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# Kinetic study of the adsorption of ethylene on shoots of corn blue

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## Abstract
This work allowed us to consider the Elimination of methylene blue as material plant shoots of corn-based adsorbent. We have characterized our material adsorbing by adsorption infrared from transformed of Fourier (FTIR) spectroscopy and microscopy analysis electronic scanning (SEM).In order to optimize the operating conditions of the adsorption process, various studies on the kinetics, capacity, weight, pH solutions and original on the corn stalks and concentration was conducted. Experimental isotherms of adsorption equilibrium results were validated accurately by models of Langmuir and Freundlich.

*Keywords*: corn, Adsorption, methylene blue, modeling, isotherm, modeling

## 1. Introduction
Water pollution is beginning to take alarming proportions for both terrestrial waters and seacoast. Several physicochemical methods have been proposed to treat contaminated waters. At the high cost of certain techniques, it seems appropriate to direct the activities of the national scientific research in the field of environment, to the development of economic techniques. Among these techniques, there is adsorption on activated carbon. This treatment was effective but in most cases expensive [1]. For this, several studies have been devoted to finding new materials that can replace the activated carbon. The use of biological resources such as bacteria [2], sawdust [3], algae [4] and shells [5] has emerged as a potential alternative to conventional treatment methods (physico-chemical): The clay minerals [6-7], china [8], bauxite [9], bagasse [10] and molasses [11-12]. This work aims to study the prospective elimination of methylene blue using as adsorbent material plant corn stalks.

## 2. Theoretical and experimental part:
*2-1 Adsorption isotherms*

The adsorption isotherm is a representation of the equilibrium distribution of adsorbate between the solid and the liquid phase. The final stage of the study is to model isotherms curves. In part, the models of Langmuir and Freundlich were tested.

*2-2 Modelling of adsorption isotherms*

a- freundlich model (van Bemmelen, 1988 [13] Freundlich, 1909 [14]) is the most commonly used. We consider that it applies to many cases, especially in the case of multilayer adsorption with possible interactions between the adsorbed molecules [15]:

$$\mathbf{q_e = K_F . C_{\ e}}$$

The most common form used is the plot in logarithmic scale variations $q_e$ according to $C_e$ :

$$\mathrm{Log}\,(q_e) = \log\,(K_F) + n \log\,(C_e)$$

The constant n (adimentionelle) gives an indication of the intensity of adsorption. It is generally accepted that:

*0.1<n<0.5 characteristic of a good adsorption
*0.5<n<1 characteristic of a moderate adsorption
*n>1 characteristic of a weak adsorption
b- Langmuir model is based on assumptions well known. The initial assumptions are that the solid adsorbent has a limited adsorption capacity ($q_m$), all active sites are identical, they can only complex solute molecule (monolayer adsorption) and there are no interactions between adsorbed molecules. This model can be expressed by equation (1):

$$\frac{q_e}{q_m} = \theta = \frac{K_l C_e}{1 + K_l C_e} \quad (1)$$

| **Tableau 1:** Principal equilibrium models | | | |
|---|---|---|---|
| Isotherms | Non linear expression | Linear expression | curve |
| Langmuir | $q_e/q_m = \theta = K_L . C_e / (1 + K_L . C_e)$ | $1/qe = 1/(C_e . K_L . q_m) + 1/q_m$ | $1/C_e$ vs $1/q_e$ |
| Freundlich | $Q_e = K_F . C_e^{\ n}$ | $\mathrm{Log}\,(qe) = \log\,(K_F) + n \log\,(C_e)$ | Log $q_e$ vs log $C_e$ |

$K_L$, equilibrium constant of Langmuir
θ, recovery rate The development of equation (1) leads to the linear form of Langmuir isotherm
The ratio $R_L = 1 / (1 + K_L . C_0)$, unitless magnitude, indicates that:
The adsorption more favorable if $R_L$ tends to 0 Adsorption much worse if $R_L$ tends to 1

## 2-2 Experimental Study

### a- Product used

The dye used in this study was methylene blue of empirical formula (C16H18CIN3S, xH2O), or the number of water molecules is between 3 and 5.

