Adsorption of methylene blue in solution on activated carbon based of banana peels residue

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Abstract— Activated carbon is considered as one of the most used materials in the field of wastewater treatment, several studies have shown the purifying efficiency of this material as an adsorbent to treat industrial dyes, these are characterized by their energy stability which returns them non-biodegradable, thus difficult to eliminate in the receiving environment which causes nuisance to the ecosystem namely the fauna and flora.

We have two aims during this work on the one hand to the valorization of a vegetable origin residue "the banana peels" by using it like an active charcoal and on the other hand the study of a retention mechanisms of the methylene blue in aqueous solution on this adsorbent material; the factors influencing the adsorption of this industrial effluent are studied, such as the contact time, the grain size, the adsorbent mass, the initial concentration of the substrate and the temperature of the reaction medium. The study of liquid-solid adsorption isotherms by using the Langmuir, Freundlich, Temkin and Elovich models allowed us to better understand the retention mechanisms of the adsorbent substrate and the determination of various equilibrium parameters, such as the maximum adsorption capacity, the adsorption energy, the interaction energy and the equilibrium constants of adsorbent and adsorbate.

keywords: Adsorption, methylene blue, calcinated banana peels, Adsorption kinetics and Adsorption isotherms.

1 Introduction

The industrial textile sector in Morocco generates several types of chemical pollution in most are synthetic dyes[1], these industrial effluents discharged into the aquatic system without treatment or with an insufficient level of treatment require prior treatment to reuse them and protect the environmental system. Various types of treatment are focused on the purification of industrial effluents including chemical [2], physical [3] and biological treatment techniques [4].

In addition, the adsorption is considered as one of the promising techniques for industrial water treatment [5]; because of their cost and reliability to treat these industrial discharges.

Activated carbon is considered as the best adsorbent material used in the context of industrial waste water treatment, its expensive cost has prompted researchers to develop adsorbents based plant debris; the peels of oranges [6], the pods of peanuts [7], eggshells [8], Banana Peels [9].

The main purpose of this work is the development of an active carbon from a Banana skins debris to purify an industrial effluent methylene blue in aqueous solution, thus we will study the adsorbent capacity of this new material by considering the factors that influence the adsorption mechanism. Kinetic modeling and the adsorption isotherms study have allowed us to better understand and assimilate the adsorbent retention mechanism.

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2 Materials and methods

2.1 Materials

The adsorbent used in this work is an active carbon made from banana peels. The collection site of plant residue; garbage containers of wholesale market in vegetable and fruit from Casablanca, whose elaboration go through several stages: since the collection of debris, washing with distilled water, drying in the open air for 15 days, shredding, calcination at a temperature of 700 ^{0}C, grinding with the mortar and finally sieving to obtain the desired fraction of carbon.

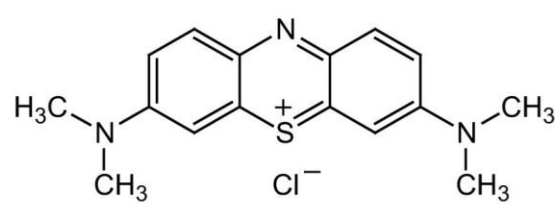

Figure 1: Molecular structure of the methylene blue.

The dye used in this study is methylene blue of very high purity. The Figure 1 shows the molecular structure of methylene blue and the main characteristics of this dye are presented in the Table 1.The initial solution of methylene blue has a concentration of 100 mg.L^{-1} , has been prepared by dissolving 100 mg of this dye in the distilled water, as well as the solutions of manipulation have been prepared by dilution of the initial solution with the distilled water.

Table 1: Characteristic principle of the Methylene blue.

IUPAC name	bis- (dimethylamino) - 3,7 phenazathionium chloride
synonyms	C.I. Basic Blue 9
Formule brute	$C_{16}H_{18}ClN_3S$
Molar mass	319.852 ± 0.022 (g · mol−1)
T fusion	decomposition at 180 °C
Solubility	50 g · L−1 eau à 20 °C
The PubChem Compound Identifier	6099

2.2 Methods

Experimentation of the adsorption kinetics of the various factors that influence the adsorption mechanism; (particle size, agitation rate, adsorbent mass and substrate concentration) thus adsorption isotherms (Langmuir, Freundlich, Temkin and Elovich models) have been performed in continuous mode; which involves contacting the methylene blue in aqueous solution with our support and follow the evolution of the residual concentration of our dye in static and dynamic mode according to the experimental conditions studied.

