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Valorization the waste of the wood industry (sawdust) and their use as adsorbent material: physicochemical characterization and modeling of optimization sorption using statistical approach

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Abstract

The present work reports on simple and effective ecofriendly approach for the valorization of waste of the wood industry in the environmental application as adsorbent biomaterials. The biomaterial was characterized using various instrumental techniques including scanning electron microscope coupled at energy dispersive spectroscopy (SEM/EDS) and Fourier transformed infrared spectroscopy (FTIR). In the other hand, other study is about optimization of sorption of Methylene Blue dye (MB) from aqueous solution onto the biomaterial prepared from waste of the wood industry using Response Surface Methodology (RSM). Effect of process parameters such as dosage of biomaterial, initial dye concentration, stirring speed, size of grains of adsorbent, and their interaction on the sorption were studied by using full factorial Central Composite Design (CCD).

1. Introduction

The effluents coming from different industries such as textile, leather, paint, pulp and paper, ceramic, pottery ... that use synthetic dyes to color their products, may lead to water pollution if they are not treated properly before their discharge to the environment **[1-10].** Methylene Blue (MB), a common dye used for dying cotton, silk and wood, has adverse effect on human health such as breathing problem, eye burns, diarrhea, vomiting and gastritis **[11–12]**. Conventional waste water treatment methods for removing dyes especially methylene blue include physicochemical, chemical and biological methods, such as coagulation and flocculation, ozonation, electrochemical techniques, fungal decolorization and others techniques. **[13-16].** But these processes are not always effective and economic where the solute concentrations are very low. Besides, most of the dyes undergo very slow biodegradation. Actually, the elimination by sorption technique has been proven to be an effective and attractive process for the treatment of dye-containing waste water **[17]**. In recent years, adsorption has been strongly recommended as an economically viable sustainable technology for the treatment of waste water streams **[18]**. The importance and usefulness of adsorption in wastewater treatment is well established **[19]**. Adsorption in environmental engineering is now in the focus and consideration of all nations, owing to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions **[20-21].**

The focus of this research is to evaluate the adsorption potential of waste of the wood industry for Methylene Blue. MB was chosen in this study because of its known strong adsorption onto solids and it often serves as a model compound for removing organic contaminants. Thus, an experimental design methodology with four

factor interaction was implemented in order to optimizing the conditions for the process sorption of this adsorbent biomaterial.

This manuscript is a continuation of the work done by L. Dahbi et al. **[22]**, From which they made a preliminary contribution to the study of the fixing of Methylene Blue (MB) on sawdust of beech, Moreover, they have demonstrated the dependence of the efficiency of this adsorbent on various operating parameters (initial pH, initial concentration of the adsorbate, agitation speed, adsorbent mass). Theoretically, adsorption isotherms of Methylene Blue (MB) by sawdust from beech wood have been validated by Langmuir, Freundlich, Temkin and Elovich models. The adsorption process was confirmed by the Langmuir model, and the application of the kinetic models based on the second Fick's law allowed us to estimate, for different initial concentrations in Methylene Blue, the parameters related to the transfer resistances of external and internal material.

2. Material and Methods

2.1. Preparation of sawdust biomaterial

The waste wood (sawdust) was collected from the waste industry (Ain Sbaa, Casablanca, Morocco). The collected materials were washed several times with boiled water and finally with distilled water to remove any adhering dirt. The washed material was then dried in the oven at 60 °C for 72 h. Finally, the resulting obtained was stored for further use.

2.2. Characterization of sawdust biomaterial

2.2.1. SEM/EDS analysis

Scanning Electron Microscope (SEM) JSM- 5800 LV, JEOL was used to determine the shape of sawdust biomaterial. Elemental composition of the sample was analyzed with energy dispersive analysis of X-ray spectroscopy (EDS) coupled to the Scanning Electron Microscope.

2.2.2. FTIR analysis

Fourier transformed infrared (FTIR) spectrum of the sample was recorded by Fourier transform infrared spectrophotometer (VERTEX 70). The FTIR spectrum ranged from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. For FTIR study, 2 mg of finely ground sample was mixed well with approximately 40 mg of KBr (MERCK) for the preparation of transparent pellets, from which functional groups were determined.

2.3. Modeling and optimization sorption

2.3.1. Preparation of dye solution

Methylene Blue (MB) is a cationic dye (Figure 1) with molecular formula $C_{16}H_{18}N_3SCl$, molar weight of 319.85 g/mol and wave length of λ_{max} = 664 nm **[23-24]**. The stock solutions of MB were prepared in distilled water. All working solutions were prepared by diluting the stock solution with distilled water to the needed concentration. Fresh dilutions were used for each adsorption study.

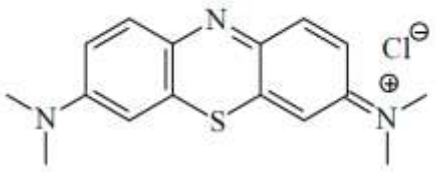


Figure 1: Chemical structure of methylene blue.

