

Kinetic and Thermodynamic Studies of Adsorption of Cationic dye on Wood Cores of Jujube in Aqueous Solution

Noureddine El Messaoudi¹, Abdellah Lacherai¹, Mohamed El Khomri¹
Safae Bentahar¹, Mohamed Ezahri²

1-Laboratory of Biotechnology and Valuation of Natural Resources, Faculty of Science,
Ibno Zohr University, BP 8106, 80000 Agadir, Morocco

2-Laboratory of Materials and Environment, Faculty of Science, Ibno Zohr University,
BP 8106, 80000 Agadir, Morocco

Abstract---- This work is a contribution to the search for new efficient and less expensive adsorbents on the one hand, on the other hand to the valuation of a natural material, namely wood cores jujube (WCJ). The efficiency of this material was tested on a dye widely used in the textile industry the methylene blue (MB), in aqueous solution. Thus, in this study, the support used is prepared and characterized by different techniques (FTIR, TGA and DTA). Also, we studied isotherms (Langmuir, Freundlich, Temkin), kinetic and thermodynamic of the adsorption phenomenon involved. The various results obtained showed that the adsorption of MB on WCJ is an endothermic reaction, spontaneous, follows a second order kinetics, and better described by the Langmuir isotherm.

Key words ---- Jujube, Adsorption, Methylene blue, Kinetic, Thermodynamic, Isotherm models

I. INTRODUCTION

Preserving the environment requires the development and optimization of technologies to reduce pollution of air, soil, and especially water. So far, in spite of the efforts deployed the industrial effluents contain a significant amount of pollutants of all kinds which is released into the environment.

Several techniques were used for the removal of dyes from industrial effluents [1, 2]. Adsorption is one of the most exploited phenomena for highlighting these removal techniques. So the activated carbon material is widely used, only it is very expensive and requires more regeneration [3, 4]. This limits its use in developing countries. What brings to remedy it by searching for new cheaper adsorbents and in particular from materials which are not classics, in particular from plant waste.

Much research has been conducted in this area by using materials of vegetable origin [5- 8].

In this perspective we were interested in a material of plant origin present in our region namely wood cores jujube WCJ, and to test its effectiveness we have chosen as a model pollutant methylene blue (MB).

The latter is a cationic dye widely used in the textile industry. MB is toxic and causes upon exposure nausea, vomiting, ocular lesions, and methemoglobinemia [9].

In this study we set ourselves the aim of studying the kinetics and thermodynamics of adsorption involved the one hand and the other hand the valorization of the material studied.

II. MATERIAL AND METHODS

2.1. Preparation and characterization of biosorbent

Wood cores jujube WCJ (*Zizyphus lotus*) was provided from region of Tata (south of Morocco). It was collected and washed with distilled water to remove the surface adhered particles, then dried in oven at 110°C for 24 h.. It was then milled and sieved to obtain a particle size in diameter range of 0.5 to 1mm. After drying for several hours the fine powder of WCJ was preserved in tight glass for use as adsorbents.

We have characterized WCJ by transform infrared spectroscopic (FTIR), Thermogravimetric analysis (TGA) and the differential thermal analysis (DTA).

2.2. Preparation of dye solutions

1g of methylene blue dye (Chemical formula: $C_{16}H_{18}N_3SCl$, molecular weight 319.85 g/mol, maximum wavelength 661 nm and IUPAC name : 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride. The structure of BM is shown in Fig.1 [10]) was dissolved in 1L distilled water (stock solution). All working solutions of varying concentrations were obtained by successive dilution. Adsorption studies were conducted with desired dilution of the stock solution.

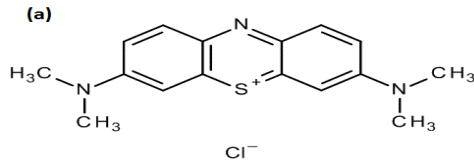


Fig.1. Structure of methylene blue.

2.3. Batch adsorption experiments

Adsorption of BM dye solution was carried out using batch experiment and the effect of various parameters like contact times (30-240min), initial dye concentration C_0 (10-60 mg/L) and temperature (15- 60°C) on the removal of BM were studied.

The adsorption studies were carried out by adding to 0,3g of WCJ powder to 50ml of dye solutions to of known concentrations. The solutions were stirred using a magnetic stirrer at predetermined times intervals and are kept in a bath at different temperature (15- 60°C) by a thermostat with external circulation [11,12].The mixture is stirred using a magnetic stirrer to different contact times (30-240min), in these sorption experiments.