The tests have been carried out in static reactors by stirring 100 ml of methylene blue solution of initial concentration C_0 (expressed in mg.l^{-1}) at room temperature, with different chosen masses of our study material. After a given stirring time, the samples taken are decanted and then measured using a UV-6300 PC UV-visible spectrometer at the appropriate wavelength of the methylene blue (λ_{max} = 664 nm).

The absorbed quantity of methylene blue is expressed by Equation 1:

$$q_e = (C_0 - C_e)V/M \quad (1)$$

- V: The volume of solution (L),
- M: Mass of adsorbent solid (mg),
- C_0: The initial concentration of methylene blue in the liquid phase (mg.L-1).

3 Results and Discussions

This part presents the different results obtained during the study of the adsorption of Methylene Blue on the calcinated banana peels:
- The main factors that influence the adsorption mechanism.
- The study of adsorption isotherms.

3.1 Factors affecting adsorption of dye

3.1.1 Effect of particle size

The effect of particle size of the coal made from banana peels has been monitored as a function of time for a mass of 90 mg and an initial concentration of methylene blue of 10 mg.L-1 (See Figure 2). After a 20 minutes of contact, the elimination rate reaches 97 % (corresponds to 11mg.g-1) for the finer diameter particles (d_1 < 80µm) and only 32 % (corresponds to 4mg.g-1) when the grain size becomes higher (80µm < d_2 < 2mm). Adsorption depends on the external surface of our adsorbent; when the particle size is small, the larger the exchange surfaces provided; promoting a high rate of the substrate transfer to the adsorbent.

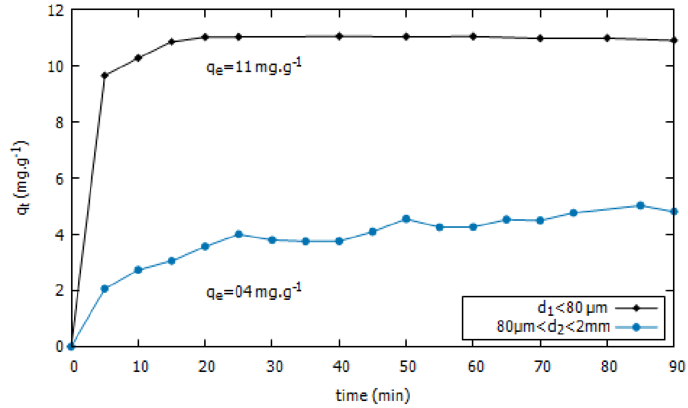

Figure2: Effect of particle size of calcinated banana peels on the adsorption of methylene blue (MB_{aq}) ; C_0=10 $mg.L^{-1}$,m_S=0.9 $g.L^{-1}$,V_{agi}=400 rpm and T=22 ^{0}C.

3.1.2 Effect of stirring

To study the effect of the stirring speed of the reaction medium on the adsorption of methylene blue MB_{aq} by our support (CBP: The calcinated banana peels), we have chosen to work with two different stirring speeds (V_1=400 rpm and V_2=2400 rpm).

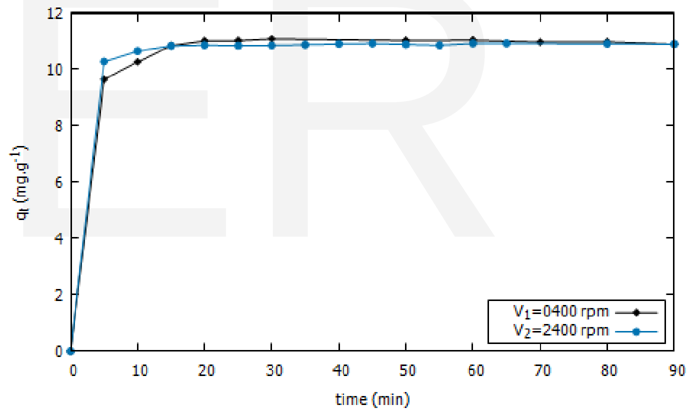

Figure 3: Effect of stirring rate on adsorption of methylene blue; C_0=10 $mg.L^{-1}$, m_S=0.9 $g.L^{-1}$, d "80 μm, V_{agi}=400 rpm and T=22 ^{0}C.

Figure 3 shows that the stirring speed chosen has no significant effect on the adsorption of our dye studied; these stirring speeds are enough to ensure the substrate transfer to the adsorbent site, subsequently we will choose to work with the lowest stirring speed (V_1 = 400rpm).