### - Used adsorbent

The adsorbent that was used in this study is the stalks corn. Before its use corn stalks was washed with water, dried in oven at T = 50 ° C, crushed, grinded and sifted at the last step. It was characterized by our adsorbent material analysis techniques include:

### c- Analysis by scanning electron microscopy (SEM) shown in Figure (1.2).

The results of the composition of corn stalks are grouped in Table 2

### d- Adsorption spectroscopy Fourier transform infrared (FTIR), Figure 3.

A more detailed analysis of the infrared spectra is presented in Table 3 [16].
The results obtained show that the adsorbent material has a microporous structure with uniform distribution of pores. According to table the composition of the corn stalks, but we note that very important content of the adsorbent material is carbon and oxygen, we also note the presence of some elements such as close, and potash with variable levels, which are probably derived substances adsorbed by the corn stalks from the soil.

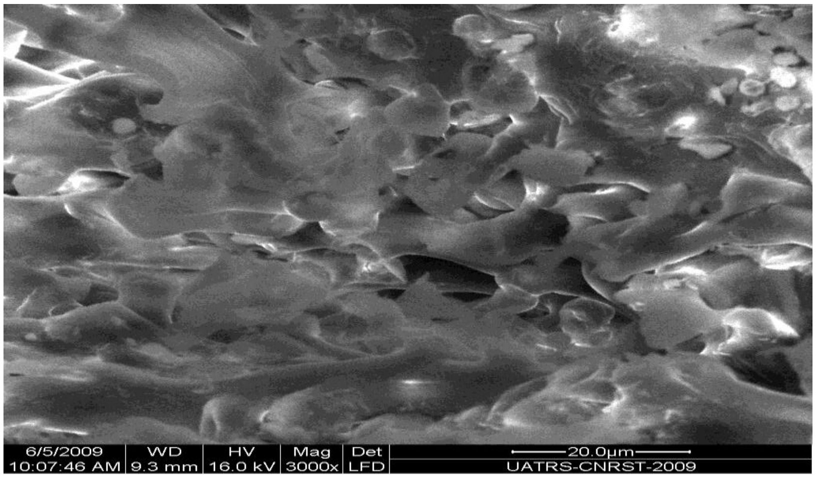



**Figure 1 :** SEM shot of the corn stalks.

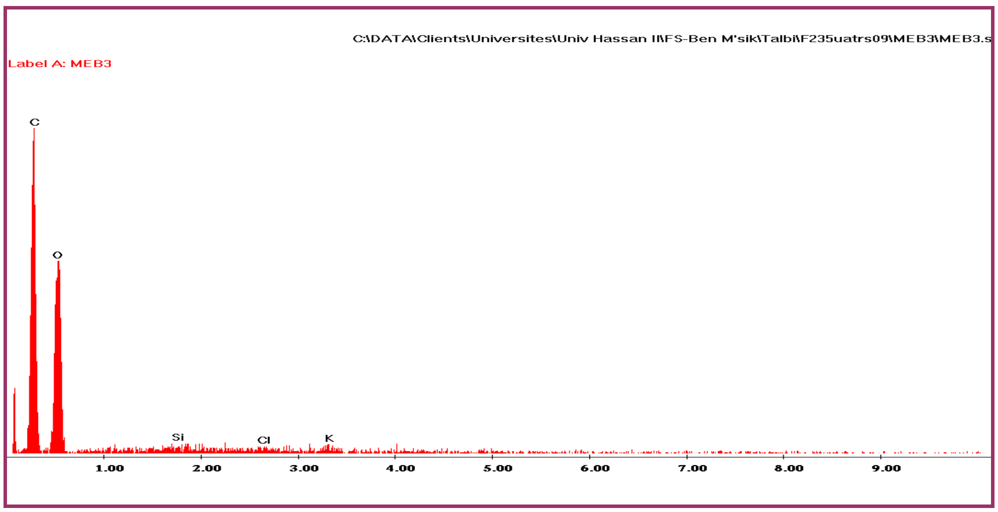



**Figure 2 :** Spectrum microanalysis X of the corn stalks.

**Table 1 :** Atomic composition mass % determined by electron microprobe X

| Elément | % massique |
|---|---|
| C | 63.19 |
| O | 36.16 |
| Si | 0.12 |
| Cl | 0.20 |
| K | 0.33 |

