J. Mater. Environ. Sci. 7 (1) (2016) 96-104
ISSN: 2028-2508
CODEN: JMESCN

Removal of cationic dye –Methylene bleu– from aqueous solution by adsorption onto corn cob powder calcined.

Y. Miyah[a]*, A. Lahrichi[b], M. Idrissi[a]

[a] *Lab of Catalysis Materials and Environment, QHSE-RG, ESTF, University Sidi Mohammed Ben Abdellah Fez Morocco*
[b] *Lab. of biochemistry, Faculty of Medicine and Pharmacy, University Sidi Mohammed Ben Abdellah Fez– Morocco.*

[*]*Corresponding Author. E-mail: youssef.miyah@gmail.com; Tel: (+2120645832284)*

Abstract
This study involved adsorption of Methylene (MB) dye adsorbed from solution on the surface of corn cob powder calcined. Various techniques for characterizing the adsorbent were used, including Scanning Electron Microscopy (SEM) coupled by EDX and Fourier Transform Infra-red spectroscopy (FTIR). The effects of different parameters such as adsorbent dose, initial dye concentration, contact time, temperature and pH of dye solution have been studied to understand the sorption behavior of the sorbent under various conditions. Concentrations of dye were measured before and after adsorption using ultraviolet (UV) spectrophotometer. The experimental isotherm data were analyzed using Langmuir and Freundlich isotherm equation. The maximum monolayer adsorption capacity was 46.28 mg/g at optimum conditions. The kinetic results of sorption obeyed a pseudo-second-order model. Different thermodynamic parameters showed spontaneous reaction with endothermic nature.

Keywords: Adsorption; kinetic; Isotherm; Modeling; thermodynamic.

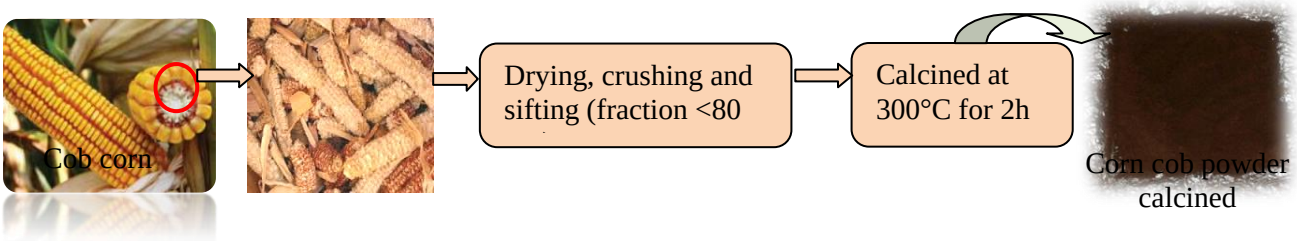
1. Introduction
Pollution caused by textile industry is the major concern for the developing countries [1]. The small and large scale operations in this textile sector cause hazardous effect to environment. The textile manufacturing processes involve large consumption of water and various chemicals which will generate waste. The major problem with regard to water usage is the untreated effluents which are discharged directly into nearby water bodies. Wastewater from the textile industry is rated as the most polluting among all industrial sectors. Dyes present even in low concentrations are highly visible. They affect the photosynthetic activity of the aquatic life due to the reduced light penetration [2-3].
Dyes are known for their stability and ability recalcitrant, making them very dangerous to human health, because they have a carcinogenic, mutagenic, teratogenic, and toxic power. Additionally it may also cause severe damage to human beings such as dysfunction of kidney, reproductive system, liver brain and central nervous system [4-5].
Therefore, the development of a sustainable competitive method from effluent management for the dyeing industry has long been an important task for the environmental protection. In general, the conventional physicochemical processes for the removal of dyes in wastewater include oxidation, photochemical degradation, reverse osmosis, membrane separation, coagulation and adsorption [6-10]. The latter is one of the most effective methods that have been successfully adopted for removal of color wastewater [11]. Among the liquid waste treatment processes, adsorption remains a relatively easy technique to implement [12].
Many investigations have studied the feasibility of using inexpensive alternative materials like nuclei of dates and olive, walnut shells, corn cob, wood, banana peel, orange peel and coffee residues [1].
Adsorbents low cost from solid and agricultural waste received wide attention of researchers in the last decade [1]. Most of these wastes have been shown to effectively remove dyes.