3.1.3 Effect of adsorbent mass

The effect of the mass of calcinated banana peels on the adsorption of methylene blue has been carried out for six different mass (40, 50, 60, 70, 80 and 90 mg) of the same particle size (d_1 = 80 µm).
- The rate of elimination increases with the mass of calcinated banana peels.
- After 40 minutes of contact, the adsorption yield reachs 82% (correspond to 20 mg.g -1) for the adsorbent mass 40 mg to 99.4 % (correspond to 11mg.g-1) for the largest mass of 90 mg;

when the adsorbent mass increases, the more sites are important to acquire the substrates.

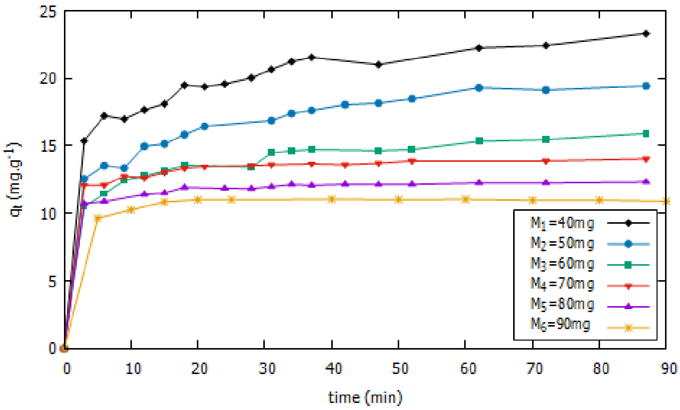

Figure 4: Effect of calcinated banana peels mass on the adsorption of methylene blue; C_0=10 $mg.L^{-1}$, V=100 mL, d_1=80 μm, V_{agi}=400 rpm and T=22 ^{0}C.

3.1.4 Effect of initial dye concentration

The initial concentrations of Methylene Blue selected in this study should not exceed certain concentrations, so that they do not interfere with the adsorption phenomenon.

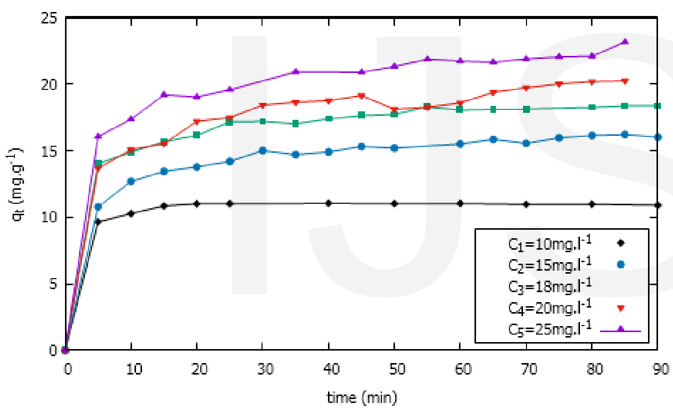

Figure 5: Effect of initial concentration of methylene blue in adsorption oncalcinated banana peels; m_S=0.9g.L−1, d_1< 80μm, Vagi=400rpm and T=22 °C.

The shape of these curves (Figure 5) shows that the amount absorbed at equilibrium for the different initial concentrations of Methylene Blue (10, 15, 18, 20 et 25 mg.L-1) decreases with the decrease of the initial concentration, the latter reaches a maximum adsorption yield of 99.4 % (correspond to 11mg.l^{-1}) after an equilibrium time of 20 minutes for an initial concentration of methylene blue of 10 mg.L-1, which shows that any increase of the initial concentration requires the good choice of adsorbent mass to avoid any loss of yield during the adsorption process.

4. Adsorption kinetics

The parameter order is very important to establish kinetics and models that describe the MB adsorption isotherms on CBP and checks if methylene blue is adsorbed well on the PBC adsorbent. It has allowed us to determine both the time needed to reach the adsorption equilibrium and determine the equilibrium constants adsorption of methylene blue. The most cited orders of reactions in the literature study of liquid-solid adsorption phenomena are:

- The pseudo first order reaction,
- The pseudo second order reaction.

4.1 Application of pseudo-first-order model on dye adsorption

The first-order reaction expressed by Lagergren's [10] Equation 2:

$+ dqt/dt= k_{1app} \cdot (q_e - q_t)$ (2)

The integration of Equation 2 between time t_0 and t, makes it possible to obtain the following expression (Equation 3):

$\ln (q_e - q_t) = \ln q_e - k_{1app} .t$ (3)

The plot of $\ln (q_e-q_t)$ as a function of time gives the straight line of slope equal to $-K_{1app}$ and the intercept equal to $\ln (q_e)$.