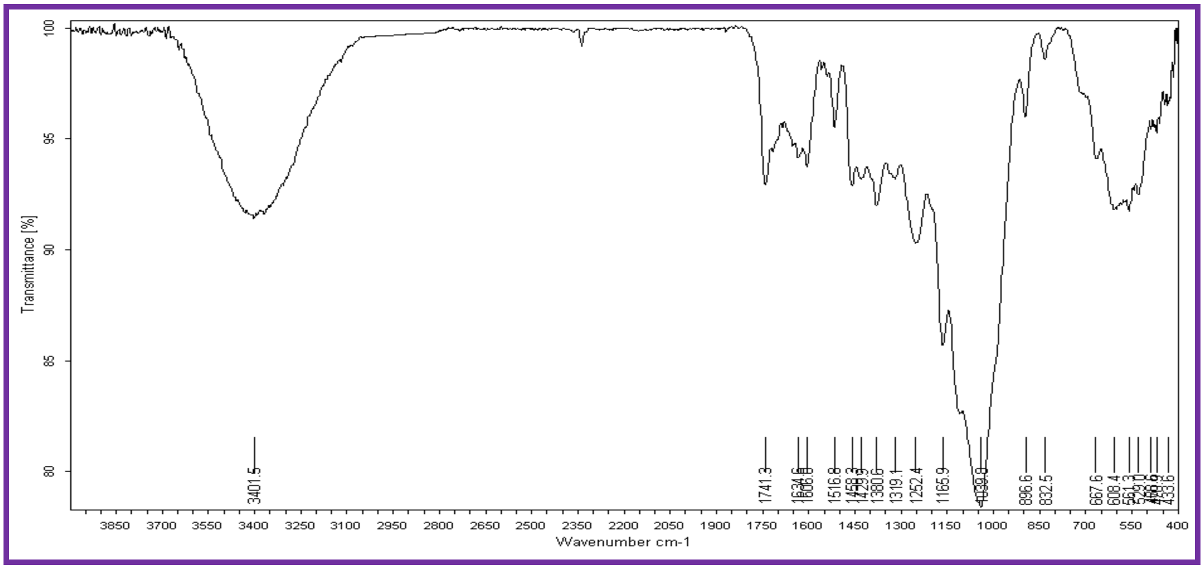



**Figure 3 :** Infrared Spectra of the stalks corn

**Table 2:** Interpretations of the Infrared Spectra of stalks corn [16]

| N° | Signals observed ($cm^{-1}$) | Interpretations |
|---|---|---|
| 1 | 597 | vinyl group |
| 2 | 808 | trisubstituted benzene: 1, 2,4 |
| 3 | 896 | CH aromatic outside the plane of deformation |
| 4 | 1033 | gr. guaiacyl CH, COH |
| 5 | 1057 | Vibration de valence. alcool sec.α-insaturé |
| 6 | 1157 | CH the aromatic within plane of deformation, guaiacyl type |
| 7 | 1266 | aromatic ethers, aliphatic alcohol, primary, secondary, tertiary, phenol, guaiacyl nucleus |
| 8 | 1317 | aliphatic chain |
| 9 | 1361 | C-H asymmetric deformation in CH3 |
| 10 | 1426 | aromatic skeletal vibration coupled with CH in the plane of deformation |
| 11 | 1460 | Asymmetric CH deformation in methyl, methylene and methoxyl |
| 12 | 1512 | asymmetric CH deformation in methyl, methylene and methoxyl |
| 13 | 1611 | Vibration. aromatic nucleus |
| 14 | 1660 | Vibration. valence. aryl-carbonyl - ketone |
| 15 | 1741 | gr. Ester |
| 16 | 3030 | vibration. valence. Aromatic C-H |
| 17 | 3400 | vibration. Valence. O-H intermolecular H bridge |

**Table 3:** Parameters of Langmuir adsorption of methylene blue in water by the corn stalks

| $C_0$ (mg/l) | $K_L$($L.mg^{-1}$) | $q_m$(en $mg.g^{-1}$) | $r^2$ | $R_L$ |
|---|---|---|---|---|
| **20** | 0.023 | 500 | 0.9858 | 0.684 |
| **30** | 0.095 | 111.111 | 0.983 | 0.087 |
| **40** | 0.1429 | 58.479 | 0.9718 | 0.149 |
| **60** | 0.313 | 29,154 | 0.9692 | 0.050 |

## 3. Results and discussions

In order to optimize process conditions for adsorption of methylene blue on corn stalks, we studied the influence of some factors which may be involved in the process of this phenomenon.

*3-1 Effect of parameters*

**a- Effect of pH**

The pH of the solution presents a parameter that has great influence on the retention of the dye. In our study we found that when the pH is between 6 and 8, better performance is obtained without precipitation of methylene blue.

