Moroccan Journal of Chemistry
ISSN: 2351-812X
http://revues.imist.ma/?journal=morjchem&page=login
Mejbar & al. / Mor. J. Chem. 6 N°3 (2019) 436-443

Studies of the adsorption kinetics process for removal of methylene blue dye by residue of grenadine bark extraction

Fatiha Mejbar [1*], Youssef Miyah [1], Aziz El Badraoui [1], Loubna Nahali [1], Assila Ouissal [1], Anis Khalil [1], Farid Zerrouq [1]

[a] QHSE Research Group, Laboratory of Catalysis, Materials and Environment, University of Fez, School of Technology, BP 2427 Fez–Morocco. Email: fatihamejbar2@yahoo.fr, youssef.miyah@gmail.com, zerrouq1959@gmail.com.

Abstract

This study makes it possible to prove that an inexpensive material, namely the residue of grenadine bark extraction (GB), can be used to remove a dye from the textile industry, in particular methylene blue (MB). For this reason, different techniques of characterization of the GB adsorbent have been used such as: scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and the zero charge point. On the other hand, batch studies have been used to evaluate the effect of initial concentration, contact time, adsorbent dose, pH and temperature on the variation in uptake capacity. In this case, the results show that a very fast adsorption kinetics reaching 98% within the first 10 minutes. Additionally, kinetic studies of dye on MB carried out the pseudo-second order at different dye concentration values. Besides, the Langmuir model describes satisfactory adsorption on the GB. Further, thermodynamic studies have indicated that dye adsorption process by grenadine bark (GB) was spontaneous, physisorption and endothermic in naturel

Keywords: *Cationic dye, Isotherm, Kinetic, Thermodynamic, Adsorption*

1. Introduction

In recent years, trash from many industries such as plastics, detergents, paper, painting, especially textiles are heavily laden with dyes that pose a serious global problem of great concern, in addition to toxicological impacts that are dangerous for the environment [1]. In addition, these dyes can be accumulated in aquatic animals and therefore, penetrate the food chain to reach humans [2]. Therefore, the development of a sustainable competitive process of effluent management for the dyeing industry has long been an important task for the protection of the environment [3]. Moreover, Conventional physicochemical processes for the removal of dyes from wastewater include oxidation, photochemical degradation, reverse osmosis, membrane separation, coagulation and adsorption [4-7]. In this respect, it is known that adsorption is the most suitable treatment for the removal of dyestuffs with activated carbon which is the most efficient and widely used adsorbent [8]. However, this adsorbent has a high cost and remains difficult to regenerate. For this reason, the growing demand for efficient and low-cost treatment methods and the significance of adsorption have given rise to low-cost alternative adsorbents namely: walnut bark, corn support, wood, banana and orange peel, cotton, coffee and tea residues, bone meal and fish, eggshells [9-11]. Since most industries require a rapid removal rate to support increased pollutant capacity, the development of these adsorbents for industrial applications have become impossible. Therefore, the need to develop waste as adsorbents that are economical and offer both high removal rates and high adsorption capacities is of paramount importance [12]. The development of simple and effective methods for the removal of industrial dyes has been achieved using natural adsorbent

materials of vegetable origin such as the grenadine bark extract residue. In the present work, we are interested in the study of the adsorption of methylene blue dye on grenadine bark. For this purpose, we carried out a parametric study of the adsorption by studying the effect of several important parameters on the decolorizing power of the material used particularly contact time, adsorbent concentration, pH and temperature. A kinetic study has been accomplished and kinetic models have been applied to the experimental results such as the pseudo-first order, pseudo-second order model. Adsorption isotherms have been executed for the dyes, their modeling was fulfilled by applying known models such as Langmuir and Freundlich. The effect of temperature on the adsorption of the dye has also been studied and the thermodynamic parameters have been determined.

2. Materials and Methods

2.1. Preparation of adsorbent

Grenadine was collected in the Mouzar area, Morocco. These grenadine barks were washed several times with ultrapure water. This latter having been carried out in the soxhlet mounting for both the elimination of the active principle and the obtaining a residue of the bark of grenadine. This residue dried at 90 °C for 24 h. Then were ground using a grinder (IKA M20) and sieved at 80 µm to take out a material called the grenadine bark extract residue (GB).