The results of different values of the first-order model are presented in Table 2.

Table 2: Pseudo first order parameters of adsorption of methylene blue on calcinated banana peels (CBP).

Model	parame-ters	10 mg.L−1	15 mg.L−1	18 mg.L−1	20 mg.L−1	25 mg.L−1
pseudo first order	K_{1app}	0.0576	0.0368	0.0642	0.0433	0.0281
	q_e(calc)	0.6732	5.6277	8.6928	9.5020	7.9066
	r^2	0.6521	0.9087	0.8605	0.8171	0.8005

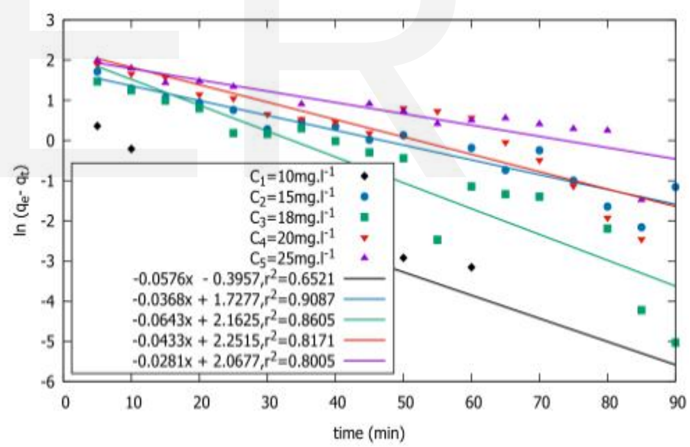

Figure 6: Application of pseudo-first order model of adsorption of methylene blue on calcinated banana peels (CBP).

4.2 Application of pseudo-second-order model on dye adsorption

The second order model is based on the solid phase adsorption capacity. It is generally used to describe chemisorption type of adsorption phenomena.

The pseudo-second order model can be represented by the following Equation 4:

$+ dq_t/dt= k_{2app} \cdot (q_e - q_t)^2$ (4)

The integration between time t_0 and t leads to Equation 5:

$1/q_t= 1/q_e + (1/ k_{2app}. q_e^2).1/t$ (5)

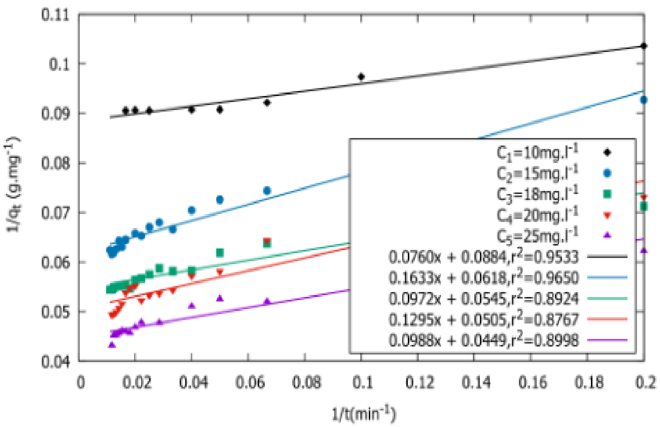

Figure 7: Application of the pseudo-second order model of methylene blue adsorption on calcinated banana peels.

The second pseudo model is better apply compared to the first order, this amplify show that the adsorption of methylene blue on our adsorbent is a chemisorption.

Table 3: Pseudo second order parameters of adsorption of methylene blue on calcinated banana peels.

Model	parameters	10 mg.L−1	15 mg.L−1	18 mg.L−1	20 mg.L−1	25 mg.L−1
Pseudo-second order	K_{2app}	0.103	0.023	0.031	0.020	0.020
	qe(calc)	11.312	16.181	18.349	19.802	22.272
	r^2	0.953	0.965	0.892	0.877	0.900

5. Adsorption isotherms

The adsorption isotherms in this study play an important role to determine the following parameters:

- The maximum adsorption capacities q_m.
- The constants of the adsorbate - adsorbent equilibrium.
- Identification of the adsorption type.

