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Adsorption study of the methylene blue on sawdust beech and red wood.

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Abstract

Two adsorbents were studied from sawdust, one with using the beech wood, and the other was from red wood, the adsorbents were characterized by several techniques (FTIR, SEM).Then they were used for the study of the adsorption of the methylene blue on wood sawdust.

This study allowed us to highlight the influence of the pH of the solution, the duration of contact, the concentration of the methylene blue and the mass of the used adsorbent, on the adsorption of the methylene blue. The results show that the percentage of adsorption increases in a defined interval of each parameter and then it stabilizes at precise values, this stabilization is due to the saturation of the active sites of the adsorbent. The results obtained show that the equilibrium is established after the first 10 minutes of the adsorption, it can reach a maximum of 96% at the room temperature and the initial pH of the solution. The kinetic adsorption of methylene blue on the two waste woods is described by a pseudo-second order model.

The experimental design method using the full factorial design, allowed us to define and study the influence of the adsorption parameters of methylene blue on sawdust; it enabled us to bring out the interaction between them. In order to optimise the factors acting on the adsorption of the methylene blue on red wood and beech wood sawdust, we used a central composite design. After an appropriate choice of four variables, 27 experiments led to a mathematical model of the second degree linking the response (percentage of fixation) with the factors and allowing a good mastery of the adsorption process. After carrying out the tests and analysing the data, the study made it possible to know the optimum conditions necessary for obtaining a higher percentage of adsorption. These operating conditions are: a mass of wood sawdust of 0.305 g, a methylene blue concentration of 0.2 ppm, a contact time of 90 min and pH of 2.

1. Introduction

Morocco has an estimated forest heritage of 9 million hectares with a production of about 1.6 million m^3 of wood. Half of this volume is processed in sawmills leaving nearly 108000 tonnes of waste per year [1]. The treatment of the wood waste is now subject to constraints linked to the principles of sustainable development and requires the development of specific recycling and recovery methods. The valorisation of this type of waste becomes a necessity more than ever for the protection of the environment and forest heritage. One of the most widely used methods for valorisation this wood waste is used them for the adsorption of different dyes.

Dyes are an important class of synthetic organic compounds used in many industries [2, 3], especially textiles. Consequently, they have become common industrial environmental pollutants during their synthesis and later during fibre dyeing [4]. Environmental pollution is one of the major and most urgent problems of the modem world. Industries are the greatest polluters, with the textile industry generating high liquid effluent pollutants due to the large quantities of water used in fabric processing. In this industry, wastewaters differing in composition are produced, from which coloured water released during the dyeing of fabrics may be the most problematic since even a trace of dye can remain highly visible [4]. Dyes and additives used by industries pose a serious threat to the environment because their presence in water, even at very low levels, is highly visible and undesirable. Current research is then directed towards low-cost processing methods using materials such as clays, bentonites and other adsorbent materials such as wood waste which may be a good alternative for the adsorption of dyes and adjuvant organic.

Among the most used dyes in industries is methylene blue which is the most used substance for a several materials of textiles such as cotton, wool, and silk dyeing [5, 6]. The exposition to methylene blue causes serious injuries to human and animals eyes and in some cases could lead to mental confusion and methemoglobinemia [7]. Thus, a treatment of wastewater containing these dyes has attracted the attention of scientific researchers in order to reduce their negative impacts on human health [7].

To reduce the negative impact of these dyes, various physical and chemical methods are used, such as chemical precipitation, membrane separation, electroplating and solvent extraction. The adsorption has also proved to be an effective technique for this objective. Activated carbon is the most commonly used adsorbent; the steps of activation and regeneration are delicate and too costly, limiting its use [8]. In this context, the importance of finding renewable, inexpensive, abundant and easy to handle adsorbents is necessary. Indeed, the efficiency of the adsorption technique depends essentially on the nature, the cost, the regeneration and the availability of the adsorbent. In order to replace activated carbon, several adsorption studies of dyes on bioadsorbents have been carried out [9] such as the wood sawdust.

The present work aims at valorisation of two types of the wood waste sawdust (beech and red wood) by using the adsorption of the methylene blue. The first part consists to a physicochemical characterization of sawdust from our samples. Once the waste is characterized by infrared spectroscopy, scanning electron microscopy, they are subjected to an adsorption study of methylene blue as a colorant. Several parameters have been studied, namely: pH of solution, contact time, concentration of methylene bleu and mass of adsorbent. Then, the optimisation of the parameters influencing adsorption was studied using the method of experimental design.

2. Materials and methods

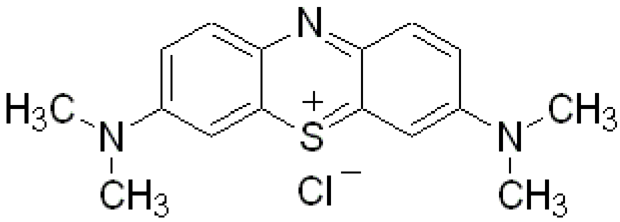
This study presents the adsorption of a cationic dye, methylene blue, on the sawdust of two types of wood (red wood and beech wood).

2.1. *Adsorbent*

The study is performed on two types of waste wood, red wood and beech wood, collected from an industrial unit located in Fez. The samples of sawdust acquired from the industry consist primarily of particles with a diameter less than 1 mm for red wood sawdust and less than 200 µm for beech wood sawdust while a particle size analysis was performed on the sawdust in order to separate the fine particles with these characteristics [10].

2.2. *Dye*

The dye used is the metylene blue which is a cationic dye of the chemical formula $C_6H_{12}ClN_3S$. It is an organic molecule used to test the adsorptive powers of solids and to determine their specific surface area. Its molar mass is 319.852 g / mol.



Molecular Structure of Methylene Blue

2.3.*Adsorption procedure*

The residual concentration of the dye in samples is measured by UV / Visible spectrophotometer at the wavelength characteristic of the dye (λ of the methylene blue = 664 nm).

The percentage of fixation (% ads) is calculated by the following equation:

$$\% Ads = \frac{C0 - Ce}{C0} \times 100$$

Where C_0 is the initial concentration and C_e is the final concentration(ppm).

2.4. *Study of adsorption kinetic*

The Lagergren pseudo first order and Blanchard pseudo second order models are used to describe the adsorption kinetics of methylene bleu on samples of wood sawdust.

2.4.1. *Model of the pseudo first order kinetics: Lagergren model*

The Lagergren pseudo first order model used by researchers to study adsorption kinetics is presented by the following equation:

$$\text{Ln}\ (q_e - q_t) = \ln q_e - K_1.t$$

With K_1 is the rate constant of the pseudo first order (min^{-1}), $q_e$isthe adsorption capacity at equilibrium (mg / g) and q_t is the adsorption capacity at time t (mg / g).

Experimentally, we trace ln (q_e - q_t) as a function of the time t, in order to calculate the kinetic parameters of the Lagergren first order model. We obtain a straight line with a slope ($-K_1$), and an ordinate at the origin equal to ln (q_e).

2.4.2. *Model of the second order kinetics: Blanchard model*

The pseudo-second order model is expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

With K_2 is the rate constant for second-order kinetics ($g.mg^{-1}.min^{-1}$),

The kinetic parameters for the Blanchard model are represented graphically by drawing t / $q_t$as a function of time t. A straight line with a slope 1 / q_e and an ordinate at the origin 1 / K_2qe^2 is obtained.

2.5. *Experimental design*

An experiment design consists of a group of mathematical and statistical techniques that can be used to optimize a set of experiences in order to quantify the relationship between the responses and the factors. After identification of the most influential factors, a more detailed study can be performed in order to detect possible interaction effects between the factors, meaning that the influence of some factors could be different according to the value of the other factors [11].