2.3.2. Tests of sorption

The adsorption tests were carried out in a static reactor under the same operating conditions. Known mass of the adsorbent is introduced into a solution containing a concentration of methylene blue. The mixture is stirred at room temperature for a sufficient time of equilibrium (2 hours), and then the experiment's stopped for one hour to determine their residual concentrations. It's noted that all the experiments are repeated in triplicate in order to have an average and a standard deviation from the results. The yield removal of dye was calculated as follows:

$$Yield(\%) = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

Where C_0 and C_e (mg/L) are the liquid phase concentrations of MB at initial and equilibrium, respectively.

In the other hand, all experiments were performed at a temperature (25 ± 2 ° C). We first prepared the sawdust sifting for various aggregates (63.80 and 100 µm) from which we weighed the different mass (0.1, 0.2 and 0.3g / l), then, added to stock solution of 100 mg/l, we have prepared by dilution concentrations (10, 15 and 20 mg/l). The sorptions are performed for different stirring speeds (800, 1200 and 1600 rpm) at the equilibrium time of two hours.

2.3.3. Design of experiments

Response Surface Methodology is a statistical method that uses experimental data obtained from specified experimental design to model and optimize any process in which response of interest is influenced by several variables **[25]**. Primarily, this optimization is done by following three major steps viz., performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the responses and examining the adequacy of the model **[26]**. RSM helps to enumerate the relationships between output variables called responses (Y) and input variables called factors (X_i) **[27].**

$$Y = f(X_1, X_2, X_3, ..., X_n) \quad (2)$$

A standard RSM design called Central Composite Design (CCD) was applied in the present work. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters **[28].** Generally, the CCD consists of a 2^n factorial runs with 2n axial runs and n_c central runs **[29].** The centre points are utilized to evaluate the experimental error and the reproducibility of the data. Thus, for carbonization process having three independent parameters (n = 4), the total number of experiments required is:

$$N = 2^n + 2.n + n_c = 16 + (2 \times 4) + 2 = 26 \quad (3)$$

The experimental sequence was randomized in order to minimize the effects of uncontrolled factors **[30].** The outcome of each experimental run was analyzed and the response was correlated with three input factors for carbonization of parthenium for preparation of adsorbent through an empirical second degree polynomial equation as given by the following equation:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n} \sum_{j=1}^{n-1} \beta_{ij} X_i X_j \quad (4)$$

Where, Y is the predicted response (Yield of sorption in this study), β_0 the constant coefficient, β_i the linear coefficients, β_{ij} the interaction coefficients and β_{ii} the quadratic coefficient **[31].** ANOVA was used to model the system represented by independent parameters and dependent output response and to optimize the system by estimating the statistical parameters. The minimum (−1), intermediate (0) and maximum (+1) level of dosage of biomaterial, initial dye concentration, stirring speed, size of grains of adsorbent were 0.1, 0.2 and 0.3 g/l, 10, 20 and 30 mg/l, 800, 1200 and 1600 rpm and 60, 80, 100 µm respectively. The statistical experimental design as specified by the software is shown in Table 1.

3. Results and discussion

3.1. Physicochemical characterization

Sawdust (industrial waste) used in this study is derived from beech (*Fagus sp*.), which is a widely used wood in construction and furnishings (Figure 2). Beech is a very hard, heavy, white to reddish wood, very alterable and not very durable, but it is impregnated, dyed, painted, turned and easily bent. High quality beech is used in the manufacture of plywood. But it is also very appreciated for furniture and turnery. Poor quality wood is used for particle board and pulp.

Figure 2: Beech (wood).

Figure 3: Wood waste from beech.

Physico-chemical analysis of this material was carried out by scanning electron microscope (SEM) coupled at energy dispersive spectroscopy (EDS) and Fourier transformed infrared spectroscopy (FTIR).
Analysis by scanning electron microscopy is carried out on wood samples at 200 µm and at 300 µm. The plates are shown in Figure 4. This analysis shows that this material is microporous.