The adsorbent was then removed by filtration the equilibrium concentrations of the samples were analyzed using spectrophotometer (UV-visible 2300- TECHCOMP). Calibration curve were obtained with standard MB solutions by recording the absorbance values of various concentration of methylene blue dye at maximum absorbance of wavelength $\lambda_{max}=661nm$.

Each experiment was carried out in duplicate and the average results are presented.

The adsorption capacity q_e (mg/g) and color removal efficiency $R(\%)$ were calculated using following equations (1) and (2), respectively.

$$q_e = \frac{(C_0 - C_e) \times V}{w} \quad (1)$$

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

Where, C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of MB solution, respectively, V (L) is the volume of solution, and $W(g)$ is the mass of biosorbent used.

III. RESULTS AND DISCUSSION

3.1. Characterization of biosorbent

The FTIR spectrum (JASCO FT/IR 4100) of the WCJ before dye adsorption is shown in Fig.2. The absorption with maxima at 3343 cm^{-1} is assigned to the O-H group stretching vibration and the band about 2901 cm^{-1} is attributed to stretching of C-H. The band observed at 1703 cm^{-1} is assigned to a carbonyl band (C=O) of

unionized carboxylate stretching of carboxylic acid or ester [13], while the peak at 1552 cm^{-1} is attributed to C=O stretching of carboxylic acid with intermolecular hydrogen bond [13]. The band in the 1210 cm^{-1} is due to the bending modes of O-C-H, C-C-H and C-O-H. The band at 1021 cm^{-1} is attributed to C-O stretching.

The FTIR results indicated that the biosorbent studied presented functional groups such as, OH, COO⁻ and CO, that could be potential adsorption sites for interaction with the cationic MB dye also confirmed the lignin presence of the lignin on the wood cores [14].

The WCJ was analyzed by TGA and DTA (SHIMADZU D60) between 25° and 600° C with a heating rate of $10^\circ\text{ C} / \text{min}$. The TGA and DTA curves are shown in Fig. 3. The analysis of these curves shows that they can be divided into four phases in function of the temperature [15]. The first endothermic corresponds to loss of water ($T < 270^\circ\text{ C}$). The second is exothermic ($270 < T < 360^\circ\text{ C}$) and the third endothermic ($360 < T < 500^\circ\text{ C}$). The latter two may be due to the decomposition of organic matter. The last phase is the formation of carbon ($> 500^\circ\text{ C}$) at an exothermic process.

3.2. Adsorption Kinetic studies

Figure 4 shows the effect of contact time on the retention rate at three different initial concentrations of the dye. For the three used concentrations, the retention rate grows with reaction by following two different slopes. One is rapid and is located in the first 180 minutes, whereas the second is slow and could express the equilibrium between the fractions retained dye and those desorbed.

Overall retention is comparable for all three concentrations with a yield that decreases when the concentration increases, with the values of 94.09, 76.71 and 56.93% respectively for concentrations 10, 25 and 40 mg / l.

Most of transferred dye onto the adsorbent is obtained in the third hour with amounts on the order of 91.94, 76.07 and 55.68% respectively for concentrations 10, 25 and 40 mg / l. The adsorption capacity increases, too, with the increase in concentration of the solution to reach values of about 1.56, 3.19 and 3.79 mg / g for the respective concentrations of 10, 25 and 40 mg / L.

The mechanism of adsorption and the potential rate controlling steps involved in the process of adsorption had been investigated using kinetic models such as pseudo-first-order, pseudo-second-order and intra particle diffusion model.

Pseudo first-order model

The pseudo first-order equation is generally expressed as [16]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (3)$$

Where, k_1 is the constant pseudo-first order (min^{-1}). The constants of pseudo-first order were determined by

extrapolation of the plot of $\log(q_e - q_t)$ vs. t . The results are shown in Fig. 5.

The adsorbed quantities q_e , cal values, the constants k_1 pseudo-first order and R^2 regression coefficients for the three concentrations used are given in Table 1. R^2 values were found relatively low and between 0.823 and 0.981.

The calculation of q_e for the three concentrations shows that the adsorbed amounts of dye are rather low compared with experimental quantities. These observations lead us to say that the adsorption of methylene blue does not express a diffusion process controlled since it does not follow the pseudo-first order equation.