The aim of the first study was to evaluate the influence of mass of adsorbents, concentration of methylene blue, pH of the solution and contact time on the percentage of adsorption considered as the response of our study by using a full factorial design. In the second part of this study, the four parameters were optimized by applying a response surface methodology in form of central composite design, in order to define the optimum conditions for a higher percentage of adsorption.

All the calculations (regression, statistical tests and graphical plots) were performed with Nemrodw software (New Efficient Methodology for Research using Optimal Design, LPRAI).

2.5.1. Full factorial design

In order to study the influence of the parameters on the percentage of adsorption, a full factorial design of the n^k type was used, where n and k are respectively the numbers of levels and parameters , in this study n = 2 and k = 4. Thus, the total number of experiments required for this study is 16, we choose a repetition for each experiment with two central points, and then the total number of experiments was 34. Y attribute to response variable which is the percentage of adsorption, then the four-parameter regression equation and their interaction is given by the model mathematic:

$$Y = b0 + \sum_{i} bi\ Xi + \sum_{i \neq j} bij\ Xij + \sum_{i \neq j \neq k} bijk\ Xijk + \sum_{i \neq j \neq k \neq l} bijkl\ Xijkl$$

With $b_{i\neq 0}$ is coefficient of the parameters, b_0 is the average, $X_i.X_j$ is the interactions between the parameters X_i and X_j and Y is the percentage of the adsorption.

2.5.2. Central composite design

In order to obtain the optimum conditions for a maximum of adsorption, a response surface methodology was used. The central composite start with a factorial design used in the first study (with center points) and add "star" points to estimate curvature. Its comprise 8 axial points, 3 central points and 16 experiences from full factorial design which give 27 experiences.

$$Y = bo + \sum_{i} bi\ Xi + \sum_{i} bii\ Xi\ Xi + \sum_{i \neq j} bij\ Xij$$

3. Results and discussion

3.1.*Physico- chemical characterization of sawdust*

3.1.1. Scanning electron microscopy (SEM)

Scanning electron microscopy was used to describe the surface microstructure of sawdust samples from wood (Figure 1 and 2) for the red wood we observe the presence of horizontal tubes known as tracheids. Are cells elongated in the longitudinal direction and which act as support and contact for the raw sap [12, 13, 14]. For the beech wood, the morphological examination gives the different SEM photomicrographs of the sample; it shows the presence of the elongated fibers and vessels which contain the fibers.

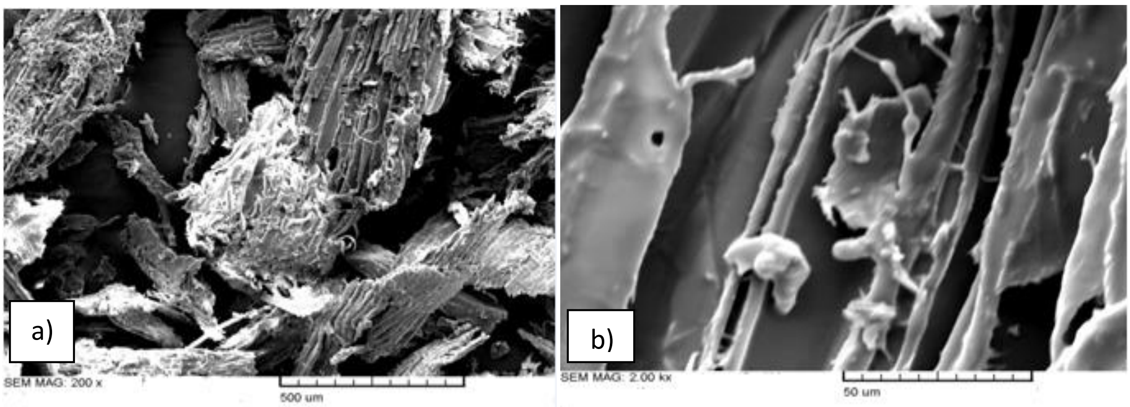


Figure1: SEM micrograph of red wood sawdust:
Enlargement a: x 200 ; b: x 2000

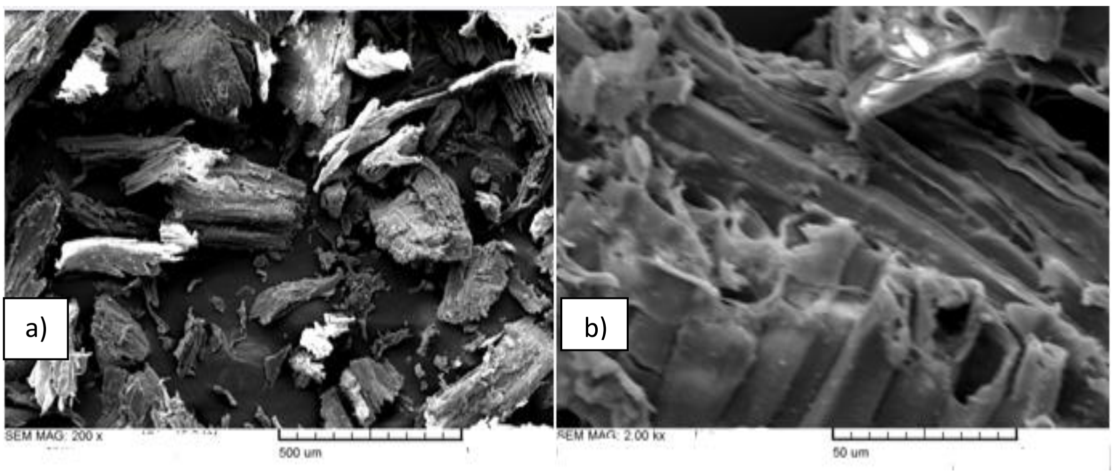
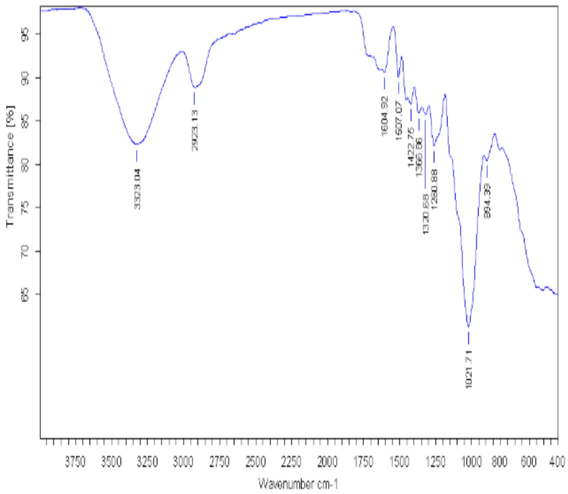


Figure 2: SEM micrograph Beech wood sawdust:
Enlargement a: x 200; b: x 2000

3.1.2. Infrared spectroscopy(FTIR)

Infrared spectroscopy shows the bands of the characteristic spectra of the wood compounds, which have been allocated in agreement with the literature data [15, 24]. The spectrum of cellulose appears between 3330 cm^{-1} and 3320 cm^{-1}, as well as the appearance of the bands characteristic of hemicelluloses and lignin.