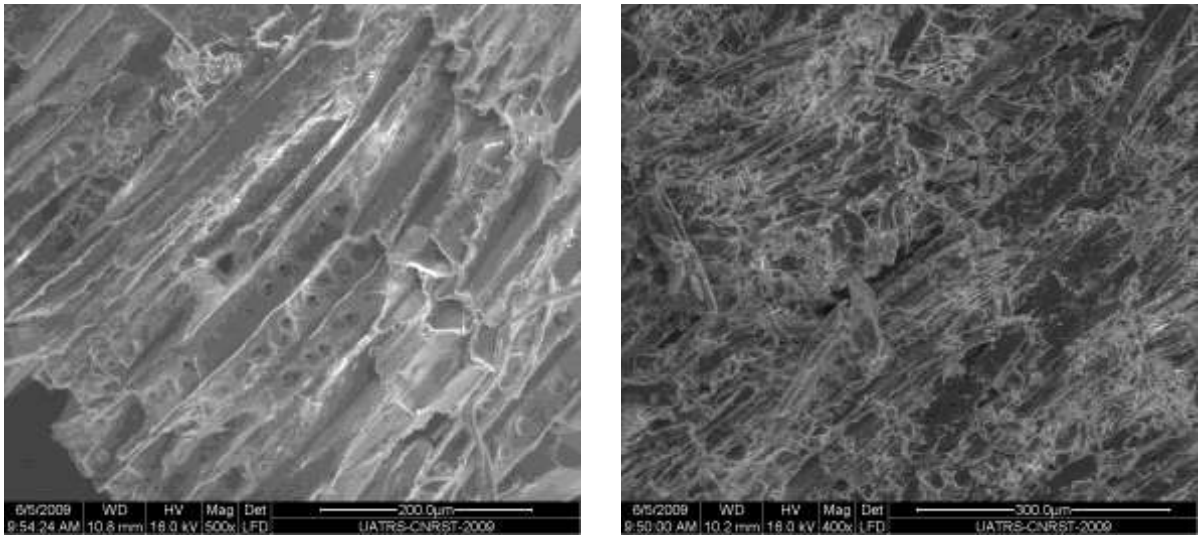


Figure 4: SEM of wood: 200 µm and 300 µm.

As a result, the microanalysis X by EDS allows the qualitative and quantitative determination on the scale of the cubic micron of the chemical elements contained in very diverse materials: rocks, metal alloys, powder, etc. The detection limit is about 10-14 to 10-15 g which corresponds to a content of less than 100 ppm. This analysis allowed us to characterize a number of elements that the samples contain. These elements have been identified by their binding energy which is characteristic and listed in the spectroscopic tables. The relative contents of the various elements expressed as atomic percent are grouped in Table 1. The atomic composition as a percentage by mass determined by EDS showed that the content of carbon and oxygen is very important in the waste wood, this shows that both elements are the elementary constituents of wood, the presence of Some elements such as aluminum, chlorine, calcium and potash with variable grades, which probably originate from substances absorbed by the tree in the soil.

Table 1: Percent atomic composition determined by EDS.

Composition	Percentage content (%)
C	70.12
O	28.68
Al	0.22
Si	0.39
Cl	0.18
K	0.17
Ca	0.24

In the other hand, FTIR makes it possible to identify the functional groups that are characteristic of the compounds. This technique does not make it possible to precisely define the structure of a molecule as complex as lignin. However, the results obtained show major differences in the main components of wood such as lignin, cellulose and hemicellulose, so thesample spectrum of wood waste is presented in Figure 5.
A broad band in the region of 3400 cm^{-1} represented presence of hydroxyl groups (OH), Furthermore the valence vibration related to aromatic C-H is shown on the spectrum. It is characterized by absorptions at the 3030 cm^{-1} region. The characteristic functions of the basic units of lignin are aromatic functions, carbonyls (C = O), alcohols and ethers. Each of these functions is found in the infrared spectrum. The aromatic functions are characterized by infra-red absorption bands in the region of 1500 to 1600 cm^{-1}, which is characteristic of the C = C vibrations of the aromatic skeleton of lignin. Thus, fundamental studies on the vibrations of benzene have shown that the valence vibration mode of the carbon-carbon bonds conjugated from the aromatic skeleton leads to the appearance of 4 bands lying between 1650 and 1450 cm^{-1} **[32-34].**

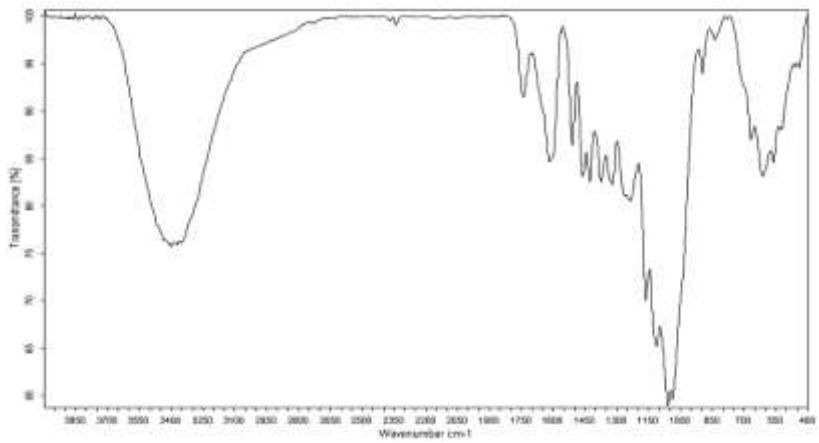


Figure 5: FTIR spectrum of sawdust (beech wood).

3.2. Modeling of optimization sorption using statistical approach

The experimental plan chosen is a composite plan centered in a cubic domain, each factor requires 3 levels, and the number of simulations is equal to 26, or the experimental design is given in Table 2. Therefore, the mathematical model associated at empirical second degree polynomial for response of correlated with four input factors given by the following equation 5:

$$Y = 86.95 - 2.62X_1 + 4.27X_2 - 0.31X_3 - 2.76X_4 - 2.22X_1^2 - 4.82X_2^2 + 2.56X_3^2 + 2.31\,X_4^2 + 3.14X_1X_2 - 0.29X_1X_3 - 1.20X_2X_3 + 1.01\,X_1X_4 - 1.44X_2X_4 + 0.12\,X_3X_4 \quad (5)$$

Table 2: Experimental design (input and response factors).