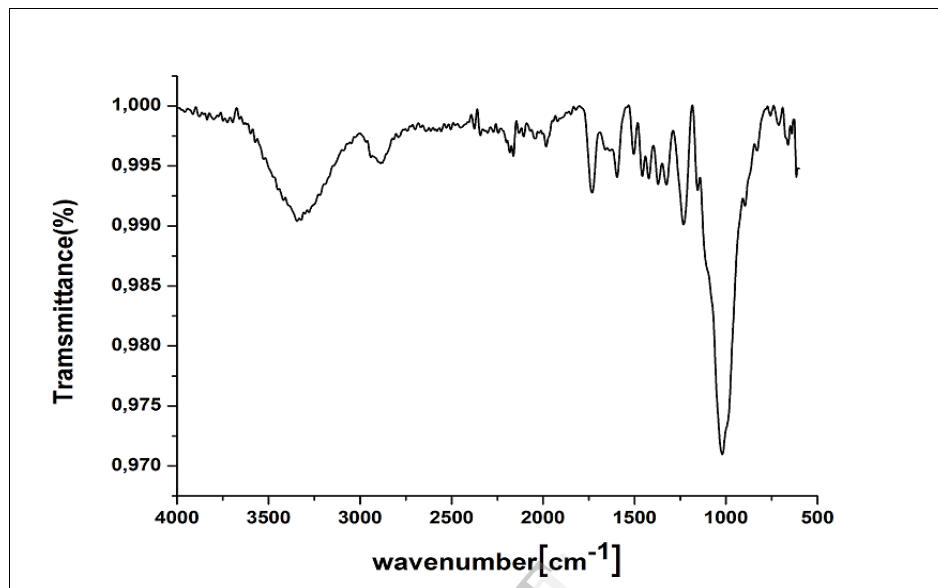


Fig.2.FTIR spectra of WCJ

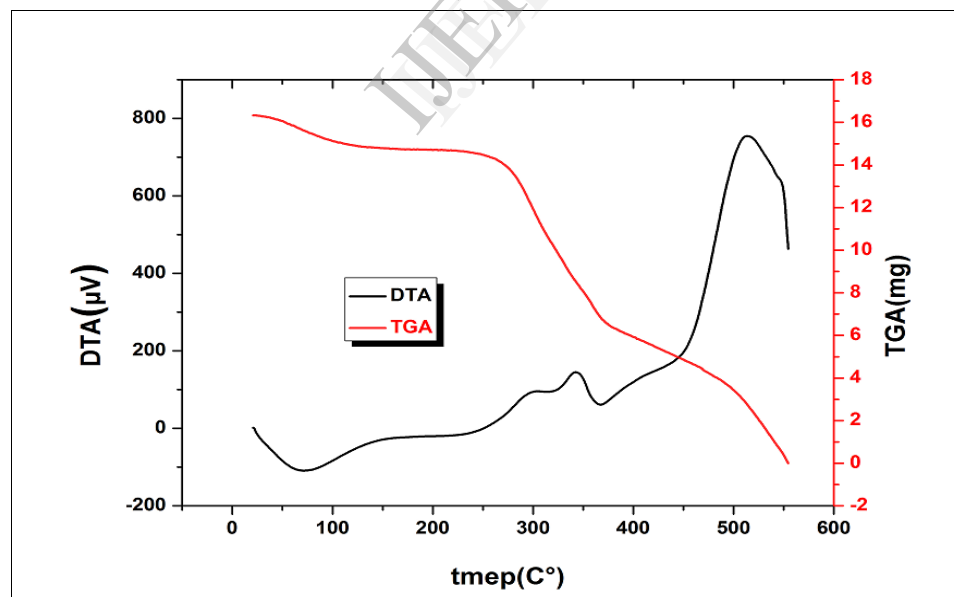


Fig.3. Curves TGA and DTA of WCJ

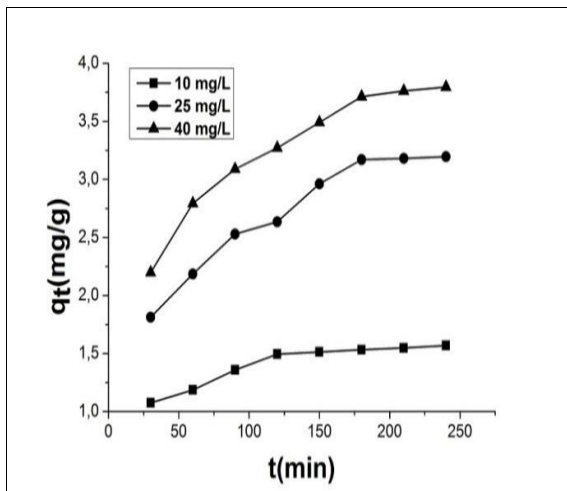


Fig.4.Effect of contact time on the amount adsorbed ($C_0=10-40$ mg /L; $T = 30^\circ$ C; biosorbent dose =6g/L).