The present research was aimed to test various two-parameter isotherm models to describe the sorption data generated from methylene bleu dye sorption by corn cob powder calcined (CCPC). For this we conducted a parametric study of biosorption, studying the effect of several important parameters on the decolorizing power of the material used, in particular, contact time, concentration of adsorbent, pH and temperature. On the other hand, various techniques for characterizing the adsorbent were used. In addition, tests regeneration of the adsorbent was conducted in the laboratory by desorption of cations methylene blue dye adsorbed to examine the possibility of reuse from the adsorbent several times.

2.1. Materials and Methods

2.2. Preparation of adsorbent

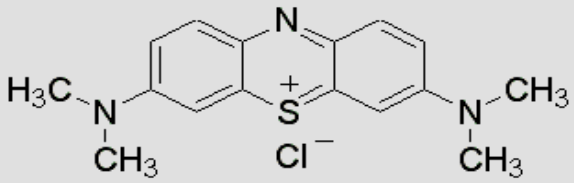
The raw material used in this work is the corn cob, they were ground and sieved to obtain fractions < 80 µm and then calcined at 300 °C for 2h.



2.3. Preparation of Adsorbate

The adsorbent used is the Methylene blue, provided by the company Ciba Specialty Chemicals Inc, All the chemicals use come from Merck. Table 1 represents a descriptive card of the methylene blue BM. Stock solution was prepared by dissolving accurately the weighed dye in ultrapure water to obtain a concentration of 1000 mg.L^{-1}.

Table 1: structure and characteristics of Methylene blue (MB)

Name	Methylthioninium chloride (CI 52015)
Chemical structure	
Molecular formula	$C_{16}H_{18}N_3SCl$
Other name	3,7-bis(Dimethylamino)- phenothiazin-5-ium chloride
Molecular weight (g/mol)	319.85

2.4. Adsorption procedure

Adsorbent CCPC was characterized by various analysis methods: FTIR technique using a range sweeping wavelength 400-7500 cm^{-1} (BRUKER Vertex70). SEM-EDX analysis equipped with probe EDAX for microanalysis of surfaces (Quanta 200 FEI).

corn cob powder calcined was tested for the adsorption of methylene blue dye reagent from aqueous solutions at room temperature using the batch processing technique. Adsorption measurements were made by mixing varying amounts CCPC for removing the potential of methylene blue dye in the series of glass beakers containing 200 ml of the colored solution at different pH values using a numerically controlled heating, and a magnetic stirrer (Stuart). Dye solutions were prepared using ultrapure water (Millipore Direct-Q, UV3 with Pump) to prevent and minimize the possible interference, the samples were performed using a syringe filter 0,45µm diameter (Minisart, sartorium Stedim Biotech). The effect of several variables such as adsorbent dose (0.5-2 g/L), pH (2-12), contact time (0-100 min), initial dye concentration (30 to 1000 mg/L) and temperature of solution (20-50 °C) were studied.

The solution pH was adjusted by adding drops of HCl and NaOH (0.1 M). After 20 min, the balance was established. At the end of adsorption experiments, the concentration of dye was given by measuring the

solution absorbance at λ = 664 nm using a UV-visible spectrophotometer (Jasco V530). All experiments were carried-out in triplicate and the medium values are presented.
The amount of equilibrium adsorption Q_e (mg/g) was calculated using the formula:

$$\boldsymbol{Q_e = \frac{C_0 - C_e}{W} V} \quad (1)$$

Where C_0 and C_e (mg/L) are the initial concentrations of liquid and at equilibrium dye, V is the volume of the solution (L) and W is the adsorbent mass of dye (g).
The dye removal percentage can be calculated as the following:

$$\% \, \boldsymbol{dye\ removal = \frac{C_0 - C_e}{C_0} \times 100} \quad (2)$$

Where C_0 and Ce (mg/L) are the initial and equilibrium concentrations of dye in solution.

3. Results and discussion

3.1. Characterization of adsorbents

Fig.1 presents the spectrum of corn cob powder calcined obtained by Fourier transform infra red spectroscopy, in the 400–4000 cm^{-1} wave number range, the absorption bands observed confirm the presence of liaison characterizing Shells Walnut Powder. Band located at 3334 cm^{-1} correspond to the stretching vibration of hydroxyl carboxylic [13-14], the band 2916 cm^{-1} is assigned to C–H stretching vibrations the aliphatic molecules [15], the band 1715 cm^{-1} corresponds to elongation of C=O bond attributed to aldehydes or saturated acid [14-15], the band 1631 cm^{-1} due to stretching vibration liaison C=C of the olefin structure [16-17], the two bonds about 1425 cm^{-1} and 1369 cm^{-1} corresponded to the C–H in-plane bending vibrations in methyl and methylene groups [17], the Bands 1317 cm^{-1}, 1241 cm^{-1} and 1027 cm^{-1} are assigned to vibration binding of C–O [14].