	X1	X2	X3	X4	
Number of trials	**C (mg/l)**	**m (g/l)**	**G (µm)**	**V(rpm)**	**Y(yield)**
1	10	0.1	60	800	88.03
2	20	0.1	60	800	76.84
3	10	0.3	60	800	95.45
4	20	0.3	60	800	93.98
5	10	0.1	100	800	91.59
6	20	0.1	100	800	75.50
7	10	0.3	100	800	91.51
8	20	0.3	100	800	91.94
9	10	0.1	60	1600	82.71
10	20	0.1	60	1600	74.03
11	10	0.3	60	1600	83.87
12	20	0.3	60	1600	87.27
13	10	0.1	100	1600	85.34
14	20	0.1	100	1600	75.93
15	10	0.3	100	1600	81.10
16	20	0.3	100	1600	83.61
17	10	0.2	80	1200	86.92
18	20	0.2	80	1200	80.29
19	15	0.1	80	1200	71.99
20	15	0.3	80	1200	90.02
21	15	0.2	60	1200	88.38
22	15	0.2	100	1200	88.38
23	15	0.2	80	800	87.50
24	15	0.2	80	1600	88.77
25	15	0.2	80	1200	90.45
26	15	0.2	80	1200	90.20

As a result, we have compared the calculated and simulated responses, hence for each row of the experimental design, and model computes a value for each of the responses. In addition, we calculated the differences between these responses. The results obtained are shown in Table 2. From the difference column of Table 3, we find that the response models (yield (%)) benefit from a good descriptive quality since the percentage difference between the responses calculated and the simulated responses is low. It can also be noted that the largest values of the percentage difference are obtained (7.53, 4.03 and 4.91) in experiments 19, 20 and 21. We will verify using statistical tests whether these experiences can be considered an atypical experience, so values of the studentized residuals as a function of the calculated response are shown in the figure 6. From this figure, it can be said that experiments 19, 20 and 21 appear to be atypical.

Table 3: Calculated responses and simulated responses.

Number of experience	Y_{exp} (%)	Y_{calc} (%)	Difference Calculated responses (%)	Difference simulated responses (%)
1	88.03	87.54	0.48	0.56
2	76.84	74.58	2.25	2.94
3	95.45	95.07	0.37	0.39
4	93.98	94.67	-0.69	0.73
5	91.59	89.65	1.93	2.12
6	75.5	75.54	-0.04	0.05
7	91.51	92.39	-0.88	0.95
8	91.94	90.84	1.09	1.19
9	82.71	82.65	0.05	0.07
10	74.03	73.73	0.29	0.40
11	83.87	84.41	-0.54	0.64
12	87.27	88.05	-0.78	0.88
13	85.34	85.23	0.11	0.13
14	75.93	75.15	0.77	1.03
15	81.1	82.20	-1.10	1.34
16	83.61	84.68	-1.07	1.26
17	86.92	87.34	-0.42	0.48
18	80.29	82.11	-1.82	2.21
19	71.99	77.86	-5.87	7.53
20	90.02	86.39	3.62	4.03
21	88.38	89.82	-1.44	1.00
22	88.38	89.19	-0.81	0.90
23	87.50	92.02	-4.52	4.91
24	88.77	86.49	2.27	2.56
25	90.45	86.94	3.50	3.88
26	90.20	86.94	3.25	3.61

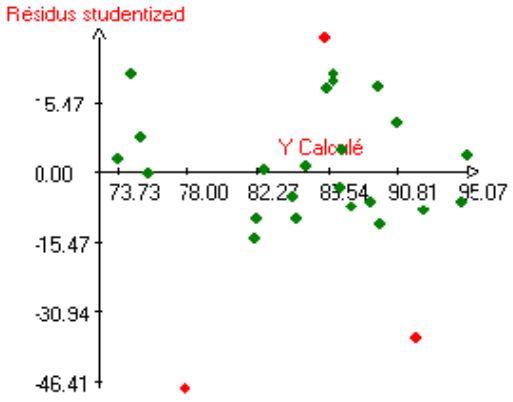


Figure 6: Normality of residues.

Table 4 presents the variance analysis (ANOVA) of the responses presented in percentage units (%). Results of this table, we see that the Fc probability value is less than 5%, so we can say that the model correctly describes the variation of the test results. In addition, the determination coefficients R^2 are shown in Table 5. It can be seen that the quality of the model is not very good since the value of determination coefficients adjusted R^2_A and predictive R^2_{pred} and are equal to 0.741 and 0.510.
Therefore, the statistical coefficients and the estimates according to the student's law are presented in Table 6. From this table, we find that the coefficients b_0, b_1, b_2, b_4, b_{11}, b_{22}, b_{33}, b_{44}, b_{12}, b_{23}, b_{14} and b_{24} have an influence on the adsorption performance.