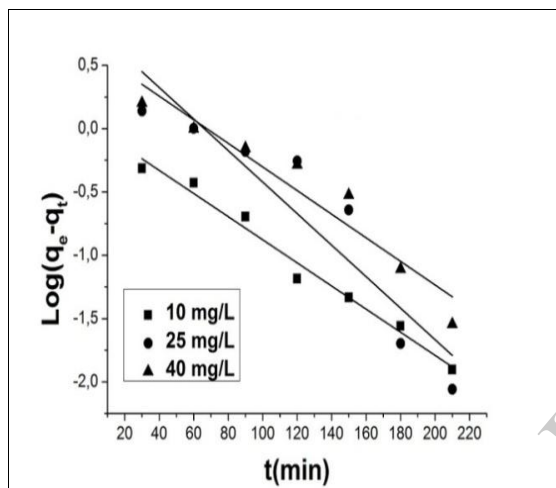


Fig.5.Pseudo-First-Order kinetic of MB adsorption by WCJ ($C_0 =10-40$ mg / L; $T = 30^\circ$ C; biosorbent dose=6g/L).

Pseudo second -order model

The equation of the pseudo-second-order can be expressed as follows [16]:

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

Where K_2 is the constant of pseudo-second order rate ($g \cdot mg^{-1} \cdot min^{-1}$). Figure 6 shows the application of the kinetic model of pseudo-second order to the results for the adsorption of methylene blue. The constants of the pseudo-second-order have been determined by extrapolating the plot of t / q_t vs. t . The values of the adsorbed quantities $q_{e,cal}$, constants pseudo second order K_2 and regression coefficients R^2 for the three concentrations used are given in Table 1.

In view of these results, it appears that the amount adsorbed at equilibrium ($q_{e,cal}$), increases with initial concentration. Moreover, the R^2 values are very high and are all above 0.99. They surpass significantly those obtained with the model of pseudo-first order. The fixed

amounts ($q_{e,cal}$) in equilibrium are in the order of 1.71, 3.75 and 4.26 mg / g respectively for the concentrations 20, 30 and 40 mg / L and are very close to the values found experimentally, the order of 1.56 , 3.19 and 3.79 mg / g.

These two last finding suggests that the adsorption process follows the model of pseudo-second order

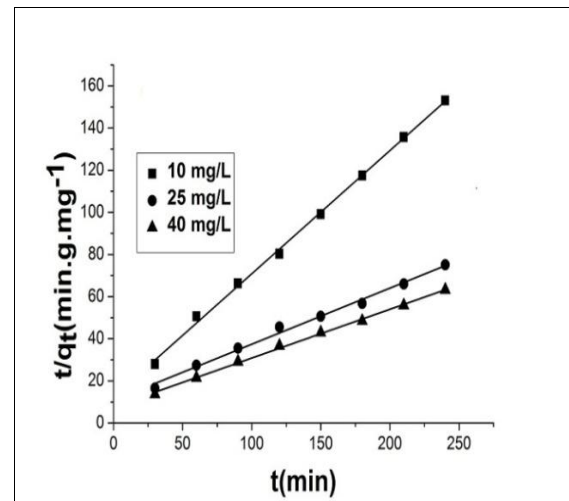


Fig.6. Pseudo-Second-Order kinetic of MB adsorption by WCJ ($C_0=10-40$ mg / L; $T = 30^\circ$ C; biosorbent =6g/L).

Intraparticle diffusion model

The possibility of intraparticle diffusion was examined using Weber-Morris theory [17]. According this theory the intraparticle diffusion model can be expressed as

$$q_t = K_{int} t^{1/2} + C \quad (5)$$

Where, q_t is the amount adsorbed (mg/g) at time t , and K_{int} is the rate constant for intraparticle diffusion ($mg \cdot g^{-1} \cdot min^{-1/2}$).

Figure 7 shows plots of the model used for the three values dye concentrations (10, 25 and 40 mg / L) . The intraparticle diffusion constant and R^2 are given in Table 1.

From figure 7, it is easy to see that the intraparticle diffusion is a significant step in the process of adsorption of methylene blue on wood cores jujube, especially after 180 minutes. This latency can be explained by the movement of dye molecules in the channels of the adsorbent cellulose.

However, the chemical surface reaction, which begins in the first few minutes of contact with the experimental points are aligned to the pseudo-second order with very high regression coefficients R^2 , indicates that the most influential step in the adsorption the dye on WCJ is the intraparticle diffusion process, since it can be considered as limiting step that controls the transfer of the dye at each time t .

