interface and adsorption spontaneity [32].

Figure 4 illustrates the effect of contact time on decolorization (dye adsorption) with *Retama raetam*. The plot (simulated aqueous solution) can be divided in three zones: (i) 0-30 min, which indicate the fast adsorption of methylene blue, suggesting a rapid external diffusion and surface adsorption; (ii) 30-60 min, show a gradual equilibrium, and (iii) 60-180 min, indicate the plateau of the equilibrium state. The adsorption was rapid at the initial stage of the contact, but it gradually slowed down until the equilibrium. The fast adsorption at the initial stage can be attributed to the fact that a large number of surface sites are available for adsorption. After a lapse of time, the remaining surface sites are difficult to be occupied.

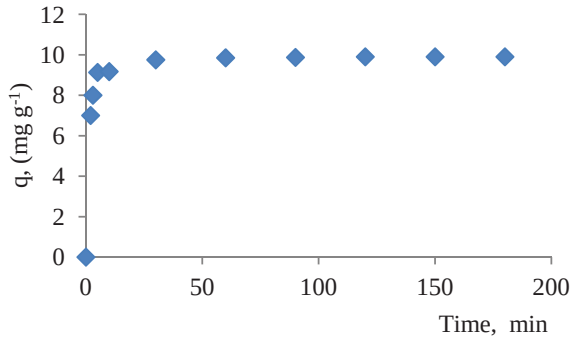

Figure 4. Adsorption kinetics of methylene blue on *Retama raetam*.

Adsorption is a complex process that is influenced by several parameters related to adsorbent and to the physicochemical conditions, under which the process is carried out [33]. For understanding the mechanism of the adsorption process, the following equations: pseudo-first order (Lagergren Model) [2], pseudo-second order [34], Esquivel [35], pseudo-third order [36], and Elovich [37] were selected to fit the experimental kinetic data. Equations of these models are presented in Table 6.

Table 6

Adsorption kinetics models and their linear and non linear forms.

Applied model	*Non Linear form*	*Linear form*	*Reference*
Pseudo-first order			
Pseudo-first order (type 1)	$q = q_e(1-e^{-k_1 t})$	$\log(q_e - q) - \log(q_e) = -\frac{k_1 t}{2.303}$	[38]
Pseudo-second order			
Pseudo-second order (type 9)	$q = q_e\left[1-\frac{1}{1+k_2 t}\right]$	$\frac{q_e}{q_e - q} - 1 = k_2 t$	[39]
Pseudo-second order (type 10)		$\frac{\theta}{1-\theta} = k_2 t$	[39]
Esquivel model (type 1)	$q = q_e\left(\frac{t}{t+K_E}\right)$	$\frac{1}{q} = \left(\frac{K_E}{q_e}\right)\frac{1}{t} + \frac{1}{q_e}$	[35]
Esquivel model (type 2)	$q = q_e\left(\frac{t}{t+K_E}\right)$	$(\frac{1}{q} - \frac{1}{q_e})q_e = K_E\frac{1}{t}$	[35]
Elovich (type1)	$\frac{dq}{dt} = k_4 \exp(-k_5 q)$	$q = k_5 \ln(k_5 k_4) + k_5 \ln(t)$	[37]
Elovich (Roginsky-Zeldovich) (type 2)	$\frac{dq}{dt} = k_7 \exp(k_6 q)$	$q = (1/k_6)\ln(k_6 k_7) + (1/k_6)\ln(t)$	[40]

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 is extent of surface coverage and activation energy of the process (g/mg), k_7 is Elovich rate constant (mg/(g min)), q_e is amount of adsorption at equilibrium (mg/g), and θ is dimensionless parameter ($=q/q_e$). For the non-linear and linear fitting procedures Excel and Origin software were used, respectively. The constants of all models were given in Table 7.

Table 7

Kinetics constants related to the adsorption of methylene blue onto *Retama raetam*.

Model	*Linear Method*	*Non-linear Method*
Pseudo-first order (type 1)		**Non-linear Pseudo-first order (type 1)**
q_e	9.900	9.782
K_1	0.403	0.517
R^2	0.854	0.996
Equation	log(qe-q) - log(qe)= -0.175*t	q=9.782*(1-exp(-0.517*t))
Pseudo-second order (type 9)		
q_e	9.932	9.908
K_2	1.926	1.97
R^2	0.946	0.999
Equation	(qe/(qe-q))-1 = 1.926*t	q=9.908*(1-(1/(1+1.97*t)))
Pseudo-second order (type 10)		
q_e	9.933	
K_2	1.926	
R^2	0.946	
Equation	(θ/(1-θ)) = 1.926*t	
Esquivel Model (type 1)		
q_e	9.901	9.908
K_E	0.485	0.507
R^2	0.874	0.999
Equation	1/q = 0.049*(1/t)+0.101	q=9.908*(t/(t+0.507))
Esquivel Model (type 2)		
q_e	9.900	
K_E	0.492	
R^2	0.874	
Equation	(((1/q)-(1/q))*qe)= 0.492*(1/t)	
Elovich (type 1)		
K_4	$2.913\ 10^{+16}$	
K_5	0.240	
R^2	0.899	
Equation	q = 0.240*ln(t) + 8.756	
Elovich (type 2)		
K_4	$1.678\ 10^{+5}$	
K_5	4.167	
R^2	0.899	
Equation	q = 0.240*ln(t) + 8.756	

Table 7 shows that q_e, k_2 and R^2 values obtained from the two linear forms of pseudo-second-order expressions were the same. The value of q_e and k_2 were calculated to be, respectively, 9.932 mg g^{-1} and 1.926 g mg^{-1} min^{-1} for linear pseudo-second-order and 9.908 mg g^{-1} and 1.97 g mg^{-1} min^{-1} for non linear pseudo-second order biosorption. The constants of all error analysis are represented in Table 8.

