

# Adsorption studies of methylene blue on methanol modified and unmodified corn stalks and egussi peeling

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**Abstract**— The adsorption of methylene blue (MB) from aqueous solution using powdered corn stalks and egussi peeling was studied in batch mode. At room temperature, parameters such as contact time, biosorbent treatment, biosorbent mass, initial concentration of methylene blue, ionic strength and the pH were studied. The results obtained showed that, the equilibrium time is independent of the initial concentration of MB and is quickly achieved, at the tenth minute for corn stalks and the twentieth minute for egussi peeling. The biosorbents treated with methanol have the highest adsorption capacity. The minimal dosage of maximum adsorption on surface of biosorbents is 20 mg. Ionic strength significantly disfavors adsorption on these materials. The adsorption potential of MB is greater at basic pH: 12 for the corn stalks treated TMT and untreated TMB, 10 for egussi peeling treated CPT and untreated CPB. The adsorption of the dye obeys a first type isotherm with the Langmuir model best described generally with ultimate adsorption capacities of 200 and 166.67  $\mu\text{mol/g}$  for corn stalk treated with methanol and crude and of 90.90 and 47.42  $\mu\text{mol/g}$  for egussi peeling treated with methanol and crude respectively, with respective elimination of 90.21 %, 88.30 %, 83.74 % and 74.41 % rate for the same mass of 20 mg. The adsorption kinetics are consistent with the pseudo-second order

model showing that the adsorption process on these biosorbents is governed by chemisorption.

**Index Terms**— Adsorption, methylene blue, biosorbents, isotherms and kinetics

## I. INTRODUCTION

Environmental pollution (water, air and grounds) has become a major problem and remains a priority [1]. Textile industries use dyes or pigments to color their final products. For example, Methylene Blue (MB), which is most common among all other dyes of its category, is generally used for dyeing cotton and silk. Dyes are synthetic in origin, have complex aromatic molecular structures, inert and difficult to biodegrade when discharged into waste streams. The effluents of wastewater in some industries such as dyestuff, textiles, leather, paper, plastics contain various kinds of synthetic dyestuff [2]. The effluents of these industries are highly colored and the discharge of these wastes into receiving waters causes severe damages to the environment [3]. The introduction of waste products into the environment is an important problem that has been highlighted by various environmentalist groups [4]. The manufacture of dyes is based primarily on properties which they must respect such as, long lifespan of the products on which these dyes are built-in, the great abrasion resistance, photolytic stability, strong resistance to chemical oxidation and to the attacks of the micro-organisms, the affinity of the dyes with fiber on which they are built-in according to whether they are basic or acid. Methylene blue (MB) dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, painful micturition, and methemoglobinemia [5,6]. Therefore the treatment of effluent containing such dye is of interest due to its esthetic impacts on receiving waters. Several methods and techniques of remediation were developed during these last years to eliminate dyes from industrial water. This methods including coagulation [7], chemical oxidation [8], photocatalysis [9,10], electrochemical [11] and adsorption techniques have been examined. Among these methods, the adsorption onto activated carbon has been found to be superior compared to other techniques. However, commercially available activated carbons are still considered expensive [12]. This is due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution control applications [13]. Several

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researchers invested in research and the experimentation of new materials and the results proved satisfactory. The focus the research was to evaluate the adsorption potential of egussi peeling and corn stalk for basic dye. The kinetic data and equilibrium data of adsorption studies were processed to understand the adsorption mechanism of MB onto these various modified and unmodified biosorbents.

II. MATERIALS AND METHODS

1-Preparation of Adsorbent

Corn stalks was collected from a pre-consumer agricultural product process industry located at Dschang (West Region) and egussi peeling from Edéa (Littoral Region) both in Cameroon. The collected rice husk and egussi peeling were sun-dried and impurities were removed manually. Each of the materials was washed several times with distilled water for 1 hour under agitation and then filtered to make it free from colored compounds. The residual material so obtained was dried at 100°C in an oven for 24 hours, and then ground and sieved to obtain particles of size less than 250 µm. In the continuation, one part of sample was treated with methanol as follows: 4 g of powder of each type of biosorbent were treated in 80 mL of a methanol solution (water/methanol in ratio 9/1).

Adsorbents obtained were characterized by Infra-Red Fourier Transform Spectroscopy to identify the functional groups and chemical bonding on the adsorbents. The IR-FT was recorded in the wave number range 4000 cm<sup>-1</sup> – 500 cm<sup>-1</sup> using a Bruker, Alpha-P Spectrometer using Attenuated Total Reflectance method.