5.1 Langmuir model

The classic Langmuir model is presented by Equation 6 [11]:

$q_e/q_m = K_LC_e\ 1 + K_LC_e$ (6)

The integration of Equation 6 allows to obtain the following expression (Equation 6):

$1/q_e = (1/K_L \cdot q_m)1/C_e + 1/q_m$ (7)

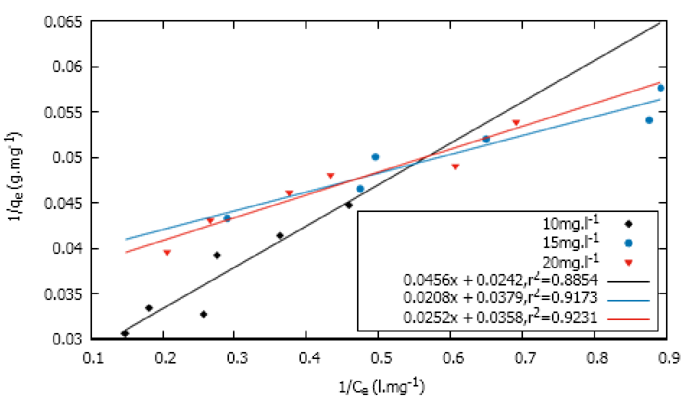

Figure 8: Application of the Langmuir model for the adsorption of methylene blue on calcinated banana peels.

A dimensionless constant separation factor R_L is used to express the essential characteristics of the Langmuir isotherm, which is given by:

$R_L = 1/(1 + K_L \cdot C_0)$ (8)

Where K_L (L.mg-1) is the Langmuir constant and C_0 (mg.L-1) is the initial concentration in the liquid phase. R_L represents the dimensionless parameter of the equilibrium or adsorption intensity.

The value of K_L indicates the adsorption isotherm model of characteristics as follows: $K_L>1$ (unfavorable); $R_L=1$ (linear); $0<R_L<1$ (favorable) and $R_L=0$ (irreversible).

For adsorption of MB onto the CBP in this study, all the R_L values listed in Figure 9 are in a range of 0.1686–0.0378, which indicate that the adsorption is a favorable process.

Table 4: Langmuir parameters of adsorption of methylene blue on calcinated banana peels.

Model	parameters	10 mg.L−1	15 mg.L−1	20 mg.L−1
Langmuir	q_m	41.3288	26.4036	27.9490
	K_L	0.5307	1.8245	1.4201
	r^2	0.8854	0.9173	0.9231

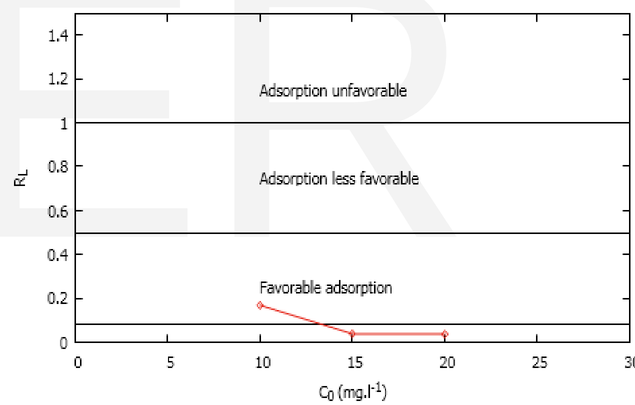

Figure 9: Evolution of R_L according to the initial concentration in methylene blue.

5.1 Freundlich model

The empirical model of Freundlich [12] is described by Equation 9:

$q_e = K_F \cdot C_e^{(1/n)}$ (9)

Figure 10 shows the linearization form of the Frendlich isotherm.

$\log q_e = \log K_F + 1/n \cdot \log C_e$ (10)

The maximum adsorption capacity q_m has been calculated from the Freundlich parameters (K_F et n) by Equation 11:

$K_F = q_m/(C_0)^n$ (11)

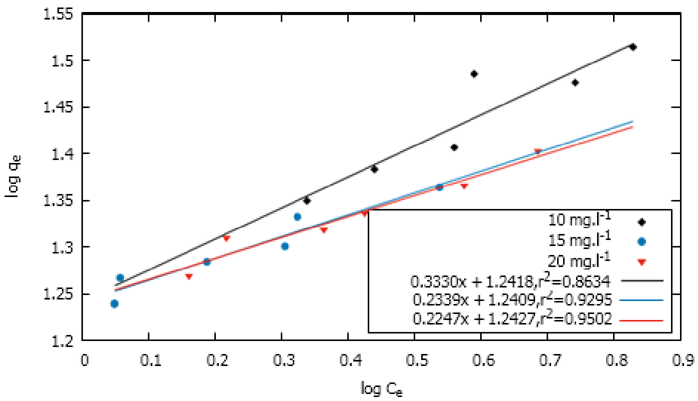

Figure 10: Application of the Freundlich model for the adsorption of methylene blue on calcinated banana peels (CBP).