2.2. Preparation of adsorbate

Methylene blue dye was 99% of purity provided by Ciba Specialty Chemicals Inc. The structure of this dye is illustrated in Fig 1 having a molecular weight of 319,852 g/mol. Besides, stock solution of MB was prepared by dissolving 1 g of accurately weighed dye in 1000 ml of distilled water. In this case, the solution was then diluted to prepare standard solutions of different concentrations to study the effect of initial dye concentration. Further, the dye concentration was measured in the UV spectrophotometer at the wavelength of 664 nm. Furthermore, the initial pH of dye solution was adjusted by using dilute hydrochloric acid (0.5M) or sodium hydroxide (0.5M) solution.

Fig.1. Structure of methylene blue.

2.3. Biosorption experiments

Adsorbent GB was characterized by various analysis methods: scanning electron microscopy SEM (Quanta 200 FEI), Fourier transform infrared spectroscopy FTIR (BRUKER Vertex70) and the zero charge point. At pH>pH_{zpc} the net surface charge is negative while at pH<pH_{zpc} the net surface charge is positive. The adsorption tests were carried out in a batch reactor by stirring the colored synthetic solution of MB in the presence of GB adsorbent at ambient temperature. In this case, homogenization of the mixtures was accomplished by a magnetic stirrer for 120 min. In addition, samples were taken at regular time intervals followed by filtration on 0.45µm diameter (Minisart, sartorium stedim biotech) filter paper to measure absorbance by a UV-visible spectrophotometer (Jasco V530). During the adsorption experiments, the effect of the critical parameters, namely the adsorbent dose GB (0.5-2 $g.L^{-1}$), the pH (4-12), the contact time (0-120 min), the initial concentration of dye is fixed from 10 to 30 $mg.L^{-1}$ and the temperature of the solution (20-60 °C) have been studied in order to optimize all these parameters in order to obtain better adsorption.

The amount of equilibrium adsorption, Qe (mg/g) was calculated using the following formula:

$$Q_e = \frac{C_0 - C_e}{W} V$$

The dye removal percentage can be calculated as follows:

$$\%\ of\ elimination = \frac{C_0 - C_e}{C_0} \times 100$$

Where C_0 and Ce (mg/L) are the liquid concentrations of dye initially and at equilibrium, V is the volume of the solution (L) and W is the mass of dye adsorbent (g).

3. Results and discussion

3.1. Characterization of adsorbents

Our adsorbent (GB) was analyzed by scanning electron microscopy SEM; the use of this technique allows us to visualize the morphology of the surface of the used adsorbent. The images (a) and (b) of Fig.2 show that they have a porous appearance which facilitates the adsorption. We acknowledged that cellulose fibers of many sizes with a high porosity of our adsorbent (GB) could be the reason for the high adsorption capacity, which explains the ease of fixation of the methylene blue dye at the surface of grenadine bark (GB).

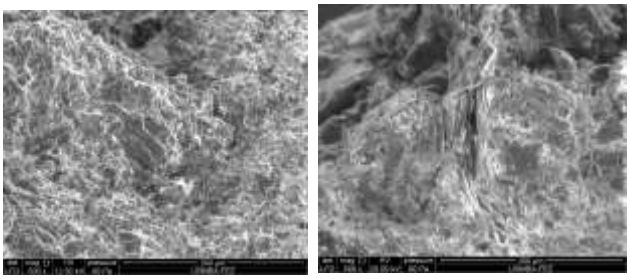

Fig.2. SEM images of grenadine bark.

Fig.3 displays the spectrum of the grenadine bark adsorbent obtained by Fourier Transform Reduced Infra Red (FTIR) spectroscopy. Among these bands are mentioned mainly: the bands of 3424 cm^{-1} and 2924 cm^{-1} correspond to the OH group elongation vibrations of the water of constitution, the bands located at range1650-1800 cm^{-1} due to the C=O bond and the band 1631 cm^{-1} corresponds to the H-OH deformation vibrations due to the molecules of adsorbed water, the bands at range1520-1030cm^{-1} identify with the vibrations of elongation of CO_3, the three bands 815 cm^{-1}, 787 cm^{-1} and 616 cm^{-1} correspond to the valence vibrations of the C─H bond [13-16].