All infrared spectra reveal the presence of a wide band at about 3323 cm^{-1} and 3324 cm^{-1} which corresponds to the elongation vibrations of the O-H bond of the aromatic and aliphatic structures of phenol, lignin group and cellulose [14]. The band which appears between 2923 cm^{-1} and 2891 cm^{-1} corresponds to the asymmetric elongation vibration of the C-H bond of the cellulose. The peak at 1731 cm^{-1} is characteristic of the (C = O) valence vibration of carboxylic acids and / or xylan esters present in lignins and hemicelluloses [21, 23]. The vibration at 1507 cm^{-1} and 1504 cm^{-1} is attributed to the deformation (C = C) of the aromatic cycles of the lignin and the bands observed at 1320 - 1324 cm^{-1} and 1260 – 1234 cm^{-1} attributed to the vibration ν (CO) of the groups methine from lignin [14]. The peak at 1021 cm^{-1} corresponds to the valence vibrations of the C-O and C-O-C bonds, of cellulose [17]. The peak at 894 cm^{-1} and the bands appearing at the frequency between 720 cm^{-1} and 400 cm^{-1} are characteristic of the C-H group in cellulose [24, 25] (Table 1).



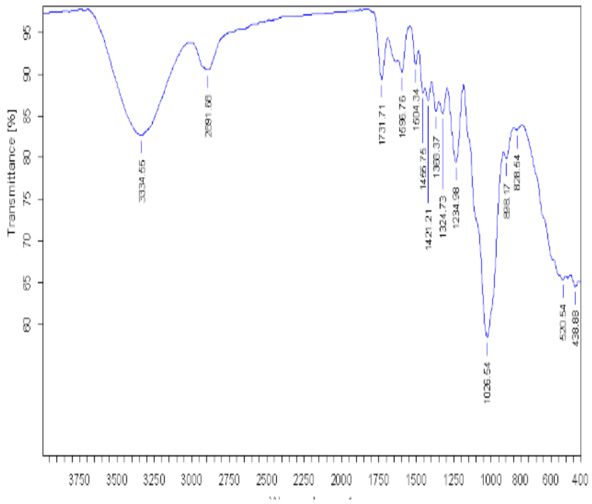


Figure 3: Infrared spectrum of red woodsawdust**Figure 4:**Infrared spectrum of beech woodsawdust

Table 1: Attribution of infrared bands of molecules

Frequency (cm^{-1})	Allocation of bands
3323 – 3324	O-H Stretching
2923 – 2891	C-H Stretching
1604 – 1596	C=O Stretching
1507 – 1504	Aromatic sequel vibration
1456 – 1455	C-H bending
1422 – 1421	Aromatic vibration
1366 – 1368	Aliphatic C-H stretching in CH_3
1320 – 1324	C-O stretching (Primary or secondary alcohol)
1260– 1234	C-O stretching (Primary or secondary alcohol)
1021	Aromatic cyclohexane

3.2. Adsorption
3.2.1. Influence of adsorbent mass

The influence of the initial amount of wood sawdust was studied at the pH of the solution without adjustment, at room temperature, at a stirring speed of 300 rpm and at a concentration of 10 ppm of methylene blue for both types of wood sawdust (red wood and beech wood). The effect of the mass of wood sawdust to remove the methylene blue from the aqueous solution was studied by varying the mass of sawdust from wood between 0.01 and 2 g.

Concerning the percentage of adsorption (% Ads), it reaches the maximum at a mass equal to 0.6 g with an adsorption of 96% for both types of wood waste (Figure 5).

The adsorption consists of interactions between the adsorbent and the adsorbate fixed on the active sites. The curve of the figure shows that a mass of 0.6 g of sawdust from red and beech wood is capable to fix a maximum of blue methylene of the order of 96%. The increase in the percentage of adsorption to this mass can be explained by the increase in the number of active sites added by the sawdust. The percentage of adsorption remains constant which can be explained by the saturation of all the active sites. After a certain mass, the percentage of adsorption decreases slightly indicating probably the presence of another type of interaction between dye and sawdust. It may be a competition between the fibers retaining dye fractions and the free fibers of the adsorbent which attract the latter, causing it to return to the solution reference [26]. It is therefore useful to work with doses of adsorbent ≤ 0.6 g and to avoid an inefficient overdose (Figure 5).

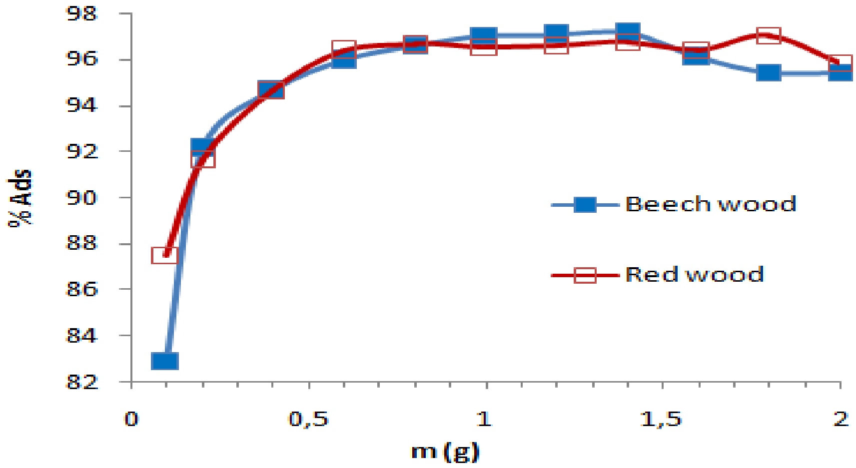


Figure 5: Variation of fixation percentage (% Ads) as a function of the mass (m)

3.2.2. Influence of pH

pH of solution of the dye is an important factor in any adsorption study because it can influence both the surface charge of the adsorbent and the structure of the adsorbate. That's why it's necessary to optimize the pH by studying the phenomenon of adsorption over a wide pH range.

The pH of adsorption of methylene blue on wood sawdust samples was realized at acidic and basic pH values from 1 to 10 by adjusting the initial pH of solutions using the nitric acid (HNO_3) and the sodium hydroxide (NaOH) solutions.

Figure 6 shows an increase in the adsorbed amount of methylene blue between pH = 1-3. For the pH range 3-10, a stability of the adsorbed amount and percentage of absorbance is observed. This can be explained by the fact that at low pH values the surface of the adsorbent would be surrounded by the H^+ ions, which decreases the interaction of the methylene blue ions MB+ with the sites of the adsorbent, it can be explained by the competition between the H + ions and the MB+ cation which prevents the dye from being fixed on the active sites of sawdust, For a higher pH values, the H^+ concentration decreases, resulting in good interaction between dye ions and surface sites [27].

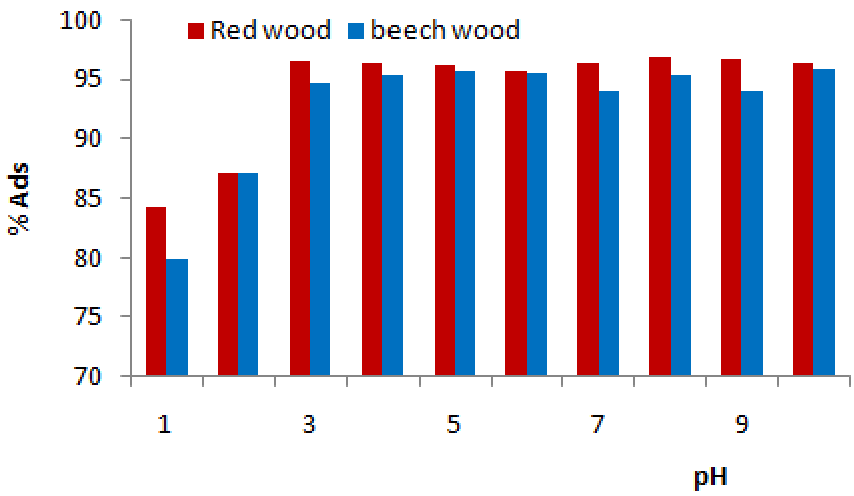


Figure 6: Variation of fixation percentage (% Ads) as a function of pH

3.2.3. Influence of concentration

The influence of the concentration was made by stirring the solution containing the adsorbate and the adsorbent for one and a half hours at a rate of 300 rpm at the initial pH of the solution, kept at room temperature. The methylene blue concentrations selected varies from 0.2 to 10 ppm.