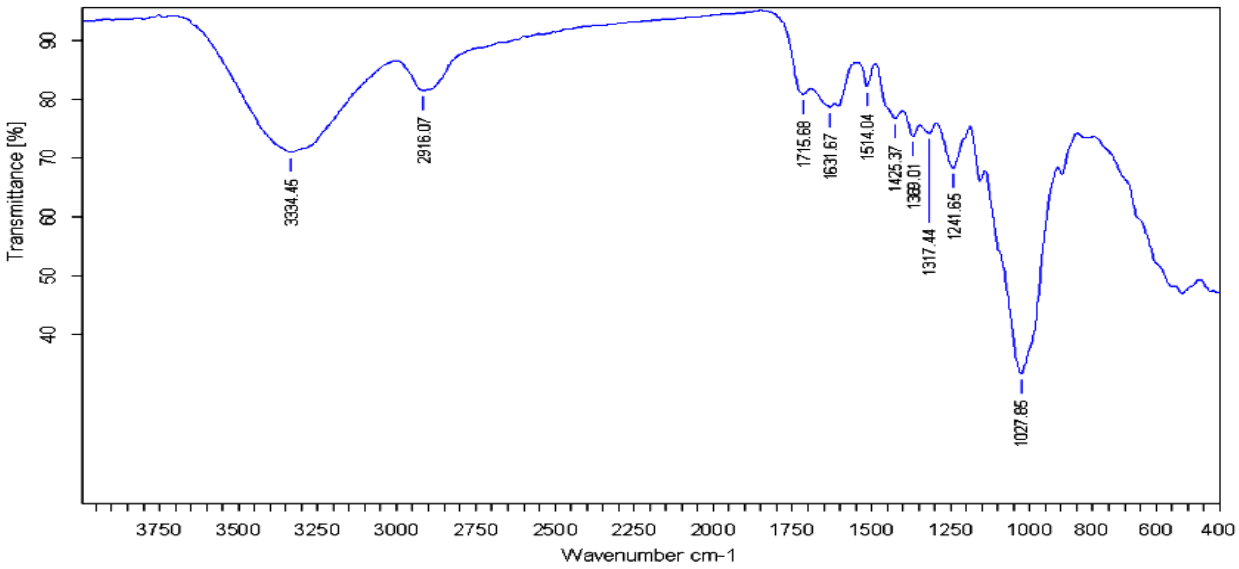
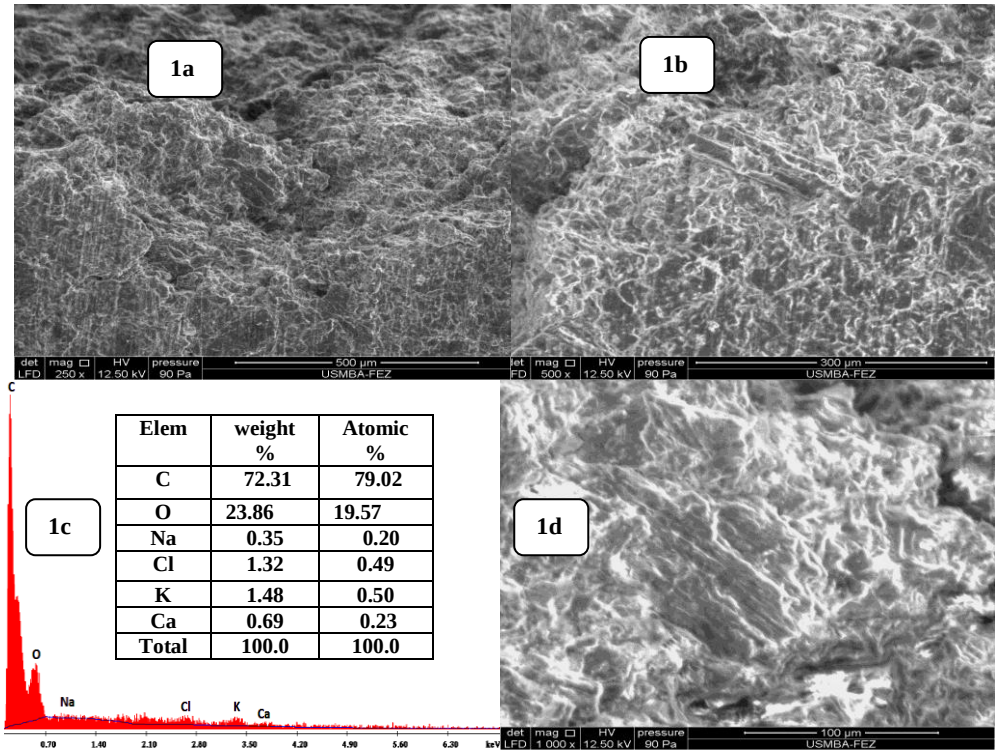