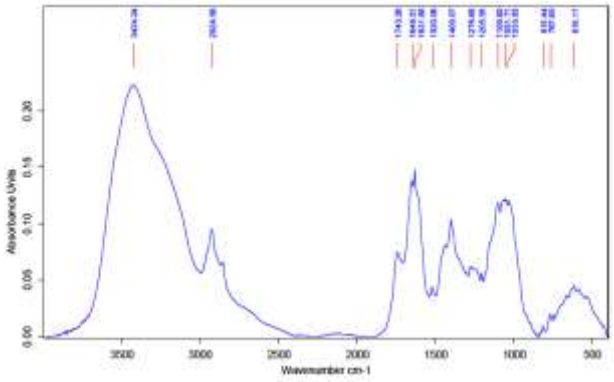

Fig.3.FTIR spectra of grenadine bark

3.2. The effect of different adsorption parameter

3.2.1. The influence of contact time on the adsorption of methylene blue (MB)

The kinetic survey of the adsorption of methylene blue on the GB adsorbent to evaluate the effect of contact time has been performed with BM solutions in the initial concentration range from 25 to 75 mg/L, adsorbent dose 1g/L and at a temperature of 20 °C for duration of 120 min. In this respect, the determination of the contact time corresponding to the adsorption equilibrium enabled the establishment of the adsorption isotherms for GB. The knowledge of this time is essential for the calculation of the maximum adsorption capacity. Thus, the results are presented in Fig.4.

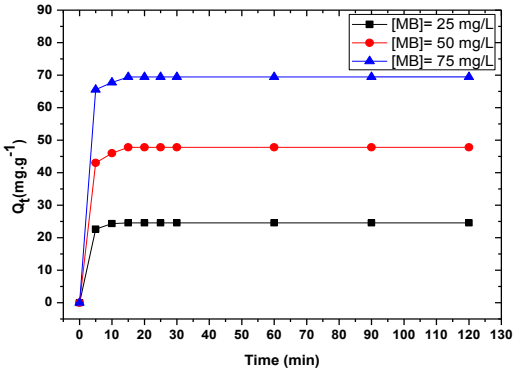

Fig.4: The influence of the contact time on the adsorption kinetics of methylene blue (MB) on GB.

The results obtained exhibit a rapid increase especially in the first 10 minutes and a slight increase after 15 min and then we observe a plateau indicating a saturation of the pores. This explains than the adsorption balance of the dye by grenadine bark (GB) is very fast. It is also noticed that the initial concentration of BM has no significant effect on the equilibrium time; moreover it has an important effect on the adsorption capacity of the support. Thus, the amount adsorbed increases with the increase in the initial concentration of methylene blue (Table 1). This can be illustrated by the fact that the presence of a large number of molecules that will diffuse to the sites of the surface of the adsorbent (GB).

Table 1: adsorbed amounts by grenadine bark (GB) at different initial concentrations of MB.

[Methylene blue]$_0$ (mg.L^{-1})	25	50	75
Q_{ads} (mg.g^{-1}) GB	24.55	47.80	69.46

3.2.2. Influence of the adsorbent dose on the adsorption of methylene blue (BM)

The study of the influence of the grenadine bark mass on the adsorption capacity of the methylene blue (MB) dye led us to vary the initial adsorbent quantity while maintaining the initial concentration adsorbate (MB) in solution. The initial MB concentration in this project was 75 mg/L and the GB dose ranged from 0.5 to 2.0 g/L. Hence, the outcomes of Fig. 5 display that the number of adsorption sites increases if the mass of the solid in the solution is large.

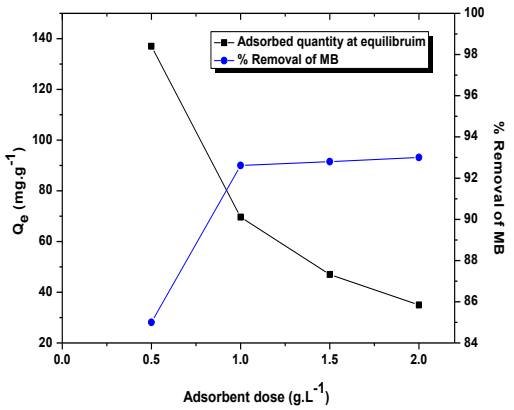

Fig.5. The evolution of the quantities of methylene blue adsorbed as a function of the adsorbent dose (GB).