Table 4: ANOVA results.

Source of variation	Sum of squares	Degree of freedom	mean square	Fc	Probability Fc
Regression	918	14	65.6	2100	1.94 *
Residues	118	11	10.7	-	-
Validity	118	10	11.8	377	4.13*
Error	312	1	0.03	-	-
Total	1036	25	-	-	-

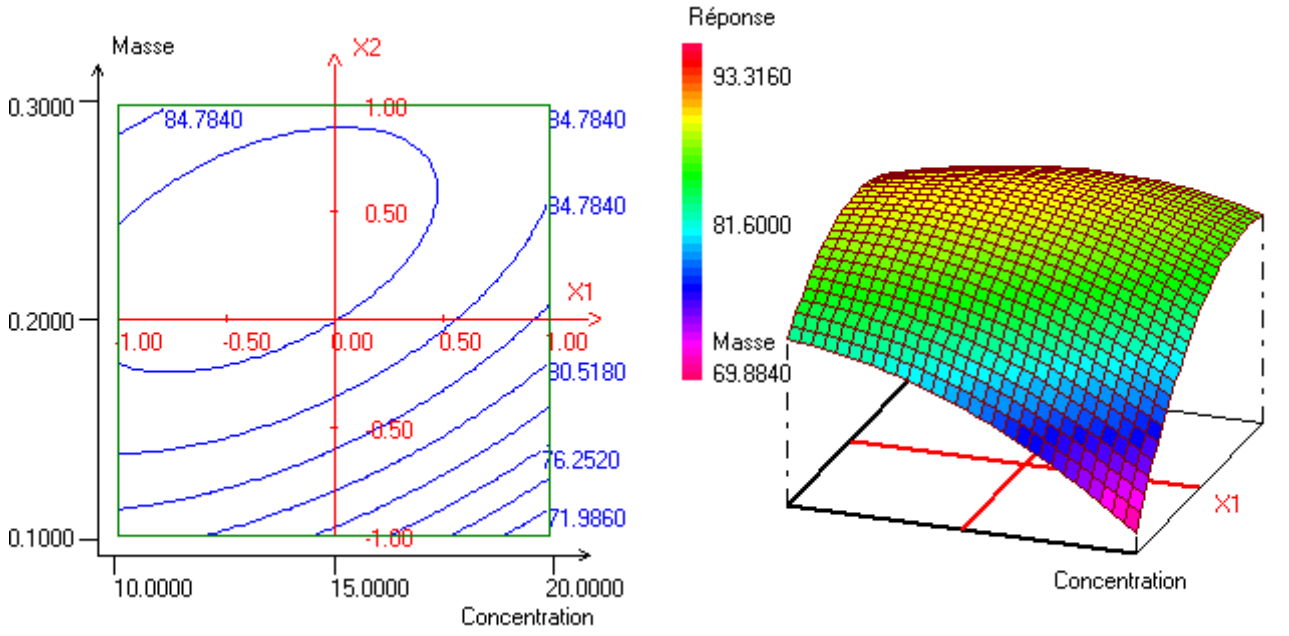
Table 5: Descriptive and predictive qualities of models.

Standard Error of the response	0.177
Determination coefficient R^2	0.886
Adjusted of determination coefficient R^2_A	0.741
Predictive of determination coefficient R^2_{pred}	0.510

Table 6: Estimates and Statistical Coefficients.