**b- Mass Effect**

The adsorption kinetics of methylene blue with three different masses is shown in Figure 6. From these results, the biosorption is important for a mass of 4g/l of adsorbent material during a relatively short time.

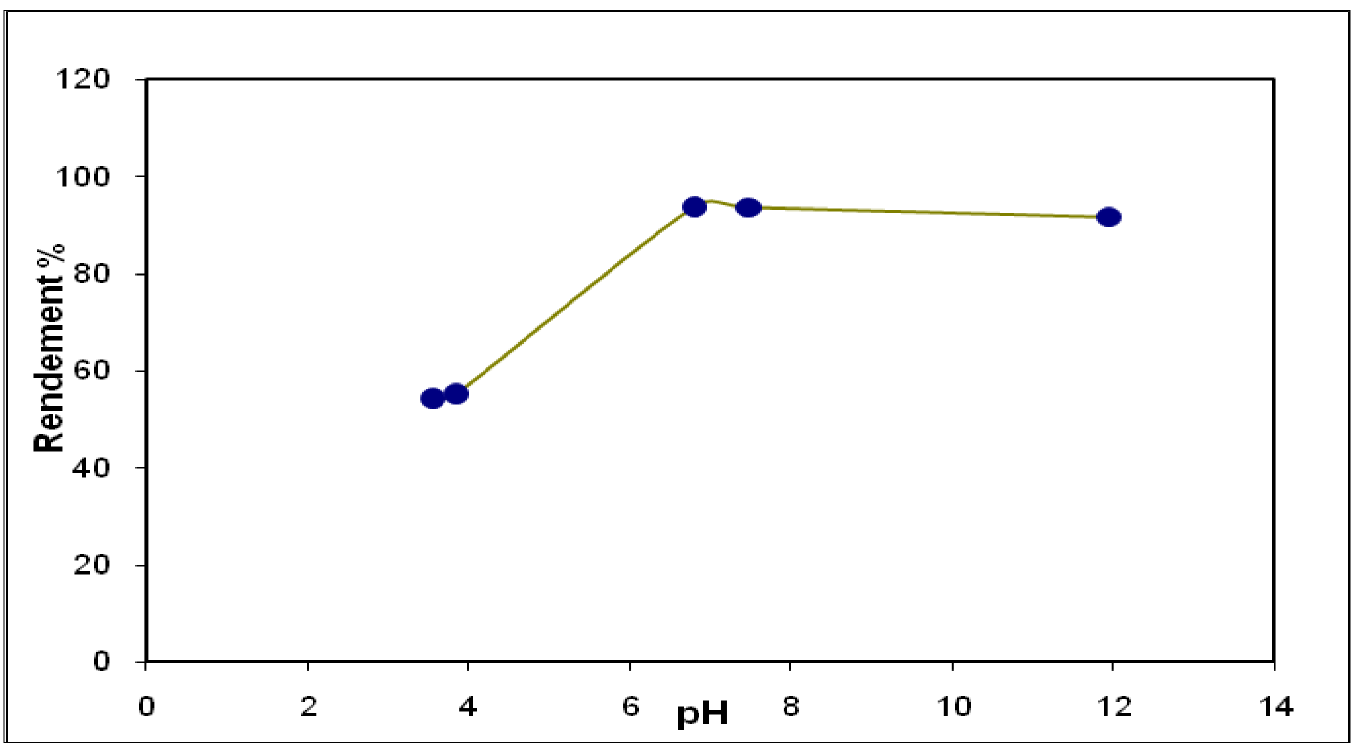



**Figure 5:** Effect of pH; m= 0,25 g/l , $C_0$= 10 mg/l, 0,2 <G<0.315 mm, T= 20 °C

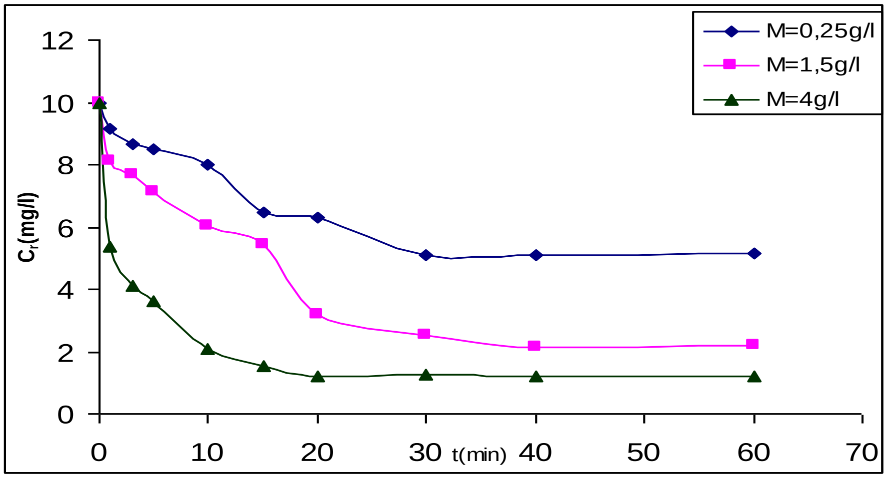



**Figure 6:** Mass Effect of the stalks corn $pH_{initial}$ = 6.8; $C_0$= 10 mg/l, 0,2 <G<0.315 mm, T= 20 °C

**c- Effect of particle size**
In this study we used three size fractions.
The adsorption kinetics of methylene blue is shown in Figure 7.
The adsorption capacity is better for a size range between 0.08 and 0.2. This is because the adsorption depends on the external surface of the adsorbent material increases with the fineness of its particles.

**d- Effect of initial concentration**
The figure 8 shows the adsorption kinetics of methylene blue at different initial concentrations. We notice a decrease in the residual concentration over time. After thirty minutes, it reaches a constant value whatever the initial concentration; this shows that the equilibrium time is independent of the initial concentration of the dye.