3.2.3. The effect of pH on the adsorption of methylene blue (BM)

The pH is among the main variables that affects the adsorption process, influencing not only the surface charge of the adsorbent, the degree of ionization of the material present in the solution and the dissociation of the functional groups on the active sites of the adsorbent, but also the chemical properties of the solution of the dyes [17]. In this respect, the behavior of methylene blue dye adsorption on grenadine bark has been studied over a wide range of pH (4-12), the zero charge point (NCP) of grenadine bark (GB) is of the order of 7.8. The initial MB concentration in this study was 75 mg/L. The Fig. 6 shows that the amount of methylene blue adsorbed on the GB increases slightly with increasing pH. Additionally, it can be noticed that the increase in the adsorbed quantity of methylene blue (MB) with the increase of the pH can be explained by the fact that the addition of the H^+ cations to lower the pH leads to the neutralization of the negative charge on the surface of the Grenadine bark (GB), which unfavorable the adsorption of cationic methylene blue (BM) in a highly acidic medium. On the other hand, when the pH increases there is a decrease in H^+ cations, therefore the charge of the grenadine bark (GB) is clearly negative, which favors the adsorption of methylene blue (Fig. 6).

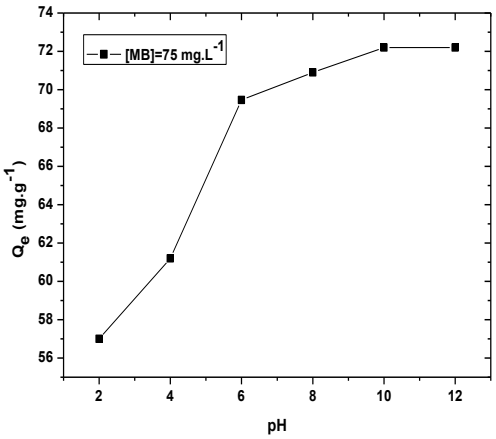

Fig.6. The influence of pH on the adsorption quantity of methylene blue (MB).

3.2.4. The influence of temperature on the adsorption of methylene blue (MB).

The adsorbed quantity of methylene blue Qe (mg.g^{-1}) by grenadine bark (GB) increases with temperature in the studied range and the adsorption time to reach equilibrium decreases with the increase of the temperature meaning that the adsorption process is endothermic (Fig.7). Miyah et al., mentioned that the number of sites for the dye molecules on the surface of the adsorbent can be increased by increasing the temperature [12]. This clarifies the reason why temperature is a highly significant parameter in the adsorption process.

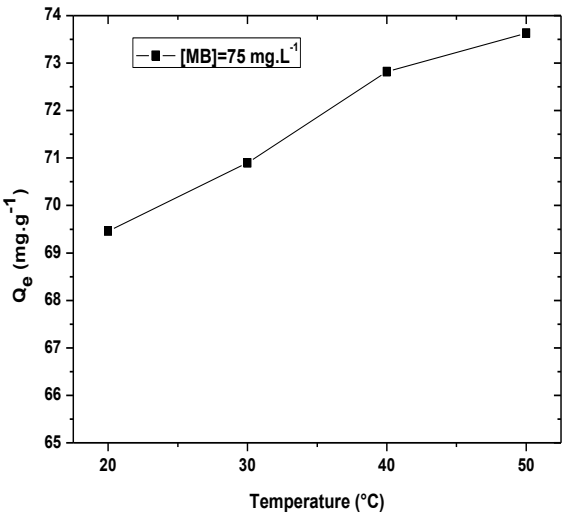

Fig.7: The evolution of the amount of methylene blue adsorbed by GB as a function of temperature.

3.3. The adsorption kinetics of methylene blue (MB) on grenadine bark

This study aims to determine the order of kinetics and models that describe well the adsorption isotherms of MB on GB and to verify if the methylene blue well adsorbed. In this case, it allowed us to determine the time required to reach the equilibrium adsorption state and to define the adsorption equilibrium constants of methylene blue. From the kinetic point of view, the curves show that adsorption occurs in two stages: fast reaction and slow reaction. During the first 10 minutes, more than 90 % of BM is adsorbed on GB and after 10 minutes, the speed becomes slightly slower until 15 minutes which corresponds to equilibrium time. Similarly, the order of the reaction is a very important parameter in the determination of the reaction mechanisms. Hence, the most cited adsorption orders for biosorption in the literature are: the pseudo-first order model and the pseudo-second order model.