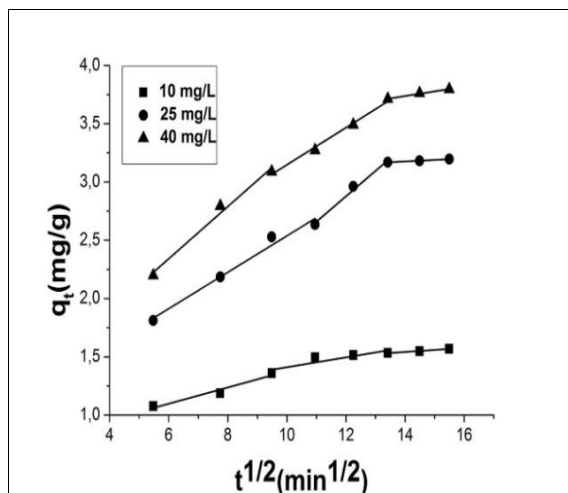


Fig.7. Intraparticle diffusion of MB adsorption by WCJ (C₀=10-40 mg / L; T = 30 ° C; biosorbent dose =6g/L).

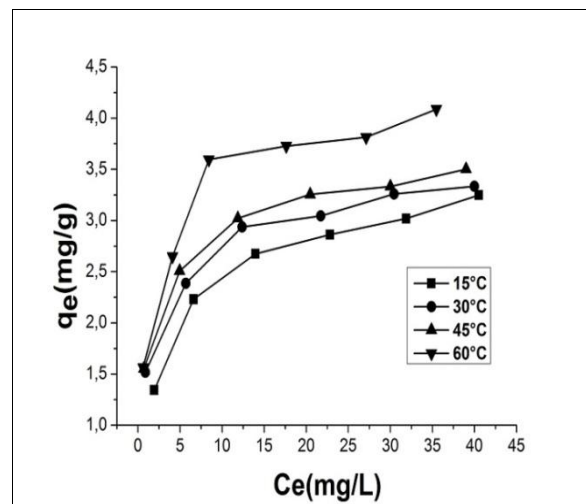


Fig.8. Adsorption isotherm of MB on WCJ at different T°C (C₀=10-60 mg / L; t = 180 min; biosorbent dose=6g/L).

Table1. Kinetic parameters for adsorption of MB by WCJ

Pseudo-first-order model				
C ₀ (mg/L)	q _{e,exp} (mg/g)	q _{e,cal} (mg/g)	K ₁ (min ⁻¹)	R ²
10	1.56	1.08	0.021	0.981
25	3.19	6.65	0.027	0.823
25	3.19	4.26	0.020	0.923
Pseudo-second-order model				
C ₀ (mg/L)	q _{e,cal} (mg/g)	K ₂ (g .mg ⁻¹ .min ⁻¹)	R ²	
10	1.71	0.027	0.999	
25	3.79	0.743	0.993	
40	4.32	0.115	0.998	
Intraparticle diffusion model				
C ₀ (mg/L)	K _{int}	C	R ²	
10	0.017	1.299	0.987	
25	0.147	1.065	0.968	
40	0.158	1.498	0.973	

3.3. Isotherms studies

The adsorption process was carried out at different temperatures of 15-60 ° C with an initial concentration of between 10 MB and 60 mg / L, stirring for a period of 180 minutes was used for all concentrations of BM in this study. Figure 8 shows that the adsorption capacity of MB on WCJ increased with temperature elevation from 15 to 60 ° C, due to an increased surface activity and an increase in kinetic energy of the dye molecule.

Since the adsorption increases with temperature, therefore, the system is endothermic.

It is important to study the equilibrium adsorption isotherm for the conception of the system adsorption. Three isotherm models of adsorption were used for this study namely Langmuir, Temkin and Freundlich.

The Langmuir equation can be described by the linearized form

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{6}$$

Where, K_L is the Langmuir constant (L/mg) and q_m is the maximum amount of adsorbate retained on the medium used (mg/g).

This isotherm (Fig.9) has several advantages. The value of K_L is related to the strength of interaction between the adsorbed molecules and the solid surface on the one hand, and on the other hand the value q_m expresses the quantity of solute fixed per gram of solid, the surface is considered completely covered by a monomolecular layer [18]. In addition the parameters KL and q_m have a physical meaning.

Equilibrium parameter «or» separation factor, which characterizes the adsorption, is defined by the following equation [19]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

Where, C₀ is the initial concentration of the adsorbate (mg / L).

The R_L value indicates the mode of sorption of the isotherm process, if the process is unfavorable (R_L> 1) or linear (R_L = 1) or favorable (0 < R_L <1) or irreversible (R_L = 0).