The figure 7 shows the influence of the concentration on the percentage of fixation. The curves obtained indicate that the adsorption increases with the increase of the concentration of the dye until it reaches a maximum which is 7 ppm, This is due to the saturation of the active sites of the adsorbent.

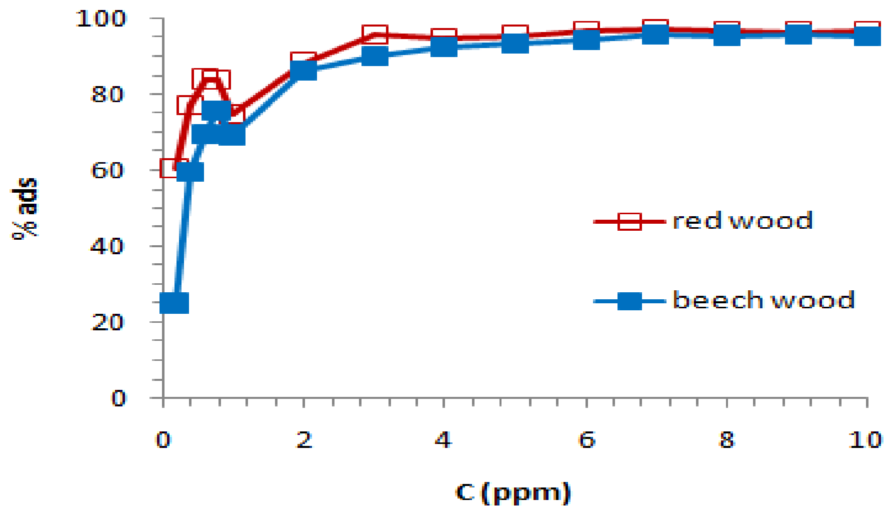


Figure 7: Variation of fixation percentage (% Ads) as a function of concentration

3.2.4. Influence of contact time

This study aims to determine the time value from which the adsorption reaction reaches equilibrium.

For this reason, the study was done at the different contact duration in which the supernatant of the reaction medium was taken for each sample of the sawdust from the wood.

The results obtained are illustrated in the figure 8 which represent the evolution of the percentage of adsorption of methylene blue on each wood sawdust samples as a function of the contact time.

According to the graphs, we notice a rapid adsorption at the beginning and then a spreading with saturation. A rapid increase in the adsorption capacity of the dye and the percentage of fixation takes place within a few minutes (10 minutes), due to the adsorption of methylene blue to the surface of the particles of the adsorbent. This first phase constitutes the essential part of the phenomenon of adsorption because the kinetics of fixation is limited by the low residual concentration of dye. In the second stage, the occupation of deep adsorption sites requires diffusion of the adsorbate within the micropores of the adsorbent. A second, slower phase is thus observed. After this phase, a saturation bearing is observed.

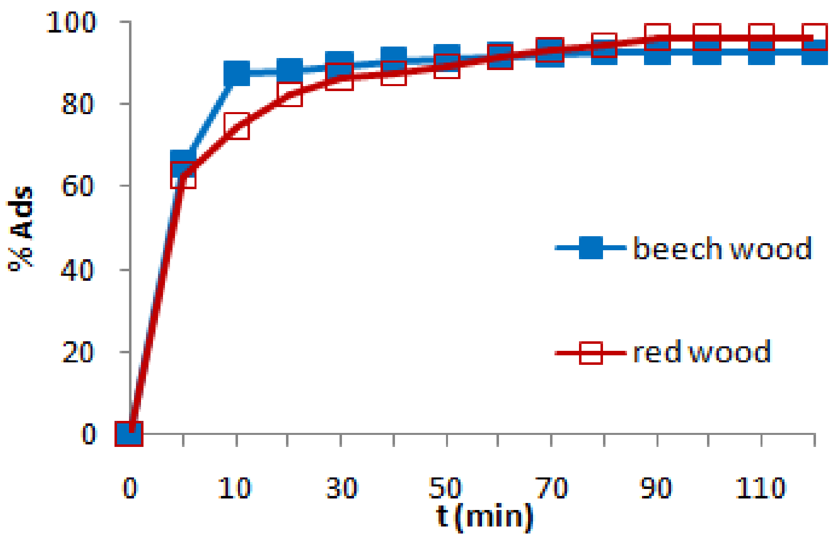


Figure 8: Variation of fixation percentage (%Ads) as a function of time contact

The comparison of the results of the percentage of fixation and the exchange capacity between the sawdust of the red wood and the sawdust of the beech wood indicates that the adsorption power of the two types of wood is almost the same with a small difference.

3.2.5. Study of adsorption kinetic

The figures 9 and 10 represents the Lagergren and Blanchard models corresponding to the adsorption kinetics of the methylene blue on the two samples of the sawdust.

According to the graphs, the equations of the first order for the red and the beech wood becomes successively ln $(q_e - q_t)$ = - 0.037 t – 1.090 and ln $(q_e - q_t)$ = - 0.026 t – 2.541.

The equations of the second pseudo-order becomes: t / q_t =1 t + 4.663 for the red wood and t / q_t = 1.061 t + 1.568 for the beech wood.

Table 2: Kinetic parameters of 1st and 2nd order

	Model of Lagergren (1st order)			**Model of Blanchard (2nd order)**		
	R^2	**$K_1(min^{-1})$**	**q_e (mg/g)**	**R^2**	**K_2 (g/mg min)**	**q_e (mg/g)**
Red wood	0.928	0.037	0.336	0.999	0.214	1
Beech wood	0.924	0.026	0.0788	0.999	0.719	0.942

According to the Table 2 and the figures 9 and 10, which show the curve of the first-order model, the curve of the second-order model and the experimental results of adsorption, we find that the second order kinetic law gives a better description of the Kinetics of adsorption with a correlation coefficient of 0.999.