3.3.1. Pseudo-first order model (Equation of Lagergren)

The first-order kinetics model is more suitable for lower concentrations of solute. It has been assumed that in this model the adsorption speed at time t is proportional to differentiate between the amount adsorbed at the equilibrium qe and the quantity qt adsorbed at that instant and thus the adsorption is reversible. This model is presented by the Lagergren [18] relationship based on both adsorbed quantity and on the first established speed equation to describe the adsorption kinetics in a liquid/solid system [19]. The law of speed is written:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (3)$$

The integration of equation (3) gives:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (4)$$

Where

q_t: amount of adsorbate adsorbed at time t ($mg.g^{-1}$); qe: amount adsorbed at equilibrium ($mg.g^{-1}$); K_1: adsorption speed constant of the pseudo-first-order model (min^{-1}); t: the time (min).

If Lagergren's relation is checked, carrying ln (q_e-q_t) as a function of time, we must get a straight line of slope -K_{ads}.

Si la relation de Lagergren est vérifiée, en portant ln (q_e-q_t) en fonction du temps, nous devons obtenir une droite de pente –K_{ads}. The results obtained display that the Lagergren equation is not applicable in the case of the methylene blue (MB) elimination by grenadine bark (GB).

3.3.2. Pseudo-second order model

The pseudo-second order equation is often used successfully to describe the kinetics of the dye binding reaction on the adsorbent. The pseudo-second-order model can be represented in the following equation [20-21]:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (5)$$

The integration of equation (5) gives:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where:

K_2: adsorption speed constant of the pseudo-second order model ($g.mg^{-1}.min^{-1}$).

If this equation is true, by plotting t/q_t as a function of t, we must have a straight line of slope $1/q_e$ and ordinate at the origin equal to $1/(K_2\, q_e^2)$.

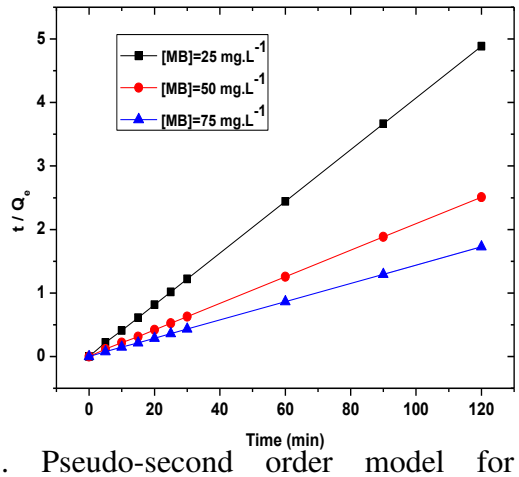

Fig.3. Pseudo-second order model for the adsorption of methylene blue (MB) on grenadine bark (GB).

The corresponding parameters have been grouped in Table 2 which also presents the correlation coefficients. In this respect, these calculated coefficients are closer to unity for the pseudo-second-order kinetic model. Thus, this indicates that the latter model well describes the experimental results of adsorption of MB on the GB adsorbent.

Table 2: Parameters characterizing the adsorption kinetics of MB on the adsorbent GB.

C_o (MB) (mg.L^{-1})	Q_{exp} (mg.g^{-1})	Kinetic of second ordre		
		K_2 (g.mg^{-1}.min^{-1})	Q_{cal} (mg.g^{-1})	R^2
[MB]=25 mg.L^{-1}	24.55	0,552	24.570	0,999
[MB]=50 mg.L^{-1}	47.80	0,110	47.619	0,999
[MB]=75 mg.L^{-1}	69.46	0,207	69.440	0,999

3.4. The thermodynamic treatment of adsorption data

Various thermodynamic parameters have also been calculated for both adsorbents using following relations [22]:

$$K_d = \frac{Q_e}{C_e} = e^{\left(\frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}\right)} \quad (7)$$

$$lnK_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

Where R: constant of perfect gas (R = 8,314 J.mol^{-1}.K^{-1}), and T: absolute temperature of solution (K); K_d: distribution coefficient; Qe: amount adsorbed on the solid at equilibrium (mg.g^{-1}), and Ce: concentration at equilibrium (mg.L^{-1}).

The values of ΔH° and ΔS° were calculated from both the slope and the interception of the lnK_d while plot as a function of 1/T. ΔG ° can be calculated using the relationship below:

$$\Delta G^0 = -RT \ln K_d \quad (9)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

The calculated thermodynamic parameters values are tabulated in Table 4. The ΔG° value is negative for all systems, indicates that the adsorption process is spontaneous [4]. Besides, the increase in temperature leads to higher negative ΔG° value. Hence the adsorption process was favorable at a higher temperature. On the other hand, the positive value of ΔH° for all systems points out that the adsorption process is endothermic. Meanwhile, the positive value of ΔS° for all system reflects the increased randomness at the solid-solution interface during adsorption.