2-Adsorption Experiments

Adsorption experiments were carried out by mechanical agitation at room temperature. For each run, 15 mL of basic dye, of known initial concentration was treated with a known weight of treated and untreated biosorbents. After agitation for a given time, the solution was filtered and the filtrate subsequently analyzed for concentration by UV/Vis spectrophotometer, Jenway model 6715. The spectrophotometer was set at the wavelength 662 nm for MB. Similar measurements were carried out by varying adsorbent doses, pH, ionic strength and initial concentrations. The percentage removal (%R) and the amount (Q<sub>ads</sub>) adsorbed were calculated using the following expressions:

$$Q_{ads} = \frac{(C_o - C_e)V}{m} \dots \dots \dots (1)$$

$$\%R = \frac{(C_o - C_e)}{C_o} \times 100 \dots \dots \dots (2)$$

Where C<sub>o</sub> is the initial concentration, C<sub>e</sub> is equilibrium concentration, V represents the volume of the solution and m is the mass of the adsorbent.

III. RESULTS AND DISCUSSION

1-Characterization of Adsorbents

The IR spectrum of materials used as adsorbents are presented in figure1 and ¶the functional groupings likely to be available to the surface of these materials are shown in table 1 below:

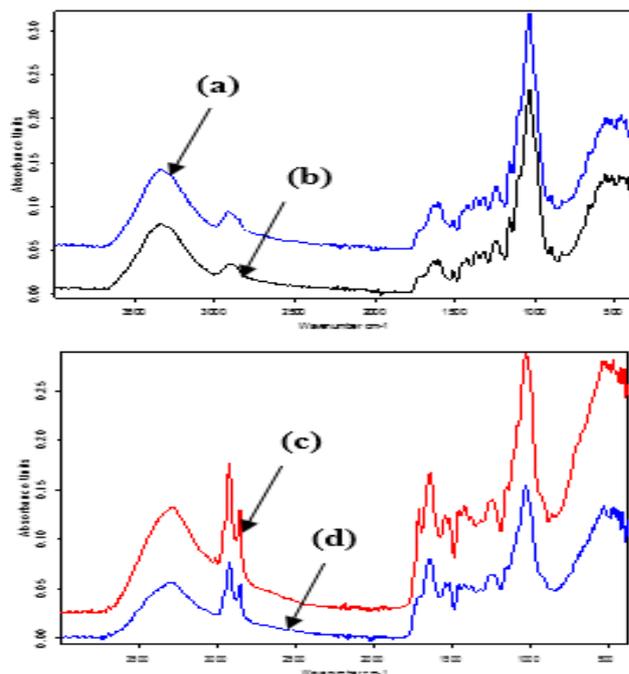


Figure 1: Spectra IR of different adsorbents: (a) corn stalk, (b) corn stalk treated with methanol, (c) egussi peeling and (d) egussi peeling treated with methanol

Table 1: IR vibration bands of crude and methanol treated cellulosic materials (corn stalks and egussi peeling)

Pics	Wave numbers (cm <sup>-1</sup> )	Attribution
1	3330	v (O-H) alcohols, phenols, polysaccharides and lignins
2	2850	v (C-H) aliphatic CH and CH <sub>2</sub>
3	1730	v (C=O) aldehydes, esters, ketones and acetates
4	1645	v (C=O) carboxylates and carboxylic acid
5	1580	v (C=C) aromatic skeleton of lignin
6	1030	v (C-O) carboxylic acids, alcohols, phenols, ethers and esters
7	900-600	v (C-H) aromatic polynuclear systems

2-Effect of contact time

The variation of the adsorption rate of MB dye over time (initial concentration 1x10<sup>-5</sup> mol/L is shown in figure 2. It’s observed that the maximum amount of dye adsorption taking place within the contact time of 10 minutes with corn stalks (fig 2-1) and 20 minutes with egussi peeling (fig 2-2) becomes gradual thereafter. This indicates that the rate of adsorption is very fast. Thus, after that no significant change in the extent of observed adsorption. As shown in figure 2, it would be for that a large number of vacant surface sites are available for adsorption during the initial stage of the treatment time, and after a few time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between MB

dye adsorbed on the surface of different adsorbents and solution phase.

### 3-Effect of adsorbent mass

At constant initial concentration of the MB, an increase in the mass of biosorbents leads to increased methylene blue binding sites as shown in figure 3. This is explained by the fact that increase in the mass increases the number of sites of adsorption on the surface of adsorbent. It should be noted that adsorbent TMT has the greatest percentage of elimination than the others. The capacity of adsorption (expressed as a percentage) increase from 81.40 to 88.30, 83.57 to 90.18, 48.18 to 78.40 and 49.01 to 84.01 for TMB, TMT, CPB and CPT respectively when the mass increases from 5 to 40 mg.