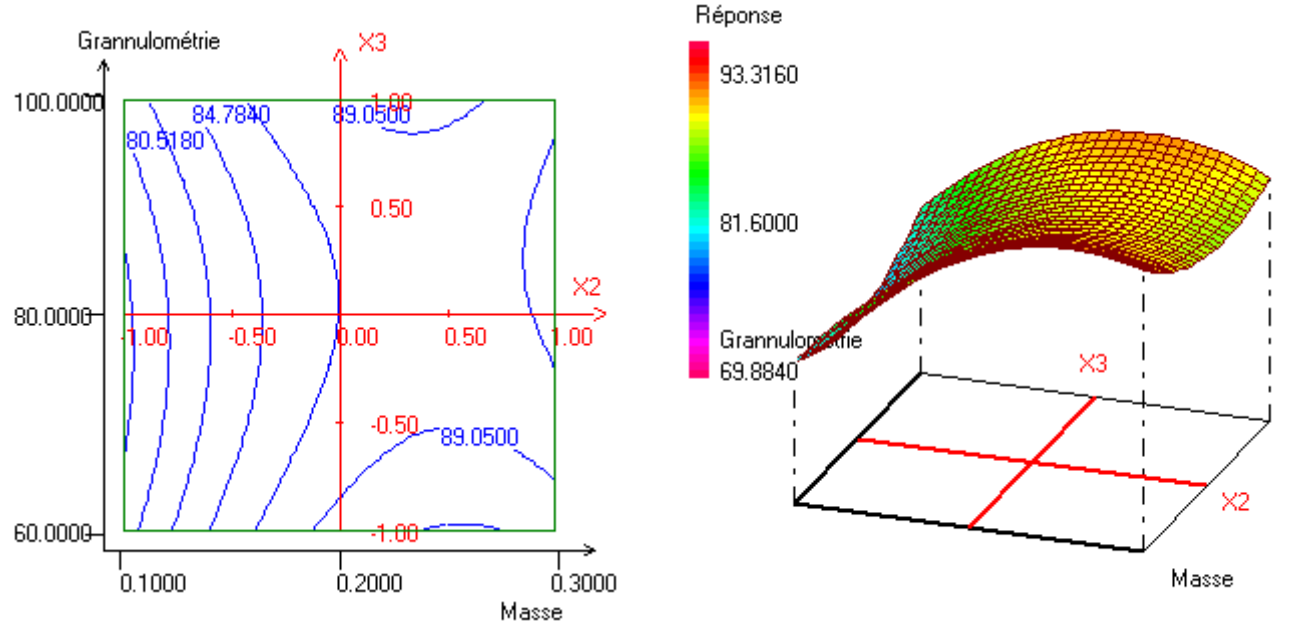
Name	Coefficient	F. Inflation	Standard Deviation	$t._{exp.}$	Sig. %
b_0	86.95	-	0.07	1199	0.51 **
b_1	-2.62	1.00	0.04	-60.73	1.28 *
b_2	4.27	1.00	0.04	98.93	0.97 **
b_3	-0.31	1.00	0.04	-7.26	8.9
b_4	-2.76	1.00	0.04	-64.05	1.24 *
b_{11}	-2.22	2.16	0.11	-19.41	3.21 *
b_{22}	-4.82	2.16	0.11	-42.17	1.64 *
b_{33}	2.56	2.16	0.11	22.39	2.80 *
b_{44}	2.31	2.16	0.11	20.21	3.09 *
b_{12}	3.14	1.00	0.05	68.64	1.19 *
b_{13}	-0.29	1.00	0.05	-6.35	10.3
b_{23}	-1.20	1.00	0.05	-26.19	2.43 *
b_{14}	1.01	1.00	0.05	22.08	2.84 *
b_{24}	-1.44	1.00	0.05	-31.53	2.07 *
b_{34}	0.12	1.00	0.05	2.53	24.8

Finally, figures 7, 8, 9, 10, 11 and 12 present graphical studies in two forms: response surfaces (two-dimensional 2D) and iso-response curves (three-dimensional 3D). A major advantage of the design of this experiment is the ability to generate multiple graphic representations of the data.



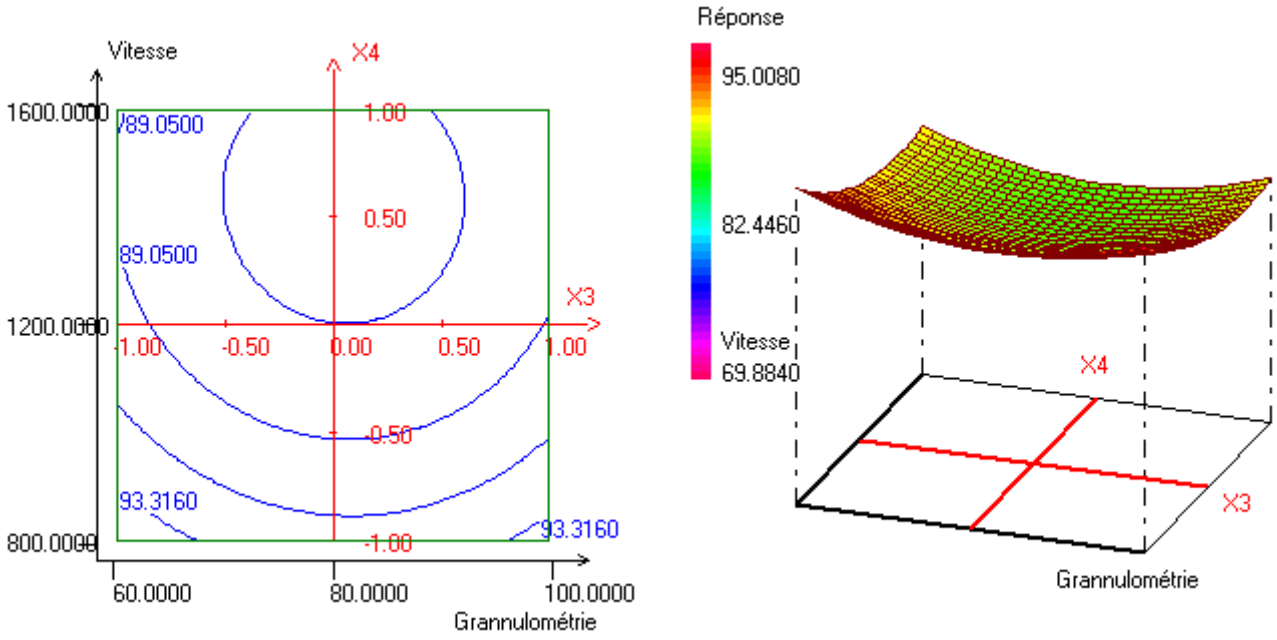
2D 3D

Figure 7: Response surface in 2D and 3D. (Change in the response - Efficiency in the plan: Concentration, Mass ; Factors fixed: - Particle size = 80 micrometer - speed = 1200 rpm)