Fig.1. Spectroscopy infra red of corn cob powder calcined (CCPC).

The surface morphology of the corn cob powder calcined was characterized via scanning electron microscopy (SEM) coupled by EDX. The use of these techniques makes it possible to visualize the surface morphology of adsorbents. The SEM micrographs of native sorbents are shown in Fig.2. The images obtained show the amorphous nature and heterogeneous morphology of corn cob powder calcined with cellulose fiber of various sizes and forms. In spectrum EDX confirms the presence of the percentages of carbon and of oxygen are raised, which confirms the organic nature of adsorbent material.



Elem	weight %	Atomic %
C	72.31	79.02
O	23.86	19.57
Na	0.35	0.20
Cl	1.32	0.49
K	1.48	0.50
Ca	0.69	0.23
Total	100.0	100.0

Figure 2. SEM Microscopy coupled by EDX, for CCPC (1a, 1b, 1c, 1d)

3.2. Influence of contact time on Methylene bleu adsorption

A specific weight of CCPC adsorbent (0.4 g) with 50 mL of MB dye solution was kept constant for the batch experiments. Initial MB solutions of 30, 50, 70, and 100 mg/L were performed at 20 °C on a magnetic stirrer operated for 1 h. Results of this study are shown in Fig. 3. It was observed that the removal of MB is increased with increasing the contact time at all initial MB dye concentrations. Furthermore, the % removal dye is increased with the decrease in initial dye concentration. It is because of the fact at lower concentration, the ratio of initial number of dye molecules to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye depends upon concentration. For the first 30 min, the adsorption uptake was rapid then it proceeds at a slower adsorption rate and finally it attains saturation at 45 min [11].

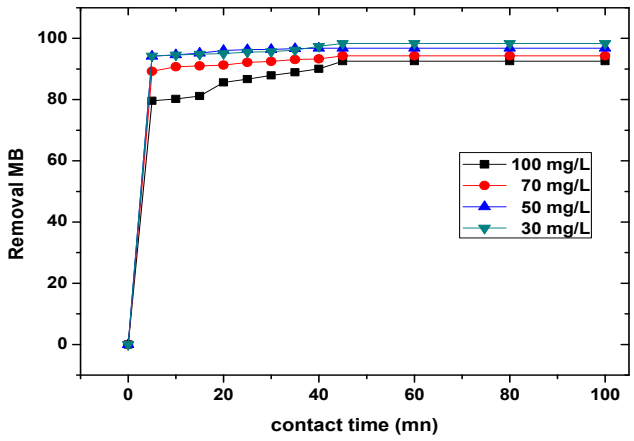


Fig.3. Effect of contact time and dye concentration adsorbent. Interval of initial concentration (30 to 100 mg/L), adsorbent dose: W= 0.4 g, V= 200 mL, pH=6.8, T= 20 °C and agitation time 100 min.

3.3. Effect of adsorbent dosage

With end to optimize the quantity of CCPC added to coloured solution BM of the experiments were provided by using 200 ml with the solution with BM (100 mg/L), to the which various quantities of CCPC were added (0.5 - 2 g/L). These results can be attributed to increasing the area available to high values of the adsorbent doses applied (Fig.4). Therefore, the probability of match (molecule-Site) also increases, thus leading to improved retention.