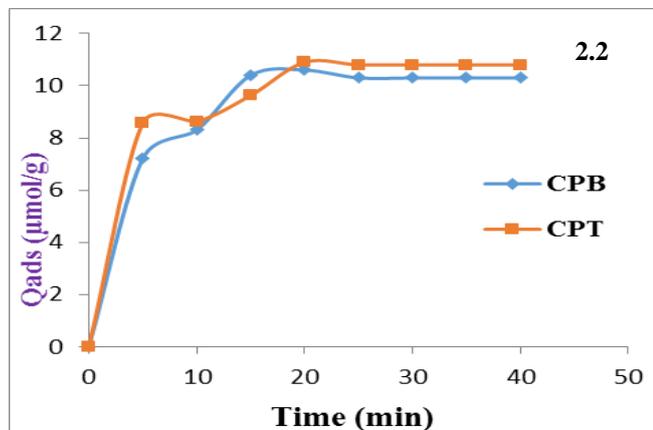
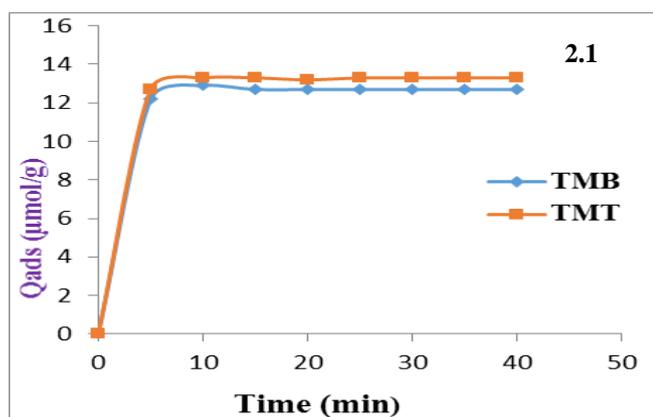


Figure 2: Influence of contact time on MB adsorption onto rough and treated corn stalks (2.1) and raw and treated egussi peeling (2.2).

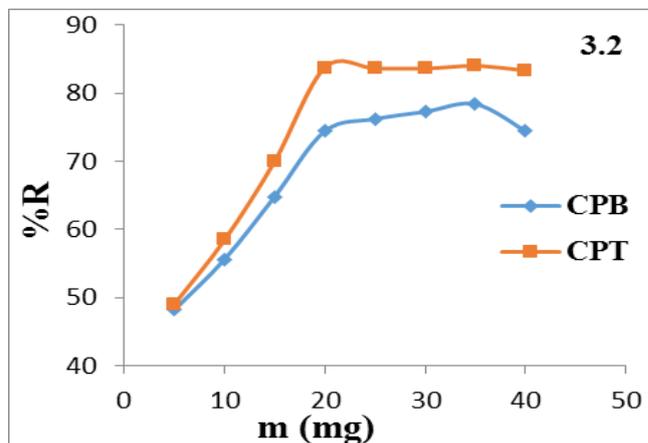
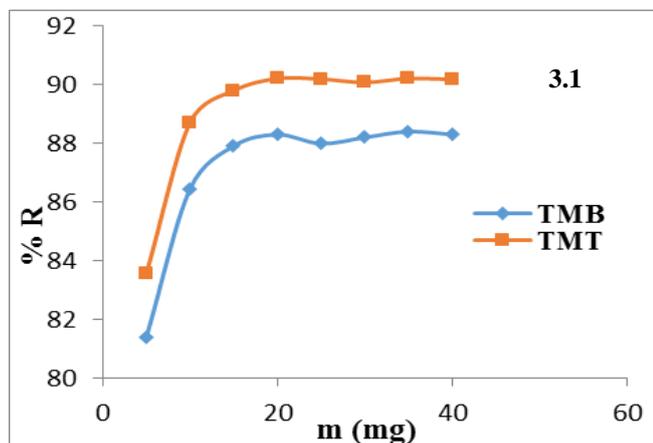


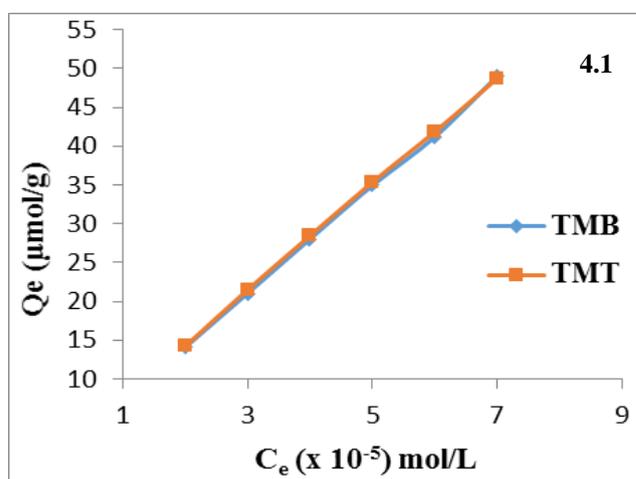
Figure 3: Influence of the mass of corn stalks (3.1) and egussi peeling (3.2) on the removal of methylene blue in aqueous solution