Table 5: Freundlich parameters of the adsorption of methylene blue on calcinated banana peels (CBP).

Model	parameters	10 mg.L−1	15 mg.L−1	20 mg.L−1
Freundlich	q_m	37.6578	32.8048	34.2752
	K_F	17.4518	17.4121	17.4860
	n	0.3330	0.2339	0.2247
	r^2	0.8634	0.9295	0.9502

5.1 Elovich model

The Elovich model assumes that the number of available sites varies exponentially during adsorption, which implies multilayer adsorption.

$\theta = q_e/q_m = K_E \cdot C_e \cdot \exp(-(q_e/q_m))$ (12)

The linearization of Equation 12 makes it possible to obtain the following expression:

$\ln(q_e/C_e) = -1/q_m \cdot q_e + \ln(K_E \cdot q_m)$ (13)

The different parameters of the Elovich model are presented in Table 6. It can be seen from Table 6 that:

- The values of the Elovich constant K_E vary in a random manner as a function of the initial concentration of methylene blue, which shows that it is not a multilayer adsorption.

Table 6: Elovich parameters of the adsorption of methylene blue on calcinated banana peels (CBP).

Model	parameters	10 mg.L−1	15 mg.L−1	20 mg.L−1
Elovich	q_m	17.1389	6.7440	6.7507
	K_E	2.0749	32.3285	31.1321
	r^2	0.7002	0.8885	0.9188

5.1 Temkin model

$\theta = q_e/q_m = R \cdot T/\Delta Q \cdot \ln(K_T \cdot C_e)$ (14)

The linear form of the Temkin isotherm [13] is given by Equation 15:

$q_e = B_T \ln C_e + B_T \ln K_T$ (15)

With:

- R: The perfect gas constant (8.314 $J.mol^{-1}.K^{-1}$),
- T: The absolute temperature (Kelvin),
- ΔQ: The variation of adsorption energy ($J.mol^{-1}$),
- K_T : The constant of Temkin ($L.mg^{-1}$),
- $B_T = q_m RT/\Delta Q$.

The values of Temkin are given in Table 7. The values of the adsorption energy ΔQ have been calculated from the values q_m extracted of the Langmuir isotherm application Equation 16:

$C_e/q_e = 1/q_m \cdot C_e + 1/q_m K_L$ (16)

Table 7: Temkin parameters of the adsorption of methylene blue on calcinated banana peels (CBP).

Model	parameters	10 mg.L−1	15 mg.L−1	20 mg.L−1
Temkin	K_T	5.4972	36.5020	57.5300
	ΔQ	11.2537	13.8068	16.4785
	r^2	0.8594	0.8553	0.9218

From the results presented in Table 7 we find that:

- At low concentrations of methylene blue, the energy decreases linearly with the constant recovery rate, which justifies that the adsorbent surface is energetically homogeneous. ΔQ = 12.53 $kJ.mol^{-1}$.
- For high concentrations, the adsorbent surface is heterogeneous.

6 . Conclusion

The study of the adsorption of methylene blue on our material based on banana peels has shown that:

1. The effect of the different factors that can influence the adsorption capacity, proved that:
   - The adsorption capacity increases as the mass of calcinated banana peels increases.

The adsorption balance is fast for the small particle size.

2. The study of the adsorption balance of methylene blue on calcinated banana peels made it possible to deduct that:
   - The forms of the curves qe = f (C_e) show that the isotherm is of Langmuir form (L),
   - The Langmuir model adequately describes the adsorption phenomenon of methylene blue on calcinated banana peels.
   - The exploitation of the Langmuir models made it possible to deduct certain parameters; the maximum adsorption capacities and the adsorbate-adsorbent equilibrium constants. To deepen our work, we have studied other models of Temkin and Elovich which showed that:

     - The adsorption is done in monolayer (Elovich model),

     - The surface and heterogeneous of our material (calcined banana skins), this is applied for the adsorption of methylene blue in low concentrations (Temkin model).

3. The study of the adsorption kinetics of methylene blue on calcinated banana peels (CBP), has shown that the pseudo-second-order kinetic model correctly describes the decisive stage of diffusion of the mass through our adsorbent, it is a chemisorption.

According to the experimental study conducted, it appears that the adsorption of methylene blue on the skins of calcined bananas gives better results, this leads us to use this adsorbent material in the treatment of industrial dyes.

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