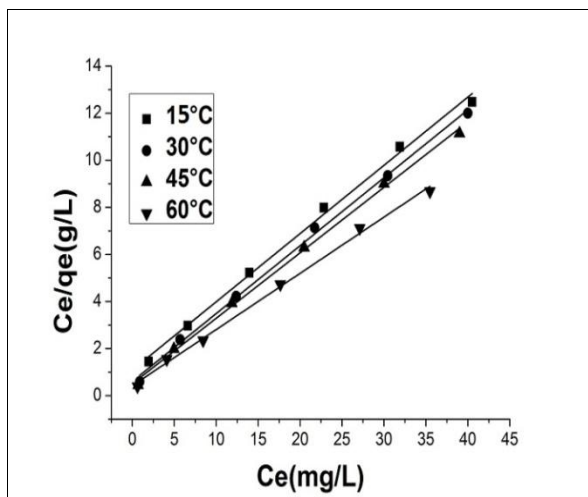


Fig.9. Langmuir isotherm of MB on WCJ at different T°C (C₀=10-60 mg / L; t = 180 min, biosorbent dose =6g/L).

The linearized Freundlich (Fig.10) equation is represented by the following equation [19]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{8}$$

Where, K_F is the Freundlich constant ((mg/g)(l/mg)^{1/n}) and 1/n is the intensity of adsorption.

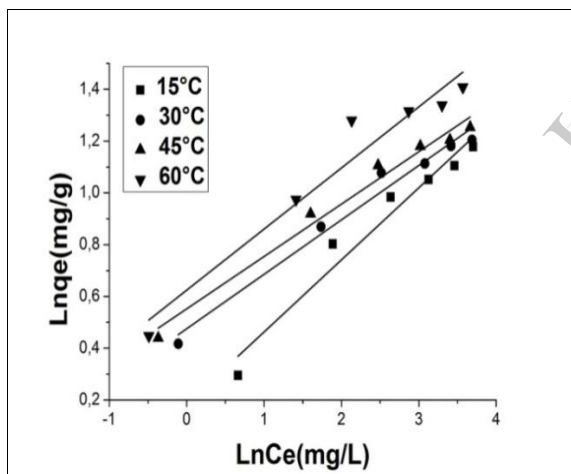


Fig.10. Freundlich isotherm of MB on WCJ at different T°C (C₀=10-60 mg / L; t = 180 min; biosorbent dose =6g/L).

The isotherm Temkin (Fig.11) also used in this studies t and may be represented by:

$$q_e = \frac{RT}{\Delta Q} \ln K_T + \frac{RT}{\Delta Q} \ln C_e \tag{9}$$

Where K_T is the Temkin constant (L/mg), ΔQ is the energy variation (J.mol⁻¹), R is the ideal gas constant 8.31447 (J.mol⁻¹.k⁻¹), T is the temperature (K).

Temkin isotherm contains a factor which takes into account explicitly the adsorptive interactions of species of adsorbents [20].

The values of the parameters q_m, K_L, R_L, K_F, 1 / n, K_T, Aq and R² for the removal of methylene blue are given in Table 2.

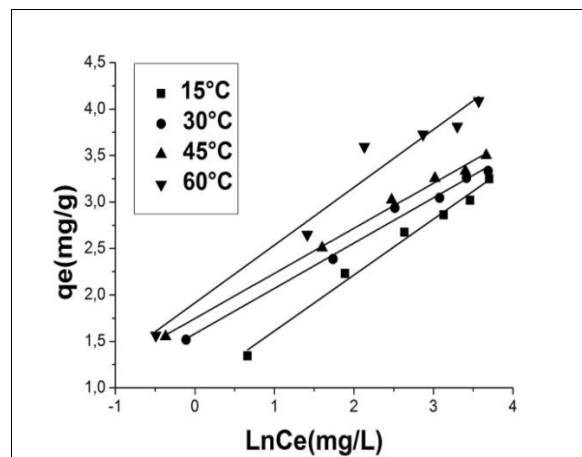


Fig.11. Temkin isotherm of MB on WCJ at different T°C (C₀=10-60 mg / L; t = 180 min; biosorbent dose =6g/L).

By adjusting the experimental points on the three isotherm models, it appears that the Langmuir model best describes the adsorption type involved. And from the R_L value obtained we can conclude that the process is favourable (0 < R_L < 1). Thus, the molecules of the dye may be adsorbed monolayers, without any dye-dye interactions. This hypothesis is reinforced by the thermodynamic results which indicate that during adsorption the order increases to give, ultimately, a organized distribution of dye molecules at the adsorption sites.