### 4-Effect of initial concentration of methylene blue

The quantities of MB adsorbed increase with its initial concentration. This to be explained by the fact that the more the concentration of MB increases, the more the number of ions in solution increases, implying a competitiveness in the occupation of the sites of adsorption of the biosorbents that increases their potentials for adsorption [14]. The pace of a line that the curves of the influence of the concentration of the MB with the corn stalk is present makes it possible to say that the size of the pores which they present at their surfaces is very broad [15] and compared with that of the egussi peeling. The increasing quantity of MB adsorbed at constant dose of biosorbents is due to the fact that the bio-adsorbent is composed of porous structure with large internal surface area. Similar process was obtained on the adsorption of MB on peanut hull [16]. It is clear that the adsorption process is highly dependent on initial concentration of solution.

### 5-Effect of ionic strength

Extensive investigations carried out on adsorption of dyes revealed that the extent of dye uptake was strongly influenced by the concentration and nature of the electrolyte ionic species added to the dye-bath [17]. The effect of inorganic salt (NaCl) on the adsorption rate of MB is presented in Figure 5. The concentrations of  $\text{Na}^+$  being much higher than that of the methylene blue, there would be competition between these cations and the MB molecules on the adsorption sites of biosorbents



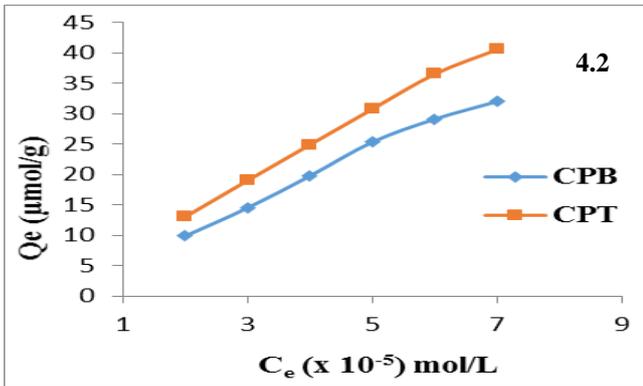


Figure 4: Influence of initial concentration of MB in aqueous solution on adsorption by the corn stalks (4.1) and the egussi peeling (4.2).

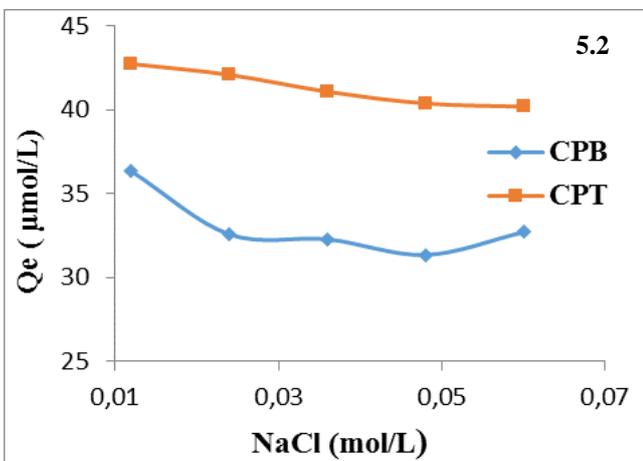
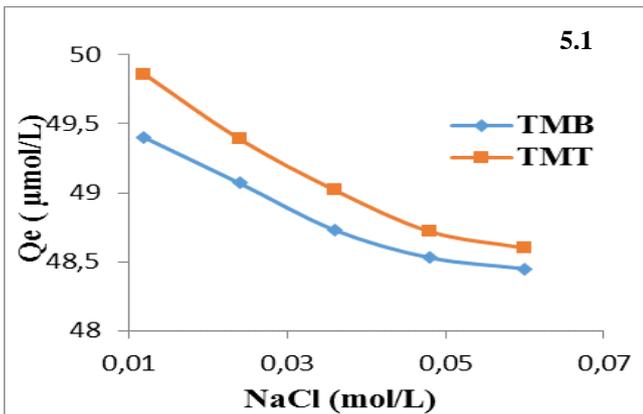


Figure 5: Influence of ionic strength on the adsorption of MB by corn stalks (5.1) and egussi peeling (5.2).