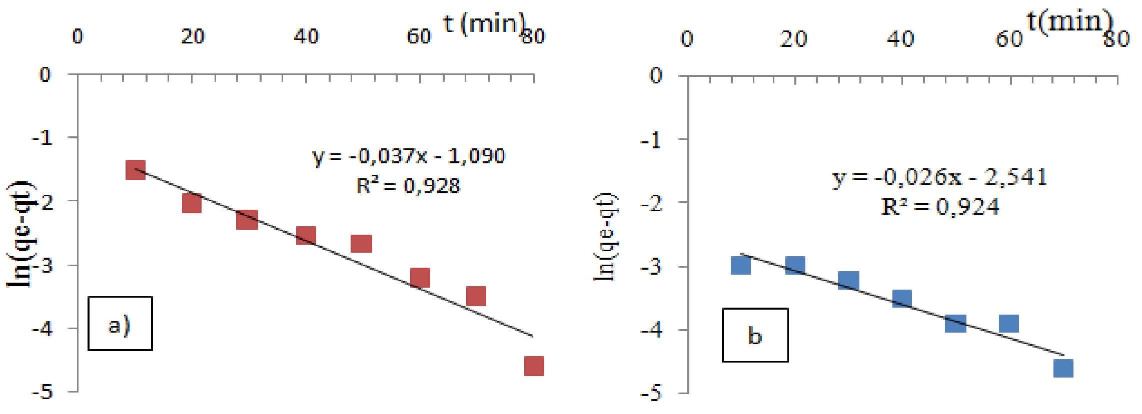


Figure 9: First order model:
a) Red wood b) beech wood

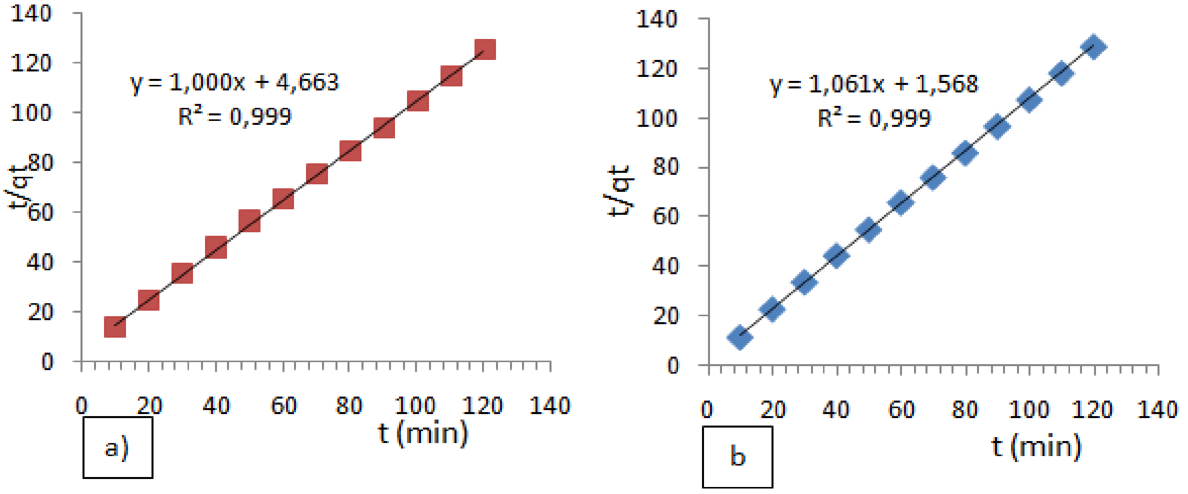


Figure 10: Second-order model
a) Red wood b) beech wood

By comparing these results with the results obtained from the bibliography and which relates to the kinetic study of the dye on sawdust from African fir [26], we observe that the three types of sawdust show a linear variation of t / qt as a function of t. Which shows that the experimentally determined equilibrium adsorbed amount is closer to that calculated using the second-order kinetic model. On the other hand, in the case of the first-order kinetics, the adsorbed quantity at equilibrium, determined experimentally, is different from that calculated.
According to the results obtained from the kinetic study of the adsorption of methylene blue on wood ashes [6], it appears that the values of R^2 are very high and are all of the order of 0.99 and far exceed those obtained with the pseudo-first order model. The quantities fixed at equilibrium qe are very close to the values found experimentally. These last two observations lead us to believe that the adsorption process follows the pseudo-second order model.

3.3. Experimental design

3.3.1. Full factorial design

The aim of this study was to evaluate the influence of the four parameters considering also the interaction effects which quantify the change in the effect of one factor when another factor is varied from its low to its high level. We postulated that the result of each experiment is a linear combination of the main effect bi and interaction effects b_{ij} of each variable X_1, X_2, X_3 and X_4.
The postulated mathematical model is a model of the first degree:
$$Y = b_0 + b_1 * X_1 + b_2 * X_2 + b_3 * X_3 + b_4 * X_4 + b_{1-2} * (X_1 * X_2) + b_{1-3} * (X_1 * X_3) + b_{2-3} * (X_2 * X_3) + b_{1-4} * (X_1 * X_4) + b_{2-4} * (X_2 * X_4) + b_{3-4} * (X_3 * X_4) + b_{1-2-3} * (X_1 * X_2 * X_3) + b_{1-2-4} * (X_1 * X_2 * X_4) + b_{1-3-4} * (X_1 * X_3 * X_4) + b_{2-3-4} * (X_2 * X_3 * X_4) + b_{1-2-3-4} * (X_1 * X_2 * X_3 * X_4).$$
With $b_{i \neq 0}$ is the coefficient of the parameters, b_0 is the average, $X_i.X_j$ is the interactions between the parameters X_i and X_j and Y the percentage of the adsorption.

3.3.1.1. Determination of the study filed

The field of study of each parameter was defined based on the results of preliminary adsorption studies.

- Mass of adsorbent

According to the preliminary study of adsorption, it was found that a mass of 0.6 g is capable to fix a maximum of methylene blue (96%), after this mass the curve remains constant, then the field of study for experimental design is limited between 0.01 g et 0.6 g.

- pH of solution

According to the results obtained by the preliminary study, the percentage of adsorption varies in the range of pH 1-3 while it remains constant throughout the interval 3-13 which is explained by the fixation of the MB + ions at the active sites of sawdust. This variation in the percentage of adsorption in the acid range was subject of the study in the experimental designs.

- Concentration of methylene blue

The results obtained from the percentage of adsorption curves as a function of the concentration of methylene blue showed that after a concentration of 7 ppm, there is a saturation of all the active sites of the adsorbent, while the adsorption remain constant even if there is an increase in concentration more than 7 ppm.

- Contact time

After 90 min, there is no variation in the percentage of fixation, which shows that it reached the equilibrium.

Table 3: Field of study of the parameters

Operating parameters	Notation	Lowlevel (-1)	High level (+1)	Coefficients
The mass of the adsorbent (g)	X_1	0.01	0.6	b_1
Concentration (ppm)	X_2	0.2	7	b_2
Contact time (min)	X_3	5	90	b_3
pH	X_4	1	3	b_4

Table 4: Experimental design describing the experiences

N°Exp	m (g)	C (ppm)	t (min)	pH	%ads red wood	% ads beech wood
1	0.01	0.20	5.00	1.00	97.42	74.16
2	0.01	0.20	5.00	1.00	92.33	70.11
3	0.60	0.20	5.00	1.00	85.13	97.73
4	0.60	0.20	5.00	1.00	80.24	97.42
5	0.01	7.00	5.00	1.00	37.68	35.25
6	0.01	7.00	5.00	1.00	34.12	36.21
7	0.60	7.00	5.00	1.00	81.28	50.16
8	0.60	7.00	5.00	1.00	75.16	52.14
9	0.01	0.20	90.00	1.00	97.22	98.33
10	0.01	0.20	90.00	1.00	95.34	98.43
11	0.60	0.20	90.00	1.00	98.84	98.89
12	0.60	0.20	90.00	1.00	95.22	98.74
13	0.01	7.00	90.00	1.00	37.68	42.73
14	0.01	7.00	90.00	1.00	40.45	37.93
15	0.60	7.00	90.00	1.00	90.25	84.39
16	0.60	7.00	90.00	1.00	85.46	84.70
17	0.01	0.20	5.00	3.00	92.78	80.41
18	0.01	0.20	5.00	3.00	90.10	74.15
19	0.60	0.20	5.00	3.00	98.48	99.30
20	0.60	0.20	5.00	3.00	98.48	99.14
21	0.01	7.00	5.00	3.00	56.15	52.17
22	0.01	7.00	5.00	3.00	51.55	56.25
23	0.60	7.00	5.00	3.00	75.40	90.25
24	0.60	7.00	5.00	3.00	70.22	91.26
25	0.01	0.20	90.00	3.00	97.57	98.48
26	0.01	0.20	90.00	3.00	97.57	98.33
27	0.60	0.20	90.00	3.00	75.20	97.72
28	0.60	0.20	90.00	3.00	70.49	98.05
29	0.01	7.00	90.00	3.00	38.28	43.23
30	0.01	7.00	90.00	3.00	34.37	39.40
31	0.60	7.00	90.00	3.00	92.37	86.88
32	0.60	7.00	90.00	3.00	92.29	84.15
33	0.30	3.60	47.50	2.00	77.56	77.09
34	0.30	3.60	47.50	2.00	80.64	78.88

3.3.1.2. Statistical validation of the model

The results shown in the table of the analysis of variance (Tables 5, 6) for both sawdust, indicate that the main effect of the regression is significant since the probability of the significance of the *p-value* risk is less than 0.05. On the other hand, the sum of the squares due to the residues has been decomposed into two variabilities: the first is due to the lack of adjustment, and the second is due to the pure error. It is a technique to refine the analysis of the variance, which can be used when at least one experiment has been repeated, and which makes it possible to test the validity of the model. According to Tables 5 and 6, the model does not exhibit a lack of adjustment since the probability of the significance of the risk (p value = 24.5 for red wood and 29.2 for beech wood) is greater than 0.05.