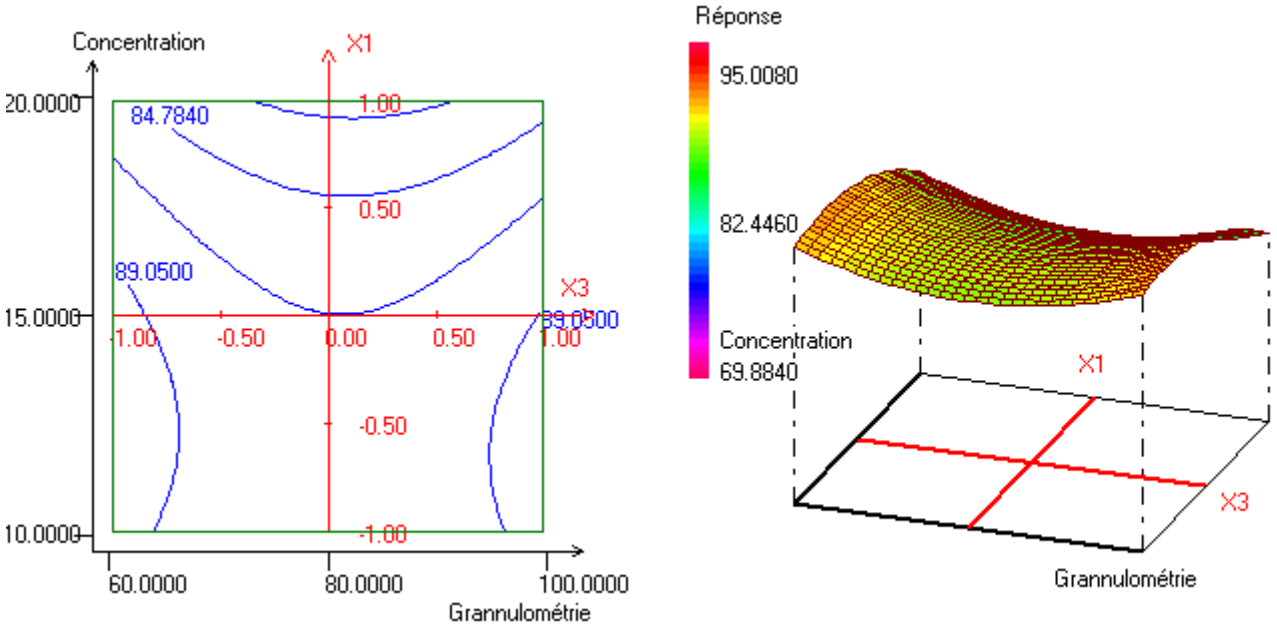
2D 3D

Figure 8: Response surface in 2D and 3D. (Change in the response - Efficiency in the plan: Masse, Grit ; Factors fixed: - Concentration = 15 mg/l - Speed = 1200 rpm)