6-Effect of initial solution pH

The pH is one of the most important factors controlling the adsorption of dye onto suspended particles. The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites [18]. The effect of initial pH of the dye solution on the amount of dye adsorbed was studied by varying pH under constant process parameters (figure 6). Figure 6 shows that the adsorption of MB on these materials is favorable at basic pH. ¶This, owing to the fact that, in aqueous mediums the surface of lignocellulosic materials is strongly

deprotonated with the presence of hydroxides ions [19], ¶which reinforces attraction between these materials and the MB thanks to its positive load. ¶With low values of initial pH, the surface of the adsorbent would be surrounded by ions H+ [20] which would decrease the interaction of the MB with the sites of the adsorbent, under the effect of repulsive forces.

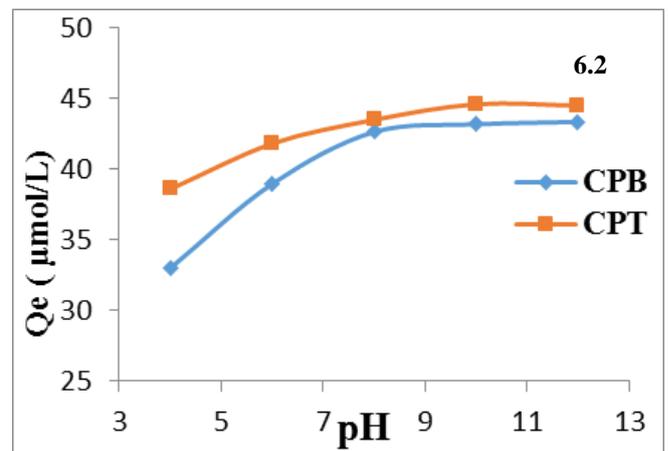
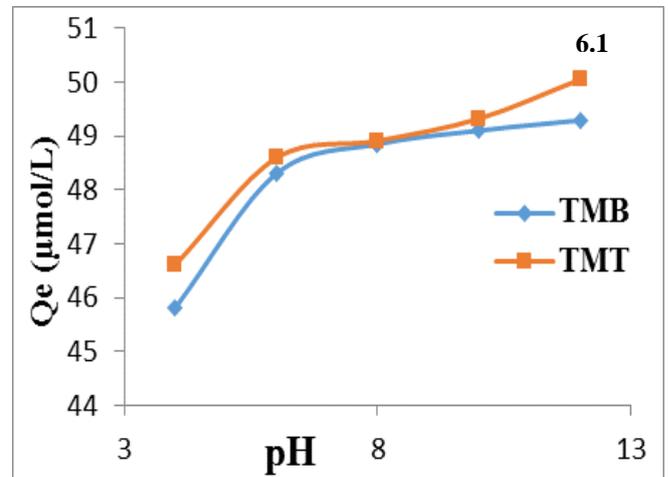


Figure 6: Influence of pH on the adsorption of MB in aqueous solution by corn stalks (6.1) and egussi peeling (6.2)

7-Adsorption kinetic study

¶Several kinetic models were tested but only the model of pseudo-second order that better describes the adsorption phenomena is presented.

Pseudo-second order model

The model of the pseudo-second order is generally used to describe the phenomena of adsorption of the type chemisorptions [21]. ¶It is expressed according to the following equation:¶

$$\frac{dQ_t}{dt} = K_2(Q_s - Q_t)^2 \dots \dots \dots (3)$$

¶Where Qs and Qt are respectively the adsorbed amount (in μmol/g) at equilibrium and at unspecified moment t; ¶K2 is the constant speed of adsorption (in g/μmol.min); Equation (3) is reduced to its simplest form by applying the boundary conditions i.e. at t = 0, Q1 = 0:¶

$$\frac{t}{Q_t} = \frac{1}{K_2 \cdot Q_s^2} + \frac{t}{Q_s} \dots \dots \dots (4)$$

The initial rate of adsorption is given by the following expression [22].

$$h = K_2 \cdot Q_s^2 \dots \dots \dots (5)$$

The plot of t/Qt = f(t) gives straight lines and ¶ values of

R2 are very close to one, showing that the adsorption process obeys the kinetic model of pseudo-second order. The constant  $Q_e$  and  $K_2$  are given in table 2.