Table2. Parameters isotherms for the removal of MB dye.

Langmuir				
T (C°)	K _L (L/mg)	q _m (mg/g)	R _L	R ²
15	0.314	3.46	0.050-0.241	0.991
30	0.173	3.47	0.087-0.366	0.992
45	0.140	3.59	0.106-0.415	0.992
60	0.090	4.20	0.144-0.501	0.997
Freundlich				
T (C°)	K _F ((mg/g)(l/mg) ^{1/n})	1/n	R ²	
15	1.202	0.278	0.959	
30	1.603	0.210	0.978	
45	1.734	0.202	0.979	
60	1.866	0.235	0.947	
Temkin				
T (C°)	K _T (L/mg)	ΔQ (kJ/mol)	R ²	
15	5.359	3.982	0.989	
30	25.750	5.170	0.990	
45	36.598	5.448	0.995	
60	21.769	4.456	0.961	

3.4. adsorption Thermodynamics

Thermodynamic behavior of the biosorption of MB on WCJ is evaluated by the thermodynamic parameters. These parameters, such as the change in Gibbs energy (ΔG), the enthalpy change (ΔH) and entropy (ΔS , reflect the feasibility and spontaneous nature of adsorption process [21].

The thermodynamic relationship $\Delta G = \Delta H - T\Delta S$ associated with the relationship Vant'Hoff $\Delta G = -RT \ln K_d$ [22] allows us to reach the Eyring equation [23]:

$$\ln k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)$$

Where, R is the ideal gas constant 8.31447 (J.mol⁻¹.k⁻¹), T is the absolute temperature (K), $K_d = C_{ad}/C_e$ is the distribution coefficient, and C_{ad} is the concentration of MB dye adsorbed (mg/L).

A plot of $\ln k_d$ versus $1/T$ is linear (Fig.12). The Values ΔG , ΔH , ΔS and R^2 for the removal of methylene blue are given in Table 3.

The negative value of ΔG indicates the biosorption is favorable and spontaneous. The positive value of change in enthalpy (ΔH) indicates the endothermic nature of adsorption process. The positive (ΔS) value suggests the increased disorder and randomness at the solid interface of MB with the adsorbent. Provides positive value implies that the conscious choice.

The increase of adsorption capacity of the biosorbent at higher temperatures was due to enlargement of pore size and activation of adsorbent surface [24]

From these results, we can conclude that the adsorption of methylene blue on WCJ was favorable.

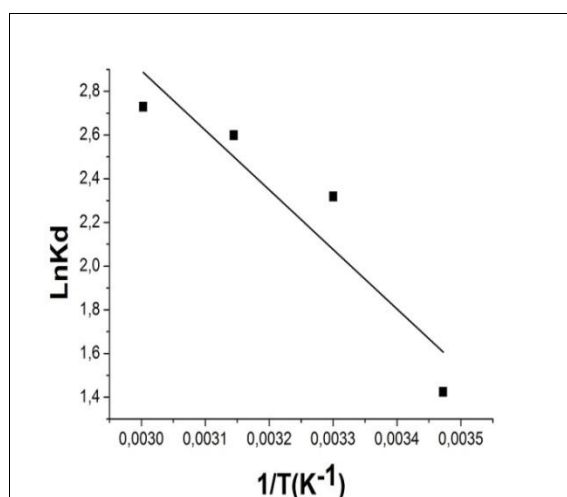


Fig.12. Plot of $\ln K_d$ vs. $1/T$ for adsorption of MB on WCJ.

Table 3. Thermodynamic parameters for the adsorption of MB by WCJ

T (k)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (j.mol ⁻¹ .k ⁻¹)	R
288	-3.407	22.653	91.99	0.877
303	-5.836			
313	-6.867			
323	-7.551			

IV. CONCLUSION

The parameters such initial dye concentration, contact time and temperature have shown significant effect on the removal of MB by CWJ from aqueous solutions.

The Langmuir, Freundlich and Tempkin isotherm models were used for the mathematical description of the biosorption equilibrium of MB onto CWJ. The 1 Langmuir isotherm model was found to provide the best fit of the experimental data in the temperature range studied.

The Kinetic studies showed that the adsorption process followed the pseudo-second-order model.

The thermodynamic results indicated the feasibility, endothermic and spontaneous nature of the adsorption process involved at 15–60 °C.

The various results obtained indicated that the adsorbent chosen for this study was efficient and could be used as an economical sorbent for the industrial effluents.