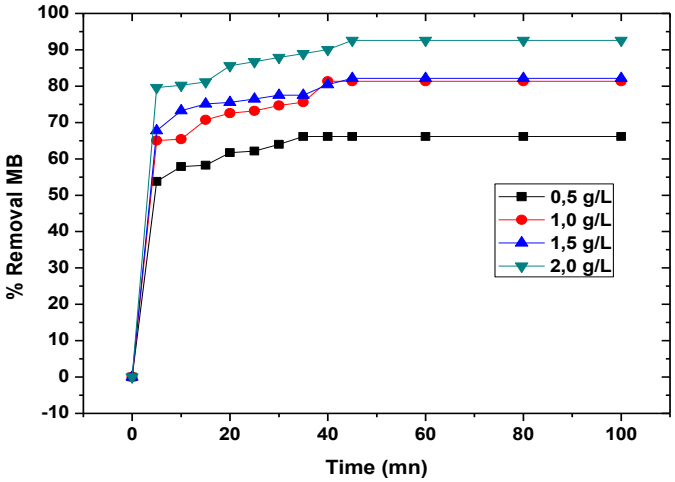


Fig.4. Effect of adsorbent amounts on dye removal of MB. Interval of adsorbent dose (0.5-2 g/L), Initial dye concentration 100 mg/L, V=200 mL pH=6.8, T= 20 °C and agitation time 100 min.

3.4. Effect of pH

One of the most important factors in adsorption studies is the effect of acidity on the medium. Different species may present divergent ranges of suitable pH depending on which adsorbent is used [18-19]. The mean of the duplicated experimental results is plotted in Fig. 5, indicating that pH considerably affected MB adsorption, particulary under acidic conditions. As can be seen in Fig. 5, percentage removal of MB onto CCPC increased from 57% to 96% when the solution pH was increased from 2 to 12. The analysis of these results shows that the quantity of the methylene bleu adsorbed on corn cob powder calcined increases with increased pH.

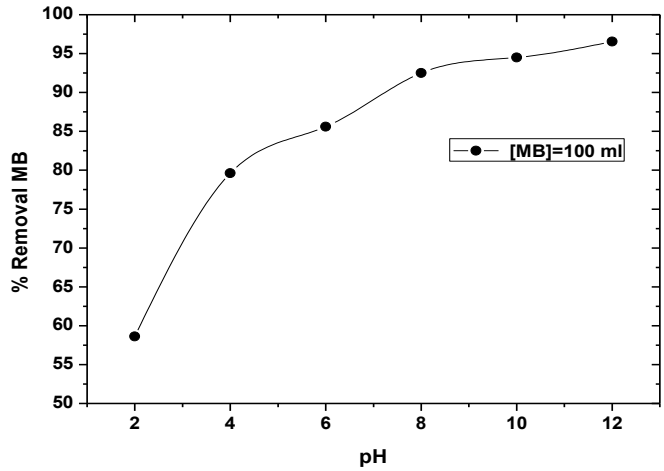


Fig.5. Effect of pH on removal of MB onto CCPC. Interval of pH (2-12), Initial dye concentration 100 mg/L. Adsorbent dose: W= 0.4 mg, V=200 mL, T= 20 °C and agitation time 100 min.

3.5. Effect of temperature

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion from the adsorbed molecules across the external boundary layer and the internal pores of the adsorbent particles, owing to the decrease in the viscosity of solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [20-21].

The percentage % of removal methylene blue on adsorbent CCPC increases with the temperature in the studied range and the time of adsorption to reach balance decreases with the increase in temperature (Fig.6). This suggests that the interaction of adsorbent CCPC and adsorbate (BM) is of nature endothermic. Generally the rise in the temperature supports adsorption.

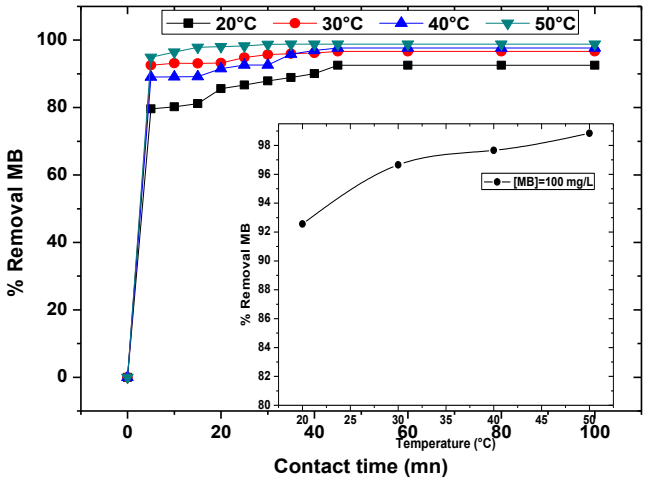


Fig.6. Effect of temperature on the adsorption kinetics of MB onto CCPC.