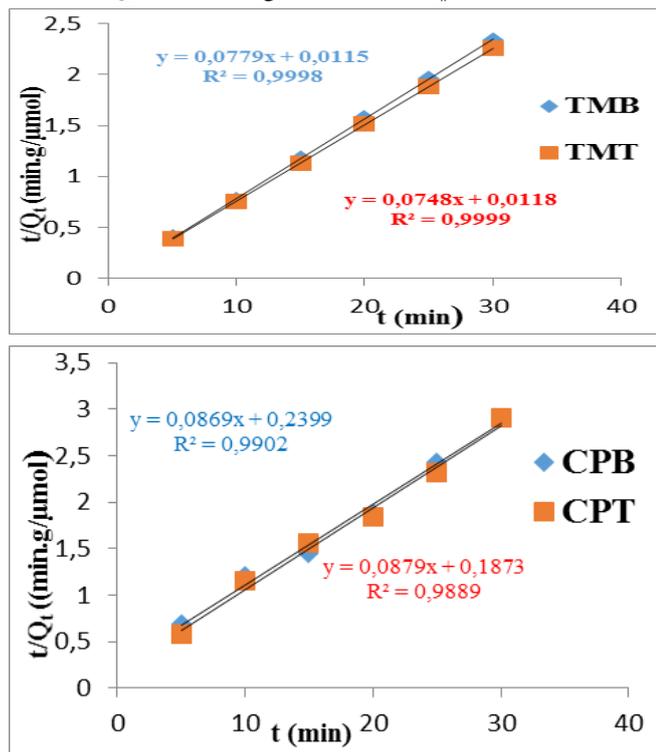


Figure 7: Linearized pseudo-second order plots

Table 2: Parameters of kinetic models of MB adsorption on TMT, TMB, CPT and CPB.

Adsorbants		T	T	C	C
		MT	MB	PT	PB
$C_0$ (mol/)		$1 \times 10^{-5}$			
Pseudo-second order model	$K_2$	0.50	0.54	0.040	0.030
	$Q_e$ ( $\mu\text{mol/g}$ )	3.51	2.98	1.50	1.62
	$R^2$	0.999	0.999	0.988	0.990

### 8-Adsorption Isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [23]. The applicability of the isotherm equation is compared by judging the correlation coefficients,  $R^2$

Adsorption isotherm is important to describe how solutes interact with adsorbents, and is critical in optimizing the use of adsorbents. Adsorption isotherm study is carried out on two well-known isotherms, Langmuir, Freundlich and Temkin

#### The Langmuir model

Langmuir isotherm model assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [24]. The linear form of Langmuir's isotherm model is given by the following equation [25]:

$$Q_e = Q_m \frac{KC_e}{1 + KC_e} \dots \dots \dots (6)$$

The linear transformation of this model brings us to the following equation:

$$\frac{1}{Q_e} = \frac{1}{C_e} \frac{1}{KQ_m} + \frac{1}{Q_m} \dots \dots \dots (7)$$

Where  $C_e$  is the equilibrium concentration of the adsorbate (MB) ( $\mu\text{mol/L}$ ),  $Q_e$  the amount of adsorbate adsorbed per unit mass of adsorbate ( $\mu\text{mol/g}$ ),  $Q_m$  and  $K$  are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When  $1/Q_e$  was plotted against  $1/C_e$ , straight line with slope  $\frac{1}{KQ_m}$  was obtained (Fig. 8), indicating that the adsorption of MB on treated and untreated lignocellulosics materials follows the Langmuir isotherm. The Langmuir constants  $K$  and  $Q_m$  were calculated from this isotherm and their values are given in table 3.

Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of biosorbent surface, i.e. each dye molecule/biosorbent adsorption has equal adsorption activation energy. The results also demonstrate the formation of monolayer coverage of dye molecule at the outer surface of lignocellulosic material. Similar observation was reported by the adsorption of acid orange 10 dye onto activated carbons prepared from agricultural waste bagasse [26] and by the adsorption of direct dyes on activated carbon prepared from sawdust [25] and adsorption of Congo red dye on activated carbon from coir pith [27].

Because of its size ( $1.43 \times 0.61 \times 0.40 \text{ nm}^3$ ), the well known MB cationic dye is commonly used to probe the mesoporous volume of materials by adsorption experiments [28]. The maximum amount of adsorbed MB allows the estimation of the sample specific surface area covered by the MB molecule (SMB) from the equation [29]

$$S_{MB} = Q_m \times A_m \times 6.02 \times 10^{23} \dots \dots \dots (8)$$

$A_m$  being the molecular surface of MB ( $1.30 \text{ nm}^2$ )

The results are summarized in table 3. According to the specific area obtained by this method, we observe that the materials treated with methanol have the higher specific area than those that are not treated. This makes it possible to affirm that methanol played its role to make the pores free of extractable and therefore more efficient.