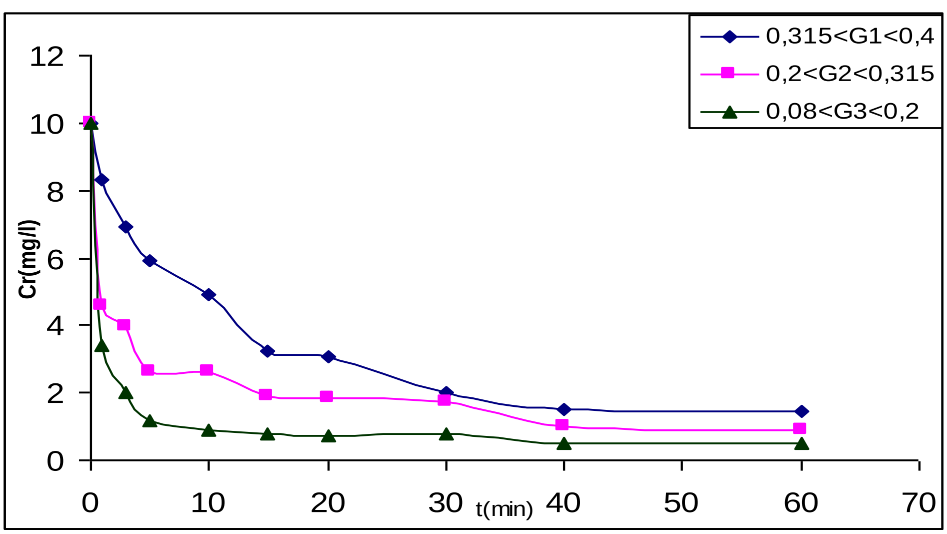



**Figure 7:** Effect of particle size of the stalks corn $pH_{initial}$ = 6.8; C0= 10 mg/l, m= 4g/l, T= 20 °C

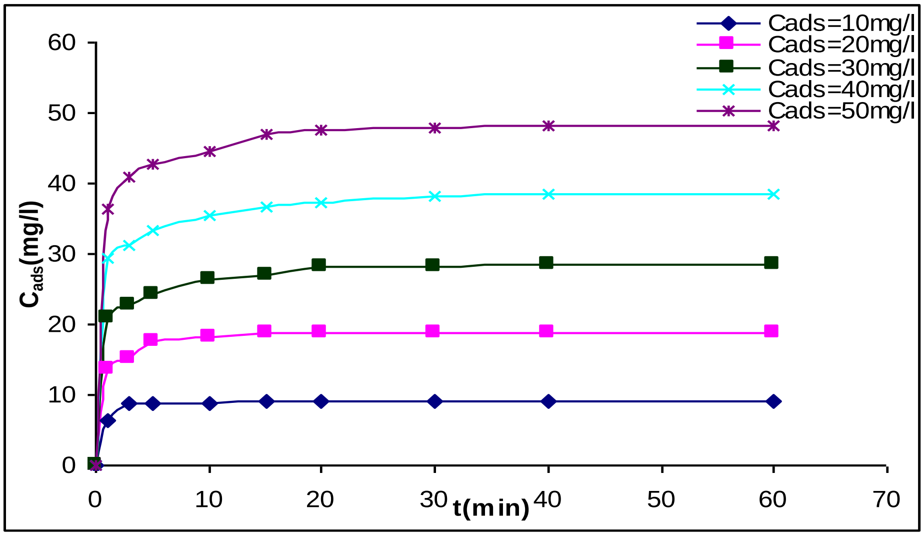



**Figure 8:** Effect of initial concentration of B.M $pH_{initial}$ = 6.8; 0,08 <G<0.2 mm, m= 4g/l, T= 20 °C

*3-2 Modelling of adsorption isotherms*

The experimental isotherms of adsorption equilibrium and maximum adsorption capacity (Figure 9) have been validated in detail by the Langmuir (Fig.10) and Freundlich model (Fig.11). The isotherms obtained were L-type according to the classification of Giles [21], which promotes a monolayer adsorption and the interaction between the adsorbate and the adsorbent is important.

**Discussions**

The results show that the maximum adsorption capacity ($q_{max}$) obtained from Langmuir model decreases with increasing the concentration value of the MB ($C_0$). It reaches its maximum value at $C_0$ = 20 mg / l. the adsorption is favorable ($R_L$ tends to 0) and moderate (0.5 < n <1).

The low values of maximum adsorption capacities obtained from the Freundlich model, confirm that the molecule of MB is not strongly adsorbed inside the pores because of its size. Only the surface functions are responsible for the adsorption