3.6. Adsorption kinetics

This study aims to determine the order of the adsorption kinetics; the most used models are the model pseudo first order and the model of pseudo second order. [22] The model of pseudo first order is more compatible with weak concentrations of aqueous solution. This model is represented by the following relation [23-24]:

$$\ln(q_e - q_t) = lnq_e - K_1 t \quad (3)$$

Where q_t: quantity of adsorbate adsorbed with time t ($mg.g^{-1}$), qe: quantity adsorbed with balance ($mg.g^{-1}$); k_1: constant speed of adsorption of the pseudo model - first order (min^{-1}), t: time (min). A straight line of ln (q_e - q_t) versus t indicates the application of pseudo-first-order kinetics model. In a true pseudo-first-order process, lnq_e should be equal to the interception of an ln (q_e− q_t) plot against t. The parameters model of pseudo first order and the coefficients from correlation are summarized in table 2.

The model of pseudo-second-order can be represented in the following form [25-26]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

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

If this equation is checked, by tracing t/q_t according to T, we must obtain a line of slope $1/q_e$ and ordinate in the beginning equal to $1/ (K_2 q_e^2)$.

The corresponding parameters were gathered in the Table 2 which also presents the coefficients of correlation. These calculated coefficients are more about the unit for the kinetic model of pseudo second-order. That indicates that this last model described well the experimental results of the adsorption from the BM on the two adsorbents.

Table 2: Comparison of the pseudo-first and second-order model adsorption rate constants, calculated and experimental qe values for different initial MB concentrations.

Dye Concentration (mg/L)	$(q_e)_{exp}$	Pseudo-first order			Pseudo-second order		
		$(q_e)_{cal}$	K_1	R_F^2	$(q_e)_{cal}$	K_2	R_S^2
30	14.51	1.07	0.049	0.926	14.70	0.462	1.000
50	23.57	1.22	0.019	0.969	23.81	0.088	0.999
70	33.57	1.15	0.18	0.926	34.48	0.093	1.000
100	46,28	2.68	0.021	0.968	47.61	0.014	0.999

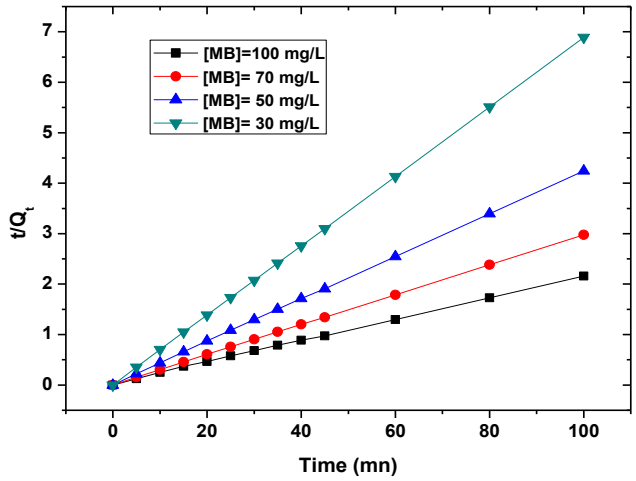


Figure 12: Model of the pseudo-second-order for the adsorption of the methylene blue on the adsorbent CCPC

3.7. Adsorption isotherms

Equilibrium adsorption isotherm data were analyzed according to the Langmuir and Freundlich models. The Langmuir equation is suitable to describe the adsorptive behaviour of homogeneous surfaces. The Langmuir adsorption model is established on the following hypotheses: uniformly energetic adsorption sites, monolayer coverage, and no lateral interaction between adsorbed molecules. A mathematical expression of Langmuir can be written as [27-28]:

$$\boldsymbol{Q_e = \frac{Q_m K_L C_e}{1+K_L C_e}} \quad (5)$$

Where qe (mg/g) is the adsorbed amount at equilibrium, Ce is the equilibrium concentration of the adsorbate (mg/L), KL is Langmuir equilibrium constant (L.mg-1) and Q_m the maximum adsorption capacity (mg/g). The linear form of Langmuir equation is:

$$\boldsymbol{\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}} \quad (6)$$

If the equation of Langmuir is checked, we must obtain while placing on the Figure 11 our experimental points in Ce/Qe= f (Ce), a line whose slope and ordinate in the beginning enable us to determine Qm and KL. The essential characteristic of Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, R_L, defined by:

$$\boldsymbol{R_L = \frac{1}{1+K_L C_0}} \quad (7)$$

Where C_0 is the initial dye concentration (mg/L). R_L values indicate the type of isotherm to be irreversible (R_L =0), favorable (0< R_L< 1), and unfavorable (R_L> 1) [29].