#### The Freundlich model

Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [22]. The equation of Freundlich is given in the following form [30]:

$$Q_e = K_f C_e^{1/n} \dots \dots \dots (9)$$

$Q_e$  is the quantity adsorbed per gram of the solid,  $K_f$  and  $1/n$  is the constants of Freundlich characteristic of the effectiveness of an adsorbent given with respect to a given aqueous solution. The logarithmic expression of equation (8) which is better used to validate or invalidate this model is as follows [31]:

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_f \dots \dots \dots (10)$$

The plot of  $\ln Q_e$  versus  $\ln C_e$  gives straight lines with slope  $1/n$  (Fig. 9), which shows that the adsorption of MB also follows the Freundlich isotherm. Accordingly, Freundlich constants ( $K_f$  and  $1/n$ ) were calculated and recorded in table 3.

#### The Temkin model

The isotherm of Temkin is represented by the following

equation [32]

$$\theta = \frac{Q_e}{Q_m} = \frac{RT}{\Delta Q} \ln K_0 \cdot C_e \dots \dots \dots (11)$$

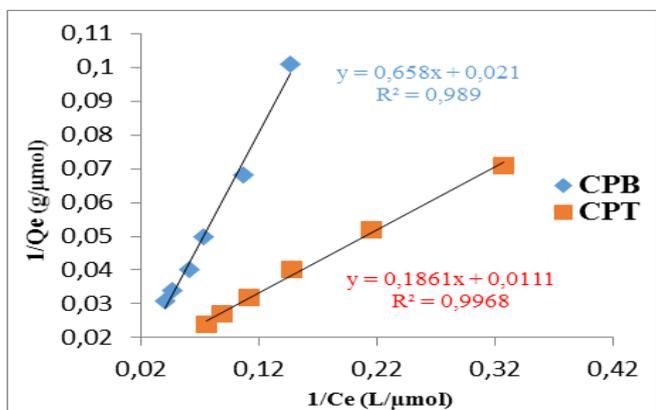
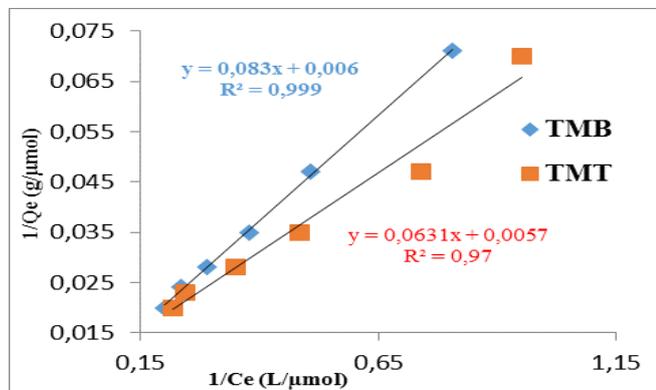
$\theta$  is the rate of covering of the surface of the adsorbent,  $Q_e$  the quantity of the product adsorbed per unit of mass of adsorbent,  $Q_m$  the theoretical maximum adsorption capacity deduced from the model from Langmuir and  $K_0$  the equilibrium Constant. The linearization form of Temkin equation leads to [32,33]:

$$Q_e = Q_m \frac{RT}{\Delta Q} \ln C_e + Q_m \frac{RT}{\Delta Q} \ln K_0 \dots \dots \dots (12)$$

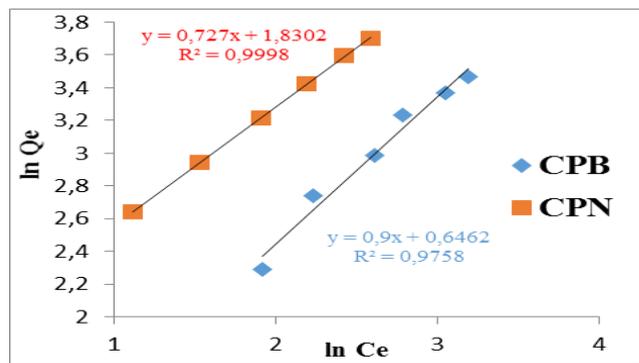
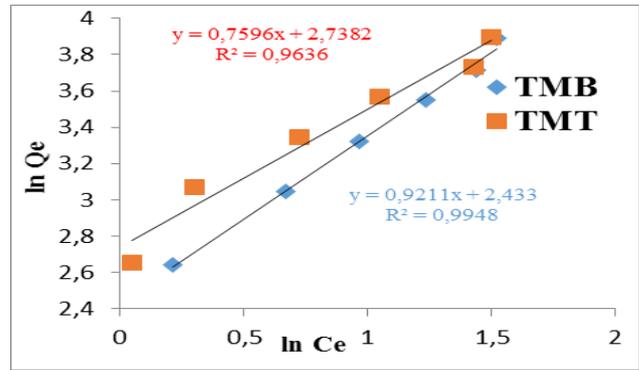
By plotting  $Q_e = f(\ln C_e)$ , one obtains a straight line whose slope and intercept make it possible to determine the heat of adsorption  $\Delta Q$  and the equilibrium constant  $K_0$ .