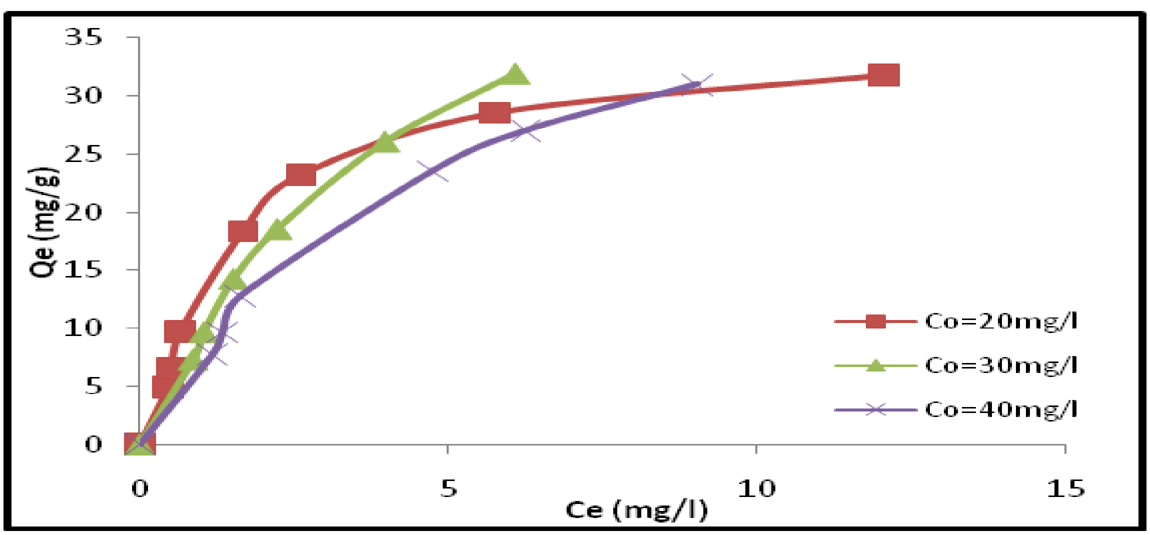



**Figure 9:** Adsorption isotherms of B.M on the corn stalks

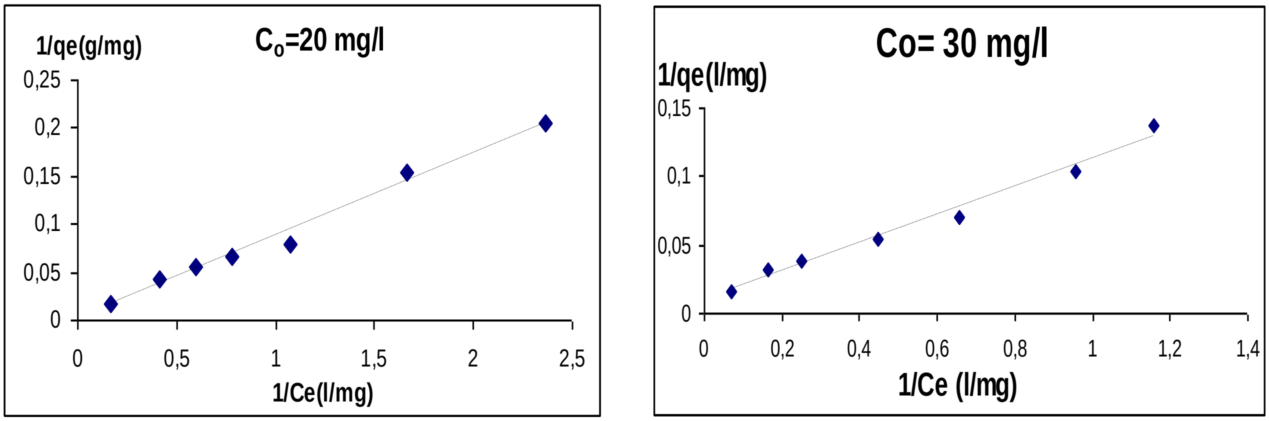



**Figure 10:** Transformed linear isotherms of Langmuir for the adsorption of the B.M knew the corn stalks.

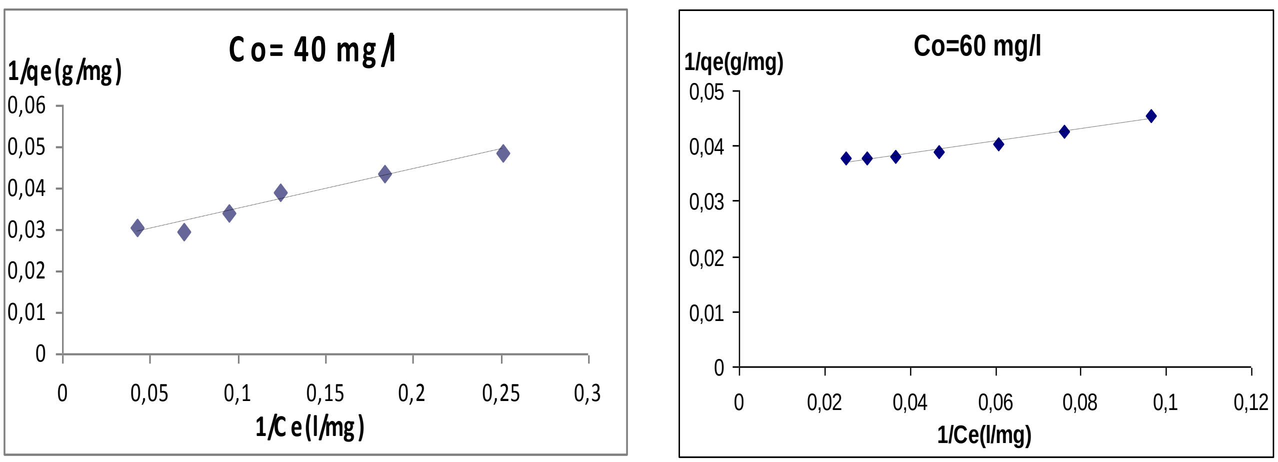



**Figure 10 bis:** Transformed linear isotherms of Langmuir for the adsorption of the B.M knew the corn stalks.

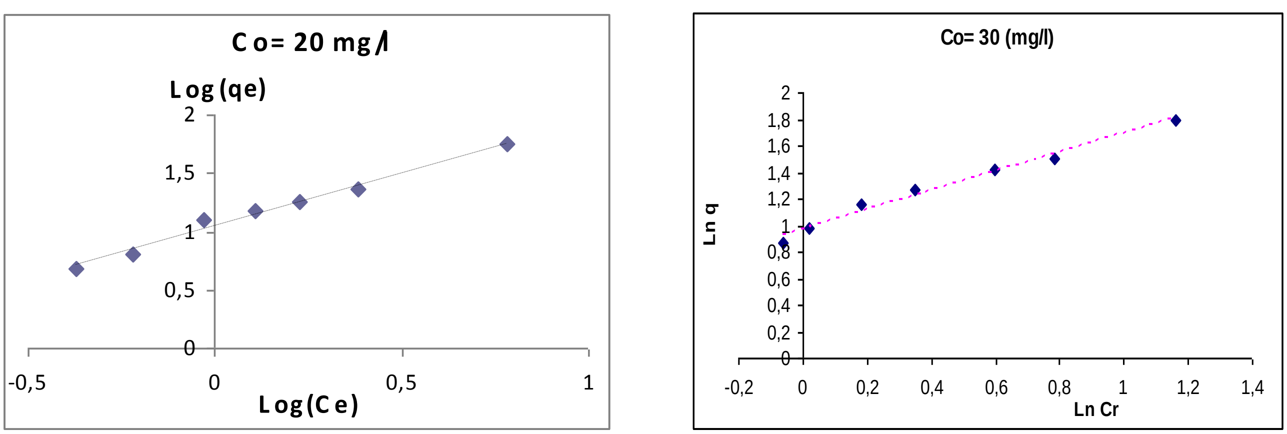
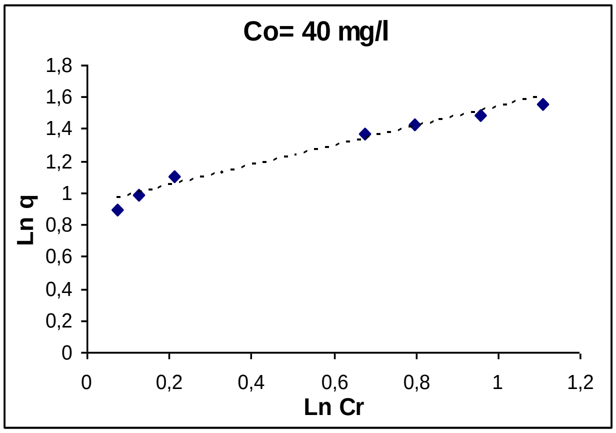



**Figure 11:** Transformed linear isotherms of Freundlich the adsorption of the B.M knew the corn stalks.



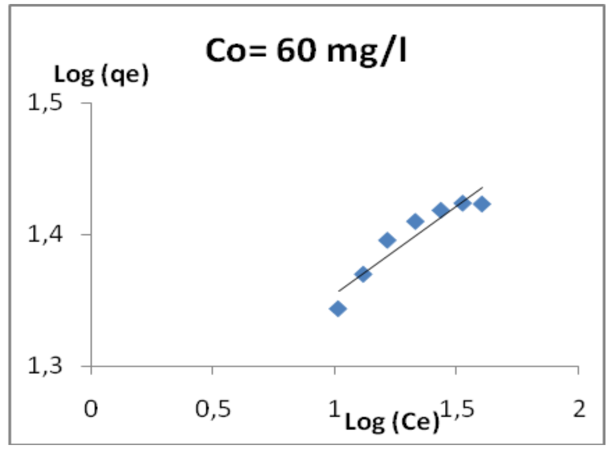