Adsorption kinetic data are the basic requirements for the design of adsorption systems. In order to optimize the design of a specific sorbate/sorbent system to remove methylene blue 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 kinetics of methylene blue onto *Retama raetam* after linear regression analysis showed that the highest R^2 value and the lowest *ARED, ARE, SAE, ARS, MPSD, Δq, SSE, 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. Hence, according to Table 4, it seems that the linear pseudo- second order type 9 and type 10 models were the most suitable models to describe satisfactorily the studied adsorption phenomenon. Therefore, based on these mentioned results, the best useful error estimation statistical tools should point out the linear pseudo- second order type 9 followed by linear pseudo- second order type 10 as the best-fitting models.

In the most studied adsorption systems, the pseudo-first-order model does not fit well over the entire adsorption period and is generally applicable over the first 20-30 min of the sorption process. The pseudo-second-order model is based on the biosorption capacity of the solid phase and it generally predicts the "chemisorption" behaviour over the whole time of adsorption [20].

Obtained results, presented in Table 4 show that the pseudo-first-order model data do not fall on straight lines indicating that this model was less appropriate. In contrast, the pseudo second order kinetics have shown very low *ARED, ARE, SAE, ARS, MPSD, Δq, SSE, MSPED,* and *HYBRID* and high R^2 values for type 9, 10 linear pseudo-second-order, and non linear pseudo-second-order expressions suggest that it is appropriate to use the pseudo-second-order model, suggesting that it is applicable to the adsorption kinetics. This suggests that, the biosorption of methylene blue onto *Retama raetam* is a chemisorption process involving exchange or sharing of electrons mainly between the dye ions and the sorbent functional groups [20]. Using linear method it was found that a theoretical pseudo-second order model represents well the experimental kinetic data of adsorption of methylene blue onto *Retama raetam* based on a Type 9 and 10 pseudo-second-order kinetic expression.

Studies regarding the use of *Retama raetam* as biosorbent are in progress. More technical and experimental optimisations and treatments should be realised to improve the adsorption capacity of *Retama raetam*. For example, use of more effective pre-treatment methods and reduction in particle size (larger specific adsorption area, m^2/g) may further improve the rate and the extent of adsorption of methylene blue onto *Retama raetam*. Besides, the methylene blue -loaded biomass itself has to be treated, in order to avoid a pollution transfer. Indeed, one of the more common questions aroused by biosorption processes involves the fate of the biosorbent after the process. Care must be taken that solving one problem, not to create another. The sorbed methylene blue can be recovered by extraction from the biomass in order to be concentrated and then stored, reused, or eliminated. Also, the decontamination of the methylene blue -loaded biomass by biodegradation is a very interesting approach.

Table 8

Error deviation data related to the methylene blue adsorption onto *Retama raetam* employing most commonly used functions.

Error functions	*ARED*	*SAE = EABS*	*MPSED*	*SSE*	*HYBRID*	*ARE*	*ARS*	*Δq(%)= 100*ARS*	*MPSD*
Linear Pseudo-first order type 1	1.801	1.334	0.035	0.635	0.024	0.018	0.033	3.283	10.741
Non Linear Pseudo-first order type 1	1.561	1.184	0.027	0.372	0.021	0.015	0.025	2.488	8.179
Linear pseudo- second order type 9	**0.599**	**0.442**	**0.013**	**0.092**	**0.008**	**0.006**	**0.012**	**1.251**	**4.090**
Linear pseudo- second order type 10	**0.599**	**0.442**	**0.013**	**0.092**	**0.008**	**0.006**	**0.012**	**1.251**	**4.090**
Non linear pseudo- second order type 1	0.701	0.523	0.013	0.088	0.009	0.007	0.012	1.225	4.012
Linear Esquivel type 1	0.708	0.530	0.013	0.090	0.009	0.007	0.012	1.232	4.036
Linear Esquivel type 2	0.729	0.546	0.013	0.089	0.009	0.007	0.012	1.227	4.022
Non linear Esquivel	0.700	0.522	0.013	0.088	0.009	0.007	0.012	1.225	4.012
Linear Elovich model type 1	0.827	0.64	0.012	0.078	0.011	0.008	0.011	1.098	3.682
Linear Elovich model type 2	0.827	0.64	0.012	0.078	0.011	0.008	0.011	1.098	3.682

Conclusions

Retama raetam plant was used for the adsorption of methylene blue 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 8 and 120 min of contact time, which lead to 90.38 % methylene blue removal.

Kinetics data correlated well with the pseudo second order kinetic model (type 9 and type 10), whereas equilibrium study was best described by non linear Freundlich isotherm model.

The adsorption kinetics of methylene blue onto *Retama raetam* can be better fitted by the pseudo- second order linear model (type 9 and type 10), as compared to the non-linear pseudo-second-order model, linear pseudo-second-order model, pseudo first order, pseudo third order, and Esquivel models. The entire experimental results showed that *Retama raetam* is suitable adsorbent for the removal of methylene blue.

The thermodynamic parameters such as: Gibbs free energy change $\Delta G°$, standard enthalpy $\Delta H°$, and standard entropy $\Delta S°$ indicated that methylene blue adsorption onto *Retama raetam* was exothermic and spontaneous.

This study identified *Retama raetam* – at its raw state and without any physical or chemical activation – as a suitable low cost adsorbent to be used for removal of methylene blue dye from aqueous solution. The very rapid adsorption and high uptake capacity for methylene blue (62.5 to 91.33 % removal rate in less than 4 minutes) make the *Retama raetam* a quite interesting alternative to more expensive materials such as activated carbons.

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