Table 5: Analysis of variance for the fitted model for the %ads of red wood

Source of variance	DF	Mean square	Sum of squares	Rapport	Signif p- value
Regression	15	$1.05658E^{+0003}$	$1.58487E^{+0004}$	140.5526	< 0.01 ***
Residual	18	7.51733	$1.35312E^{+0002}$		
Validity	1	$1.06400E^{+0001}$	$1.06400E^{+0001}$	1.4508	24.5
Error	17	7.33364	$1.24671E^{+0002}$		
Total	33		$1.59840E^{+0004}$		
R^2	0.992				

DF: Degrees of freedom; R^2 : Coefficient of determination

Table 6: Analysis of variance for the fitted model for the %ads of beech wood

Source of variance	DF	Mean square	Sum of squares	Rapport	Signif p- value
Regression	15	$1.14546E^{+0003}$	$1.71819E^{+0004}$	303.9150	< 0.01 ***
Residual	18	3.76901	$6.78421E^{+0001}$		
Validity	1	4.41901	4.41901	1.1845	29.2
Error	17	3.73077	$6.34231E^{+0001}$		
Total	33		$1.72497E^{+0004}$		
R^2	0.996				

DF: Degrees of freedom; R² : Coefficient of determination

The coefficient of determination R^2=99.2% and 99.6% for respectively red wood and beech wood are sufficient. This value gives a good agreement between the experimental and predicted values of the adapted model.

These results are confirmed by those obtained in the graph (Fig. 11), showing that the curve of the observed values as a function of the predicted values have a linear curve.

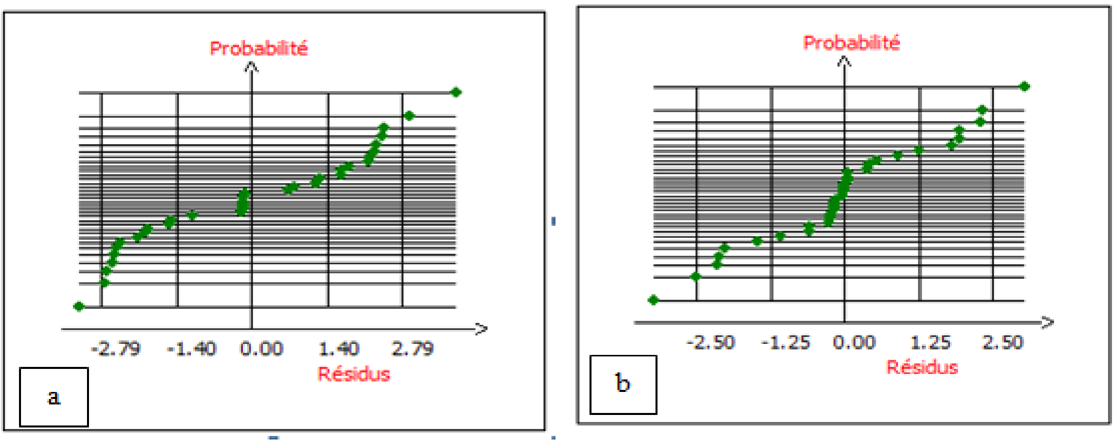


Figure 11: Study of residues
a) Red wood , b) beech wood

3.3.1.3. Study of factors effects

The main effects of the four studied variables for each wood sawdust, are shown in Tables 7, 8 and figures 12-13. Each coefficient is associated with the values of t-student and p-value. The values of t-student are used to determine the significance of the regression coefficients of each parameter and the values of p are defined as the lowest level of importance leading to the rejection of the null hypothesis H_0 (bi=0, α=0,05) [28]. In general, more the t-student's magnitude is larger, more the p-value is smaller, and more the corresponding coefficient term is significant [29, 30]. The value of the constant b_0 is respectively equal to 76.862 and 76.543 for red wood and beech wood.

Table 7: Estimated regression coefficients for the % ads for red wood

Nom	Coefficient	standard deviation	t.exp.	Signif. % (p-value)
b0	76.862	0.47021048	163.46	< 0.01 ***
b1	8.559	0.48468187	17.66	< 0.01 ***
b2	-14.678	0.48468187	-30.28	< 0.01 ***
b3	0.690	0.48468187	1.42	17.2
b4	0.234	0.48468187	0.48	63.5
b1-2	12.200	0.48468187	25.17	< 0.01 ***
b1-3	1.543	0.48468187	3.18	0.514 **
b2-3	1.159	0.48468187	2.39	2.79 *
b1-4	-1.399	0.48468187	-2.89	0.981 **
b2-4	1.551	0.48468187	3.20	0.497 **
b3-4	-2.879	0.48468187	-5.94	< 0.01 ***
b1-2-3	3.896	0.48468187	8.04	< 0.01 ***
b1-2-4	-0.619	0.48468187	-1.28	21.8
b1-3-4	-0.883	0.48468187	-1.82	8.5
b2-3-4	1.528	0.48468187	3.15	0.550 **
b1-2-3-4	4.705	0.48468187	9.71	< 0.01 ***

***: Highly significant coefficient; **: Very significant coefficient; *: Significant coefficient

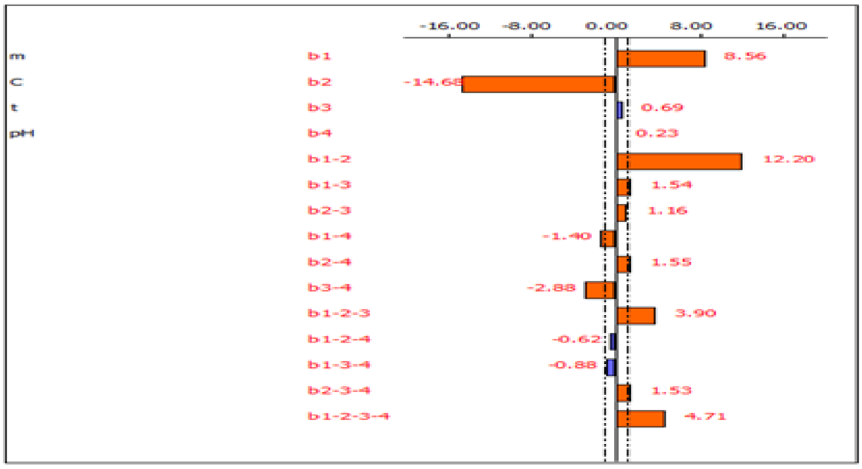


Figure 12: The factors effect's graph for methylene blue on red wood sawdust

The results show also that only the factors b3 and b4, which are related to the contact time and pH of solution respectively, as well as their interactions with the first and the second factors, doesn't have any influence on the adsorption process, since their signification risk is superior to 5%.