**Table 3:** Presentation of the various constants of the three isotherms studied for each biosorbant used.

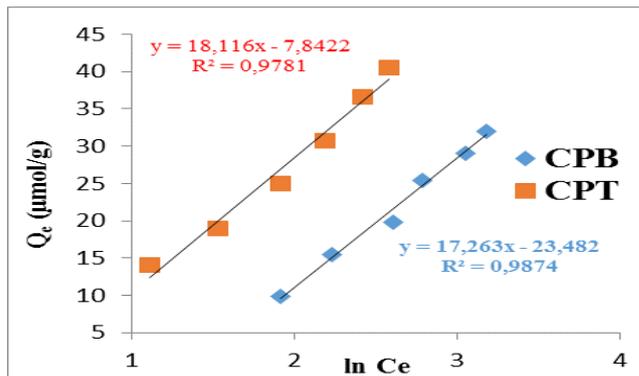
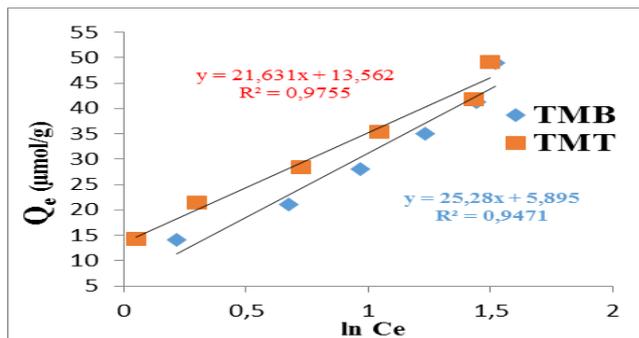
Types of Isotherms	parameter s	Biosorbents			
		TMT	TMB	CPT	CPB
Langmuir	K	0.079	0.18	0.059	0.032
	$Q_m$ ( $\mu\text{mol/g}$ )	200	166.67	90.9	47.42
	$R^2$	0.97	0.999	0.996	0.989
	$S_{MB}$ ( $\text{m}^2/\text{g}$ )	156.52	130.44	71.14	37.11
Freundlich	$K_f$	15.45	11.39	6.23	1.9
	$1/n$	0.759	0.921	0.727	0.9
	$R^2$	0.963	0.994	0.999	0.975
Temkin	$K_0$	1.87	1.26	0.64	0.25
	$R^2$	0.975	0.947	0.978	0.987
	$\Delta Q$ (kJ/mol)	22.9	16.33	12.43	6.8



**Figure 8:** Linear plot of the model of Langmuir



**Figure 9:** Linear plot of the model of Freundlich



**Figure 10:** Linear plot of the model of Temkin

Table 3 shows the values of the parameters of the three isotherms and the related correlation coefficients. As seen from Table 3, the Langmuir model yields a somewhat better fit ( $R^2 > 0.99$ ) than the Freundlich model ( $R^2 > 0.96$ ) and Temkin ( $R^2 > 0.95$ ). As also illustrated in table 3, the value of  $1/n$  is less than one, which indicates favorable adsorption [34].

IV. CONCLUSION

The studies undertaken in batch mode under the influence of the quoted parameters show that: the treatment of materials

with methanol increases their adsorption capacity from approximately 2% for the corn stalks and 14% for the egussi peeling. The biosorbents used adsorb better at weak concentrations. The ionic force disadvantage is the retention of MB on the surface of these biosorbents. The rise in the pH from 4 to 12 increases the adsorption of the MB of approximately 7.6 % and 6.56% for corn stalks untreated and treated with methanol to approximately 19.7% and 11.14% for raw egussi peeling and the egussi peeling treated with methanol respectively. Equilibrium times are quickly reached at the end of the tenth minute for the stems of corn and the twentieth minute for the pistachio egussi peeling. All the isotherms studied describe in a satisfactory way adsorption of the MB on the stems of corn and the egussi peeling of pistachios because the coefficients of correlation  $R^2$  lie all between 0.947 and 0.999 but it is the isotherm of Langmuir which better describes phenomena. The kinetics of adsorption of the MB in aqueous solution on these biosorbents (rough and treated with methanol) better follow the kinetic model of the pseudo second-order with coefficients of correlation  $R^2$  ranging between 0.990 and 0.999, which makes it possible to say that the process of adsorption of the MB on the corn stalks and the egussi peeling is controlled by chemisorption.

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