Table 3: Thermodynamic parameters for the uptake of Methylene blue

	ΔH° (kJ.mol^{-1})	ΔS° (J.mol^{-1}.K^{-1})	ΔG° (kJ.mol^{-1})			
			20°C	30°C	40°C	50°C
GB	1.908	29.539	-6.747	-7.042	-7.337	-7.633

3.5. Adsorption isotherms

The modeling of the adsorption equilibrium consists, represented by mathematical laws, the equilibrium relation between the amount of pollutant in the liquid phase (Ce) and that adsorbed on the material (Qe). In this study, the adsorption equilibrium is analyzed by applying both the Langmuir and Freundlich models, which are commonly used by researchers to study the adsorption isotherms of adsorbent / adsorbate systems [23-24]. Langmuir isotherm assumes

monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption [25]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \qquad (11)$$

Where, qe is the amount of adsorption at equilibrium (mg/g), Ce is the dye concentration at equilibrium K_L is the Langmuir adsorption constant ($L.mg^{-1}$) and q_m is the theoretical maximum adsorption capacity ($mg.g^{-1}$).

If the Langmuir equation is satisfied, we must get by placing our experimental points in coordinates 1/Qe = f (1/Ce) or Ce/Qe = f (Ce), a straight line whose slope and ordinate at origin allow us to determine Qmax and K_L.

The essential characteristic of the Langmuir isotherm can be expressed by Hall's a dimensional parameter, called the RL equilibrium parameter, which has the following form:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (12)$$

The value of factor R_L indicates either the adsorption isotherm to be unfavorable (R_L >1), favorable (0< R_L <1), linear (R_L = 1) or irreversible (R_L = 0). The Freundlich adsorption isotherm assesses that adsorption occurs on a heterogeneous surface by a multilayer adsorption mechanism and hence the amount adsorbed increases with concentration according to the following equation [26]:

$$lnQ_e = lnK_f + \frac{1}{n_f} lnC_e \quad (13)$$

Where: Q_e: the amount of methylene blue adsorbed per amount of grenadine bark mass in ($mg.g^{-1}$); K_f: a parameter essentially related to the maximum adsorption capacity in $mg.g^{-1}$ $(mg.L^{-1})^n$; Ce: the concentration of the adsorbate in the solution at equilibrium in $mg.L^{-1}$; n_f: a parameter related to the coefficients of variation of the interactions energies with the recovery rate.

The outcomes obtained exhibit that the correlation coefficient (R^2 = 0.995) of the Langmuir model is very close to unity (Table 4). The use of the linear regression line enabled us to determine the maximum adsorption capacity Q_{max} and the Langmuir adsorption equilibrium constant. The value of 1/n gives an indication of the validity of adsorption of the adsorbent-adsorbate system. A value of $1/n_f$ between 0 and 1 indicates favorable adsorption [27]. The calculated numerical values of K_F and $1/n_f$, respectively, from the intersection with the intercept and the slope of the isothermal line, are shown in Table 4.

The correlation coefficient of Freundlich (R^2 = 0.932) is lower than that of the Langmuir model (R^2=0.995). This denotes that the adsorption of the MB dye on grenadine bark follows the Langmuir model as well as Freundlich one.

Table 4: adsorption parameters of the MB dye on the grenadine bark according to the Langmuir and Freundlich models.

	Langmuir				Freundlich		
	Q_{max} ($mg.g^{-1}$)	K_L ($L.mg^{-1}$)	R_L($L.mg^{-1}$)	R^2	K_f ($mg.g^{-1}$)	n_f	R^2
GB	66.66	0.937	0.014	0.995	32.492	2.044	0.993

The values of the calculated Hall parameters are summarized in Table 4. The results obtained show that the adsorption isotherms of BM on GB are favorable.

Conclusion

The present project demonstrates that the aqueous solution of the Methylene blue dye could be removed by the batch technique which has been used under various environmentally friendly conditions to produce quantitative adsorption using the GB adsorbent. The experimental data is more suited to the Langmuir isotherm equation, showing that the adsorption of MB occurred on the surface of grenadine bark through monolayer adsorption. In addition, kinetic studies proved that the adsorption process follows the pseudo-second-order reaction model. Furthermore, thermodynamic studies indicated that the dye adsorption onto GB was a spontaneous (the negative ΔG°), endothermic and physical reaction (the positive ΔH° and ΔS°).