The statistical mathematical model representing the response in terms of the most influential variables is:

$Y = 76.862 + 8.559X_1 – 14.678\ X_2 + 12.2\ X_1X_2 + 1.543\ X_1X_3 + 1.159\ X_2X_3 – 1.399\ X_1X_4 + 1.551\ X_2X_4 – 2.879\ X_3X_4 + 3.896\ X_1X_2X_3 + 1.528\ X_2X_3X_4 + 4.705\ X_1X_2X_3X_4$

Table 8: Estimated regression coefficients for the % ads for beech wood

Coefficient	Effect	standard deviation	t.exp.	Signif. % (p- value)
b0	76.543	0.33294612	229.90	< 0.01 ***
b1	11.730	0.34319301	34.18	< 0.01 ***
b2	-16.009	0.34319301	-46.65	< 0.01 ***
b3	4.196	0.34319301	12.23	< 0.01 ***
b4	4.120	0.34319301	12.01	< 0.01 ***
b1-2	5.818	0.34319301	16.95	< 0.01 ***
b1-3	-0.688	0.34319301	-2.01	6.0
b2-3	-1.713	0.34319301	-4.99	< 0.01 ***
b1-4	1.041	0.34319301	3.03	0.715 **
b2-4	3.385	0.34319301	9.86	< 0.01 ***
b3-4	-3.989	0.34319301	-11.62	< 0.01 ***
b1-2-3	5.245	0.34319301	15.28	< 0.01 ***
b1-2-4	1.598	0.34319301	4.66	0.0197 ***
b1-3-4	-1.162	0.34319301	-3.39	0.329 **
b2-3-4	-3.027	0.34319301	-8.82	< 0.01 ***
b1-2-3-4	-1.480	0.34319301	-4.31	0.0419 ***

***: Highly significant coefficient; **: Very significant coefficient; *: Significant coefficient

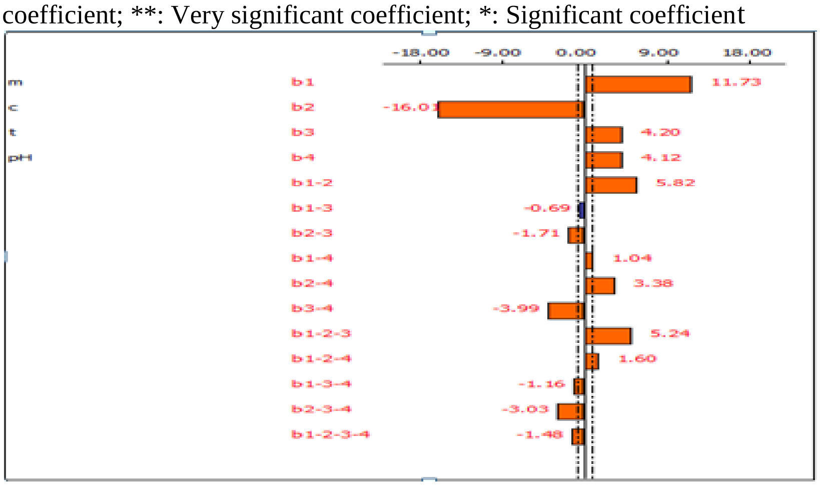


Figure 13: The factors effect's graph for methylene blue on beech wood sawdust

The results from the factors effects for beech wood show that the only interaction between mass and time contact which had no significant influence on the adsorption process, while all the other factors have an influence.

The statistical mathematical model representing the response in terms of the most influential variables is:

$$Y = 76.543 + 11.73\,X_1 - 16.009\,X_2 + 4.196\,X_3 + 4.120\,X_4 + 5.818\,X_1X_2 - 1.713\,X_2X_3 + 1.041\,X_1X_4 + 3.385\,X_2X_4 - 3.989\,X_3X_4 + 5.245\,X_1X_2X_3 + 1.598\,X_1X_2X_4 - 1.162\,X_1X_3X_4 - 3.027\,X_2X_3X_4 - 1.48\,X_1X_2X_3X_4$$

3.3.1.4. Study of interactions

Figure 12 and 13 shows that the mass of adsorbent (X1) and methylene blue concentration (X2) were the most significant individual factors affecting the percentage of adsorption. On the other hand, the %ads was affected by an interaction these factors with the contact time (Figure 14), indicating that the best condition to maximize the percentage of adsorption at 5 or 90 min, depends on the level of both factors (X1 and X2), and changing the level of one of these factors results in a change in the overall effect. Fig. 17a, which details this interaction, indicates that the % ads at t=5 min was improved when both factors were at level Xi = -1 (mass = 0.01 g and Concentration = 0.2 ppm) for red wood, whereas the % ads highly increase when the mass is 0.6g and the concentration is 0.2 ppm, for beech wood.

At t = 90 min a significantly higher percentage of adsorption was achieved, for both sawdust, if the mass of adsorbent increase from level -1 to level +1 and the concentration from +1 to -1.

The red wood has a special characteristic; it allows giving 93% of adsorption with a minimum concentration and mass whereas the beech wood allows having 98% of adsorption with a maximum mass and a minimum concentration.

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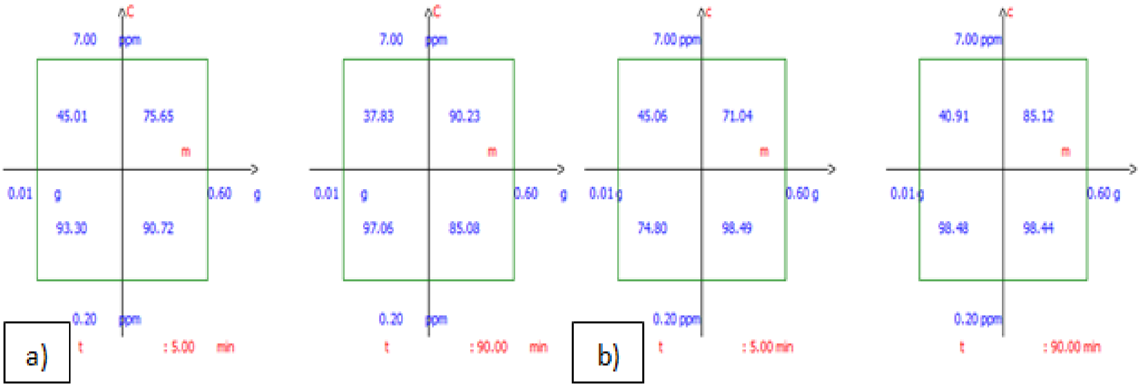

Figure 14: Diagram of the percentages of adsorption as a function of the interactions between factors X_1, X_2, X_3 a) Red wood, b) beech wood

3.3.2. Optimisation

For the study of optimisation of the factors influencing adsorption, the selected central composite design is a surface design of response which comprises a full factorial design with 16 experiences and 3 central points, to which is added 8 axial points. The total numbers of experiences are 27.