The adsorption isotherm of Freundlich [30] supposes that adsorption occurs on a heterogeneous surface by a multilayer mechanism of adsorption, and that the adsorbed quantity increases with the concentration. A mathematical expression of Freundlich isotherm was as follows:

$$\boldsymbol{Q_e = K_F C_e^{1/n}} \quad (8)$$

Where Kf (L/mg) is Freundlich constant and n is the heterogeneity factor. The K_f value is related to the adsorption capacity; while the $1/n_f$ value is related to the adsorption intensity. $1/n_f$ values indicate the type of

isotherm to be irreversible ($1/n_f = 0$), favorable ($0 < 1/n_f < 1$), unfavorable ($1/n_f > 1$) [30] can be rearranged to linear form:

$$\boldsymbol{LogQ_e = Log\ K_f + \frac{1}{n} Log\ Ce} \quad (9)$$

The estimated parameters of the adsorption isotherms of Langmuir and Freundlich, for the adsorption of methylene blue dye, by using adsorbents (CCPC), are gathered in Table 6.

Table 3: Isotherm constants for dye adsorption at different temperature onto CCPC.

Temperature (°C)	Langmuir isotherm model					Freundlich isotherm model		
	Q_L	K_L	R_L^2	R_L		K_F	n_F	R_F^2
25	41.33	2.324	0,998	0.0042		32.23	1.025	0,815

The dimensionless constant called equilibrium parameter which was calculated is grouped in Table 3. The results show that adsorption isotherms of MB on CCPC are all favorable. They found that the equilibrium adsorption data obtained for the MB adsorption on different adsorbents were well described by the Langmuir model.

3.8. Thermodynamics of adsorption

The concept of thermodynamics supposes that in an isolated system where energy cannot be gained or lost. The thermodynamic parameters which must be considered to determine the process are changes of the standard enthalpy (ΔH°), the standard entropy (ΔS°) and free standard energy (ΔG°) due to the transfer of the unit of the body dissolved starting from the solution to the solid-liquid interface [31]. The values of ΔH° and ΔS° were calculated by using the equation of Van't Hoff [32]:

$$\boldsymbol{lnK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}} \quad (10)$$

Where R: is the constant of perfect gas (R = 8.314 $J.mol^{-1}.K^{-1}$), T: absolute temperature of solution (K), K_d: partition coefficient; Q_e: quantity adsorbed on the solid with balance ($mg.g^{-1}$), and C_e: concentration with balance ($mg.\ L^{-1}$).

The values of ΔH° and ΔS° were calculated starting from the slope and the interception of the layout of $\ln K_d$ according to 1/T. ΔG° can be calculated below by using the relation:

$$\boldsymbol{\Delta G^\circ = -RT lnK_d \quad and \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ} \quad (11)$$

Table 4: Equilibrium constant and thermodynamic parameters for the adsorption of Methylene bleu MB onto CCPC biosorbents.

	ΔH° ($kJ.mol^{-1}$)	ΔS° ($J.mol^{-1}.K^{-1}$)	ΔG° ($kJ.mol^{-1}$)			
			20°C	30°C	40°C	50°C
CCPC	37.442	153.783	-7.616	-9.154	-10.692	-12.221

The negative values of ΔG° (Table 4) show that the adsorption is highly favorable and spontaneous. The positive values of ΔS° (Table 4) shows the increased disorder and randomness at the solid solution interface of MB with CCPC adsorbent that brings about some structural changes in the MB.

4. Conclusion

The results indicated that CCPC is a promising new low cost adsorbent for the removal of MB from aqueous solutions. The Langmuir model describes satisfactorily the adsorption on CCPC. The percentage of decolorization is 96%. The kinetic study shows equilibrium quickly obtained. The kinetics of adsorption is a pseudo-second-order. The adsorption is greatly pH dependent, with a low uptake of dye at low pH and high uptake at high pH. Thermodynamic studies indicated that the dye adsorption onto CCPC was a spontaneous, endothermic and physical reaction in nature.