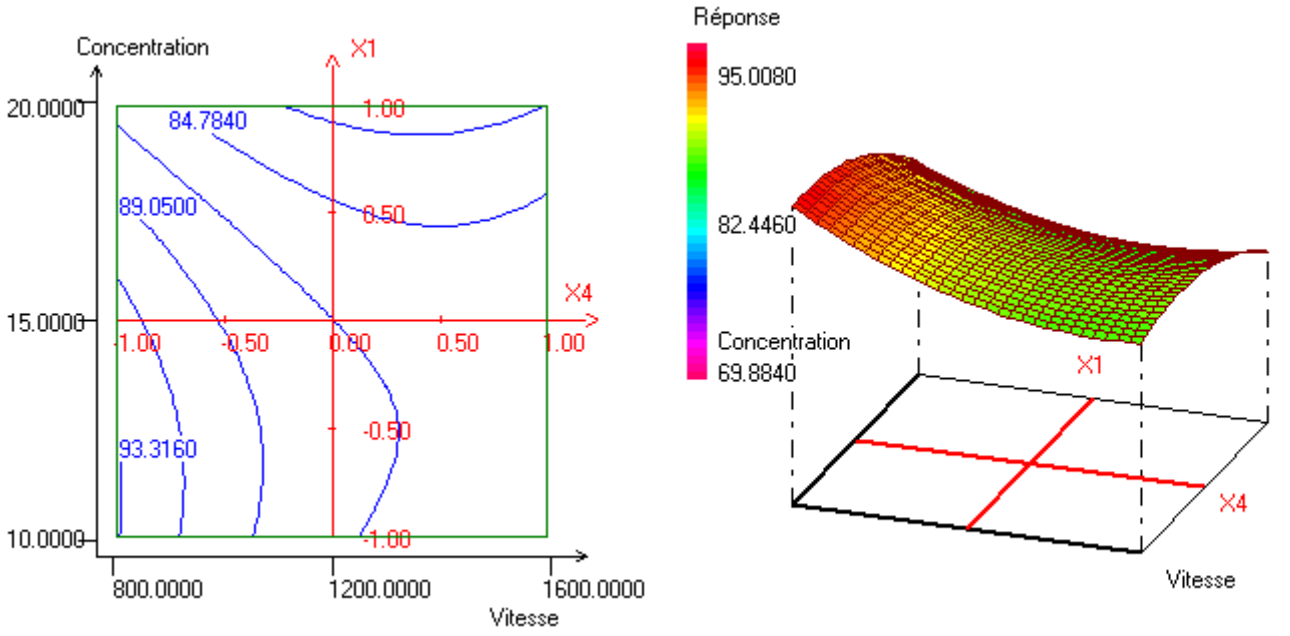
2D 3D

Figure 9: Response surface in 2D and 3D. (Change in the response - Efficiency in the plan: Particle Size, Speed ; Factors fixed: - Concentration = 15 mg/l - Weight = 0.2 g)



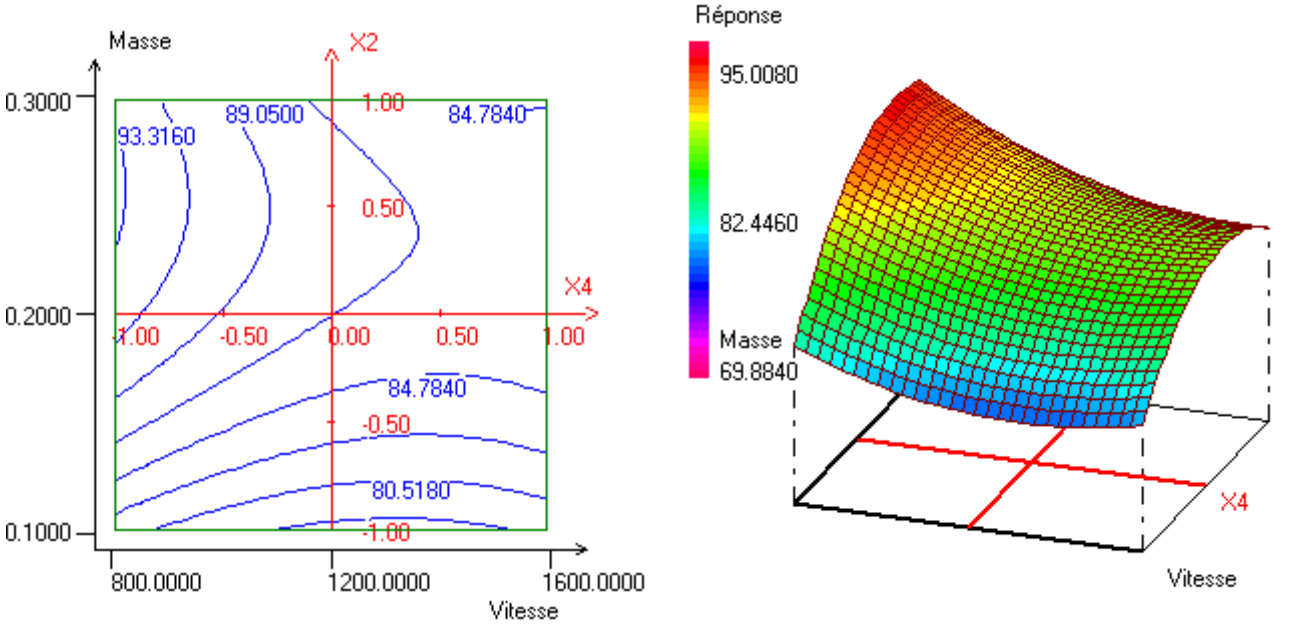
2D 3D

Figure 10: Response surface in 2D and 3D. (Change in the response - Efficiency in the plan: Particle Size, Concentration ; Factors fixed: - Weight = 0.2 g - Speed = 1200 rpm)



2D 3D

Figure 11: Response surface in 2D and 3D. (Change in the response - Efficiency in the plan: Speed, Concentration ; Factors fixed: - Weight = 0.2 g - Particle size = 80 micrometer)



2D 3D

Figure 12: Response surface in 2D and 3D. (Change in the response - Efficiency in the plan: Speed, Mass ; Factors fixed: - Concentration = 15 mg/l - Particle size = 80 micrometer)

Conclusion

From the results above, we can conclude that the sawdust wood used in this study was effective in the adsorption of methylene blue (MB), ranging widely in texture and surface properties. Indeed, the study we have undertaken on performance uses the composite design to 4 factors in the form of a polynomial of the 2nd order. It allowed us to know the influence of all parameters and derive the most influential. The optimization process was carried out and the experimental values for the BM absorption performance were found to be in satisfactory agreement with the values predicted by the models. The optimal condition was obtained using a large adsorbent mass, suggesting that adsorption increases with the surface area of the adsorbent, a fine particle size, low middle stirring speed and low initial concentration of MB.

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