REFERENCES

- [1] M.Bagane, S. Guiza, Ann.Chim.Sci.Mater.25 (2000) 615.
- [2] F.Perineau, J.Molinier, A.Gaset, Water Res. 17 (1983) 559.
- [3] KACHA S., Z. DERRICHE et S. ELMALEH (2003). Equilibrium and kinetics of color removal from dye solutions with bentonite and polyaluminum hydroxide. Water Environ. Res., 75, 15-20.
- [4] YU R., L. YEH et A. THOMAS (1995). Color removal from wastewater by adsorption using powdered activated carbon: mass transfer studies. J. Chem. Technol. Biotechnol.,63, 48-55.
- [5] HO Y.S. G. MCKAY (1998). Kinetic models for the sorption of dye from aqueous solution by wood. Trans IChemE, 76,183-191.
- [6] OFOMAJA A.E. (2007). Kinetics and mechanism of methylene blue sorption onto palm kernel fibre. Proc. Biochem., 42,16-24.
- [7] Removal of Methylene Blue Dye (Basic Dye) from Aqueous Solution using Saw Dust as an Adsorbent. D. A. Nimkar S. K. Chavan Vol. 3 Issue 4, April – 2014 (1579-1583) International Journal of Engineering Research & Technology (IJERT)
- [8] Equilibrium and thermodynamic studies for dye removal using biosorption narayana saibaba k v & p. king international journal of research in engineering & technology (impact: ijret) vol. 1, issue 3, aug 2013, 17-24
- [9] Dutta, S., Bhattacharyya, A., Ganguly, A., Gupta, S., & Basu, S. (2011). Application of response surface methodology for preparation of low-cost adsorbent from citrus fruit peel and for removal of methylene blue. Desalination, 275, 26–36.
- [10] G. Chen, J. Pan, B. Han, H. Yan, Journal of dispersion Science and Technology, 20 (1999) 1179-1187
- [11] Aerdizzone. S, Gabrielli. G, Lazzari. P, Adsorption of methylene blue at solid/liquid and water/air interfaces, Colloids Surface, 76, pp 149-157, 1993.
- [12] K.R.Hall; L.C.Eagleton, A.Acrivios, T.Vermeulen, Ind.Eng. Chem. Fundam, 5,212, (1966).
- [13] M.Minamisawa, H.Minamisawa, S. Yoshida, N. Takai, Adsorption behavior of heavy metals in biomaterials, J. Agr. Food Chem. 52 (2004)5606–5611.
- [14] J.E. Lousada Jr., J.M.C. da Costa, J.N.M. Neiva, N.M. Rodriguez, Caracterizac , ~ ao f isico-qu imica de subprodutos obtidos do processamento de frutas tropicais visando seu aproveitamento na alimentac , ~ ao animal, Rev.Cienc. Agron 37 (2006) 70–76.
- [15] DEGLISE, X., « La pyrolyse du bois, Revue du palais de la découverte » 13 (1985) 51-67.
- [16] Bouhamed F, Elouear Z, Bouzid J. Adsorptive removal of copper (II) from aqueous solutions on activated carbon prepared from Tunisian date stones: Equilibrium, kinetics and thermodynamics .

- Journal of the Taiwan Institute of Chemical Engineers 2012; 43: 741-749.
- [17] W.J.Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit.Eng. Div. Am. Soc. Civ. Eng. 89 (1963) 31-60.
- [18] EC Chitour, Surface chemistry, introduction to catalysis, 2nd Edition, Algeria (1981).
- [19] K.R.Hall; L.C.Eagleton, A.Acrivios, T.Vermeulen, Ind.Eng. Chem. Fundam, 5, 212,(1966).
- [20] P.lafrance and M.Mazet « Rétention des substances humiques sur un charbon activé en poudre, Etude de la modification de quelques caractéristiques physico-chimique du milieu lors de la l'adsorption », French reviewed the Water Sciences, No. 5, PP.291-310, 1986.
- [21] E. Demirbas, M.Z. Nas, Batch kinetic and equilibrium studies of adsorption of Reactive Blue 21 by fly ash and sepiolite, Desalination 243 (2009) 8-21.
- [22] Boureghda M.M. « valorisation d'un déchet alimentaire le marc de café, transformé en charbon actif. Etude de son comportement dynamique lors de l'adsorption des colorants textiles »
- [23] Chakir A.,bessiere J.,ELkacemei K,Marouf B.(2002)-A comparative study of the removal of trivalent chromium aqueous solutions by bentonite and expanded perlite.journal of hazardous matériakls,95,29646.
- [24] Vadivelan, V. and K. Vasanthkumar, 2005.Kinetics of crystal violet from aqueous solutions using different natural materials.J. Colloid Inter. Sci., 91: 286.

IJERT