Reference

1. Gupta V.K., Suhas., *Journal of Environmental Management*, 90 (2009) 2313–2342.
2. Jia-Shun C., Jun-Xiong L., Fang F., Ming-Ting Z., Zhi-Rong H., *Bioresource Technology*, 163 (2014) 199–205.
3. Auta M., Hameed B.H., *Chemical Engineering Journal*, 198–199 (2012) 219–227.
4. Alok M., Gupta V.K., Arti M., Jyoti M., *Journal of Hazardous Materials*, 151 (2008) 821–832.
5. Haik Y., Shahnaz Q., Ashley G., Sarmadia A., Reyad S., *Journal of Hazardous Materials*, 176 (2010) 1110–1112.
6. Ollis D., Silva C.G., Faria J., *Catalysis Today*, 240 (2015) 80–85.
7. Liang C., Sun S., Li F., Ong Y., Chung T., *Journal of Membrane Science*, 469 (2014) 306–315.
5. Mohamad Amran M.S., Dalia K.M., Wan A.W.A.K., Azni I., *Desalination*, 280 (2011) 1–13.
9. 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.
10. Idrissi M., Lamonier J.-F., Chlala D., Giraudon J.-M., Chaouch M., Miyah Y., Zerrouq F., *Journal of Materials and Environmental Science*, 5 (S1) (2014) 2303–2308.
11. Miyah Y., Idrissi M., Zerrouq F., *Journal of Materials and Env. Science*, 6 (3), (2015) 699–712.
12. El Gaidoumi A., Chaouni Benabdallah A., Lahrichi A., Kherbeche A., *J. Mater. Environ. Sci*, 6 (8) (2015) 2247-2259.
13. Çelekli A., Birecikligil S.S., Geyik F., Bozkurt H., *Bioresource Technology*, 103 (2012) 64–70.
14. Dahri M.K., Kooh M.R.R., Lim L.B.L., *Journal of Environmental Chemical Engineering*, 2 (2014) 1434–1444.
15. Ghaedi M., Mazaheri H., Khodadoust S., Hajati S., Purkait M.K., *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 135 (2015) 479–490.
16. Çelekli A., Birecikligil S.S., Geyik F., Bozkurt H., *Bioresource Technology*, 103 (2012) 64–70.
17. Yang J., Qiu K., *Chem. Eng. J*, 165 (2010) 209–217.
18. Calvete T., Lima E.C., Cardoso N.F., Vaghetti J.C.P., Dias S.L.P., Pavan F.A., *Chemical Engineering Journal*, 91 (2010) 1695–1706.
19. El Haddad M., Mamouni R., Saffaj N., Lazar S., *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 12 (2012) 48–54.
20. Al-qodah Z., *Water Res*, 34 (2000) 4295–4303.
21. Barka N., Qourzal S., Assabbane A., Nounah A., Ait-Ichou Y., *Journal of Saudi Chemical Society*, 15 (2011) 263–267.
22. Lagergren S., Kungliga Svenska Vetenskapsakademiens. *Handlingar*, 24 (1898) 1–39.
23. Ru-Ling T., Feng-Chin W., Ruey-Shin J., *Journal of the Taiwan Institute of Chemical Engineers*, 41 (2010) 661–669.
24. Yiyong C., Dejin Z., *Chemical Engineering Journal*, 254 (2014) 579–585.
25. Talal S., *Journal of Environmental Chemical Engineering* 2 (2014) 1001–1006.
26. Nahid G., Parya T., Ali K., Naser S.N., Sharifah R.W.A., *IERI Procedia*, 5 (2013) 232-237
27. Langmuir I., J. Chem. Soc., 38 (1916) 2221–2295.
28. Weber J.R., Moriss J.C., *Journal of sanitary Eng. division, American society Civil Eng.*, 89 (1963) 31.
29. Mahmoodi N.M., Arami M., *Journal of Applied Polymer Science*, 109 (2008) 4043–4048.
30. Freundlich H.M.F., *Physik. Chemie (Leipzig)*, 57A (1906) 385–470.
31. Medhat A.S., Hassan, M.A., *Chemosphere*, 111 (2014) 587–595.
32. Min L.U., Yue-ming Z., Xiao-hui G., Xiao-hui X., Ting-ting G., *Transactions of Nonferrous Metals Society of China*, 24 (2014) 1912−1917.