**Figure 11 bis:** Transformed linear isotherms of Freundlich the adsorption of the B.M knew the corn stalks.

**Table 4:** Parameters of FREUNDLICH adsorption of methylene blue in water by the corn stalks

| $C_0$(mg/l) | $K_F$ (en $mg^{(1-n)}L^ng^{-1}$) | n(sans unite) | $r^2$ | $q_m$(en $mg.g^{-1}$) |
|---|---|---|---|---|
| **20** | 2.867 | 0.901 | 0.985 | 42.624 |
| **30** | 2.643 | 0.715 | 0.983 | 30.077 |
| **40** | 2.50 | 0.617 | 0.9706 | 24.336 |
| **60** | 3.389 | 0.134 | 0.889 | 5.866 |

## Conclusion

From this study we can conclude that:

The analysis by SEM and IR showed that the adsorbent material has a microporous structure and it consists mainly of carbon and oxygen.

The equilibrium adsorption isotherms have been validated in detail by Langmuir and Freundlich models (correlation coefficients above 90%).

The low values of maximum adsorption capacities obtained from the Freundlich model, confirm that the molecule of MB is not strongly adsorbed inside the pores because of its size. Only the surface functions are responsible for adsorption.

A better performance is obtained if:

* pH is between 6 and 8
* A adsorbent mass is 4g/l
*A particle size is between 0.08 mm and 0.2mm
*The initial concentration of dye must not exceed 10 mg/l.

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