Reference

1. Awais K., Mazhar H. P., Muhammad M., Max W., *Journal of Cleaner Production,* 87 (15) (2015) 50-57.
2. Hang X., Tao Z., Chun-H., Meng Y., *Journal of Cleaner Production,* 165(1) (2017) 1499-1507.
3. Priscila M. D., Maria E. S. S., Luiz A. B. M., Marli F. F., Regina T. R. M., *Brazilian Journal of Microbiology.,* 48 (1) (2017) 25-31.
4. Miyah Y., Lahrichi A., Idrissi M., Boujraf S., Taouda H., Zerrouq F., *Journal of the Association of Arab Universities for Basic and Applied Sciences,* 23 (2017) 20–28.
5. Idrissi M., Miyah Y., Chaouch M., El Ouali Lalami A., Lairini S., Nenov V., Zerrouq F., *Journal of Materials and Environmental Science*, 5 (S1) (2014) 2309–2313.
6. Ruihua L., Baoyu G., Kangying G., Qinyan Y., Huaili Z., Yan W., *Bioresource Technology,* 240 (2017) 59-67.
7. Yu-Jun T., Li-Juan S., Bing-Tian L., Xue-Hao Z., Tong Y., Nozomu I., Kazuki I., Hong-Ying H., *Desalination,* 419 (1) (2017) 1-7.
8. Mridusmita G., Prodeep P., *Journal of Environmental Chemical Engineering,* 5 (4) (2017) 3508-3517.
9. Miyah Y., Idrissi M., Zerrouq F., *Journal of Materials and Environmental Science,* 6 (3) (2015) 699–712.
10. Gupta V.K. and Suhas, *Journal of Environmental Management,* 90 (2009) 2313–2342.
11. Miyah Y., Lahrichi A., Idrissi M., Anis Kh., Kachkoul R., Idrissi N., Lairini S., Nenov V., Zerrouq F., *Journal of Materials and Environmental Science,* 8 (10) (2017) 3570-3582.
12. Miyah Y., Lahrichi A., Idrissi M., *Journal of Materials and Environmental Science***,** 7 (1) (2016) 96–104.
13. Ferrero F., *J. Hazard. Mater*, 142 (2007) 144–152.
14. Çelekli A., Birecikligil S.S., Geyik F., Bozkurt H., *Bioresource Technology*, 103 (2012) 64–70.
15. Dahri M.K., Kooh M.R.R., BL Lim L.., *Journal of Environmental Chemical Engineering*, 2 (2014) 1434–1444.
16. Yang J., Qiu K.., *Chem. Eng. J.,* 165 (2010) 209–217.
17. Hamdaoui O., *J. Hazard. Mater***,** 135 (2006) 264–273.
18. Lagergren S., *Kungliga Svenska Vetenskapsakademiens Handlingar* 24 (1898) 1–39.
19. Jean-Pierre S., *Chemical Engineering Journal***,** 300 (2016) 254–263.
20. Shahwan T., *Journal of Environmental Chemical Engineering***,** 2 (2014) 1001–1006.
21. Weber W.J., Morris J.C., *Journal of the Sanitary Engineering Division,* (SA2) 89 (1963) 3–60.
22. Min L.U., Zhang Y.M., Guan X.H., Xu X.H., Gao T.T., *Transactions of Nonferrous Metals Society of China.* 24 (2014) 1912−1917.
23. Jingwen S., Kai M., Tifeng J., Ruirui X., Lexin Z., Jingxin Z., Qiuming P., *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 529 (20) (2017) 793-800.
24. Chunying W., Laurie B., Zigong N., Yuping H., Sabine S., José-Miguel S. P., Kanta K., Ryusuke H., *Agricultural Water Management,* 180 (B31) (2017) 205-211
25. Langmuir I., *Journal of the American Chemical Society,* 38 (1916) 2221–2295.
26. Freundlich H.M.F., *Zeitschrift für Physikalische Chemie (Leipzig),* 57A (1906) 385–470.
27. Frederick J., Warren Peter J., Butterworth Peter R. E., *Biochimica et Biophysica Acta (BBA)-General Subjects,* 1830 (4) (2013) 3095-3101.