3.3.2.1. Mathematical model

The postulated mathematical model is a second order polynomial design:

$$Y = b_0 + b_1 * X_1 + b_2 * X_2 + b_3 * X_3 + b_4 * X_4 + b_{1\text{-}1} * (X_1{*}X_1) + b_{2\text{-}2} * (X_2{*}X_2) + b_{3\text{-}3} * (X_3{*}X_3) + b_{4\text{-}4} * (X_4{*}X_4) + b_{1\text{-}2} * (X_1{*}X_2) + b_{1\text{-}3} * (X_1{*}X_3) + b_{2\text{-}3} * (X_2{*}X_3) + b_{1\text{-}4} * (X_1{*}X_4) + b_{2\text{-}4} * (X_2{*}X_4) + b_{3\text{-}4} * (X_3{*}X_4)$$

The mathematical model chosen for red wood is given by the following equation:

$$Y = 94.569 + 8.814\,X_1 - 14.009\,X_2 - 1.238\,X_3 - 9.267\,X_1^2 - 4.659\,X_2^2 - 2.147\,X_3^2 + 12.2\,X_1X_2 + 2.733\,X_2X_3 - 1.399\,X_1X_4 + 1.551\,X_2X_4$$

The mathematical model chosen for beech wood is given by the following equation:

$$Y = 92.321 + 11.913\,X_1 - 15.341\,X_2 - 3.467\,X_3 + 4.126\,X_4 - 10.394\,X_1^2 - 3.211\,X_2^2 - 1.884\,X_4^2 + 5.795\,X_1X_2 - 1.189\,X_1X_3 - 3.05\,X_2X_3 + 1.02\,X_1X_4 + 3.36\,X_2X_4 + 4.175\,X_3X_4.$$

Table 9: Study field of parameters

Operating parameters	Notation	Lowlevel (-1)	Central level (0)	High level (+1)
The mass of the adsorbent (g)	X_1	0.01	0.305	0.6
Concentration (ppm)	X_2	0.2	3.6	7
Contact time (min)	X_3	5	47.5	90
pH	X_4	1	2	3

3.3.2.2. Profile isoresponses

With the aid of the profile of isoresponses (figure 15), we can also envisage different solutions relative to the operating conditions.

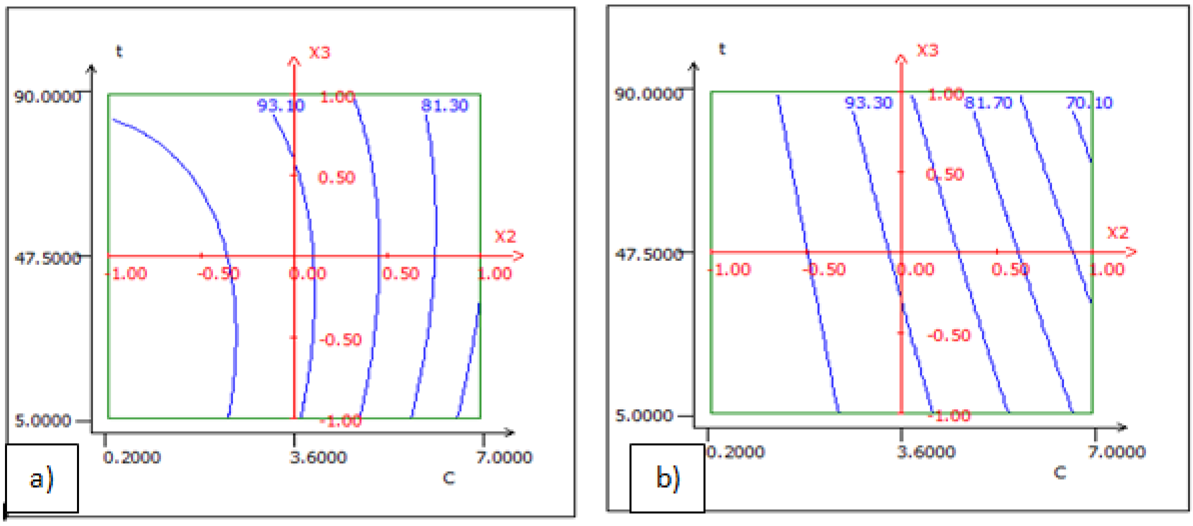

Figure 15: Variation of % Ads in 2D in the plan (c, t)
a) red wood, b) beech wood
(Fixed Factors: m = 0.305 g , pH = 2)

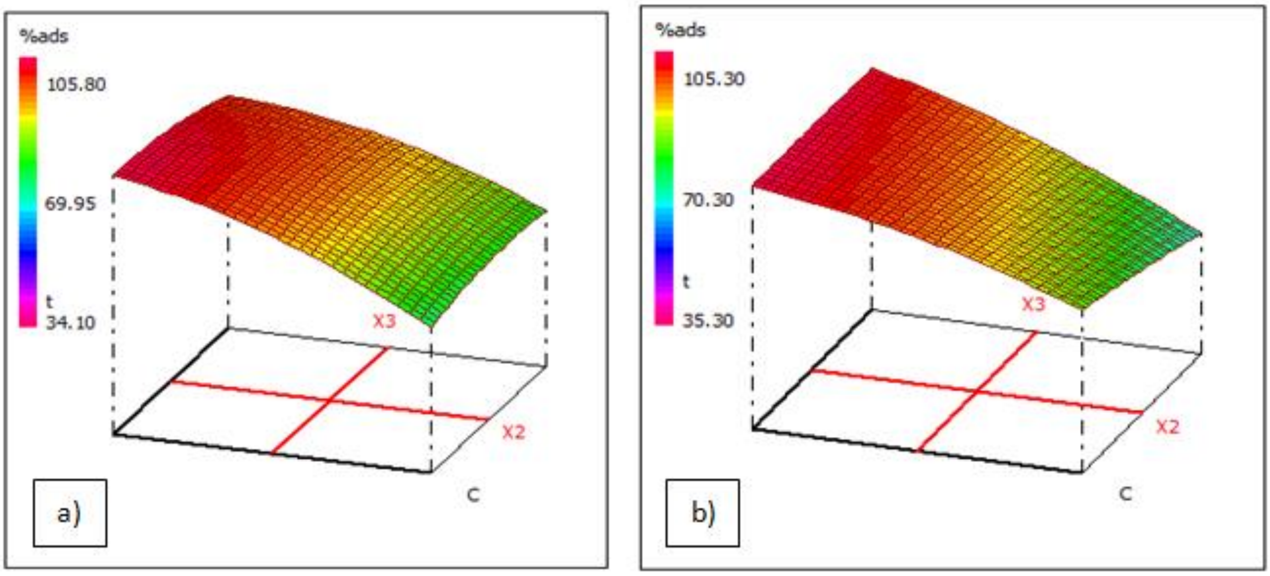

Figure 16: Variation of% Ads in 3D in the plan (c, t)
a) red wood, b) beech wood
(Fixed Factors: m = 0.305 g, pH = 2)

The graph in 2D (Figure 15) makes it possible to give isoresponse curves which have the same percentage of adsorption as a function of the level of the parameters. Moving towards areas of low mass and high concentration, it is found that the percentage of fixation decreases while it increases for larger masses of sawdust from wood. The 3D graph (Figure 16) gives response surfaces where the red color expresses the surface which has higher percentages of adsorption. It is found that in order to have a complete adsorption, it is necessary to work at the high level of the adsorbent mass, the low level of the concentration of methylene blue and of the central levels for the duration of contact, which corresponds to the values of pH = 2, 0.2 ppm of methylene blue concentration, 0.305 g of sawdust with a contact time of 90 min.

3.3.2.3. Test point

To finalize the tests of the validity of the selected model, we used the test point. Thus, we performed a test whose result corresponds to the desired response. The coordinates are: X1 = 0.305; X2 = 0.2; X3 = 90 and X4 = 2. The results mentioned in Table 10 show that there is no significant difference between the experimental and predicted responses.

Table 10: Predicted and experimental values for the test point

	Parameters	Real units	Coded units	Predicted response (%)	Experimental response (%)
Red wood	**Mass of adsorbent**	0.305	0	97.801	96.40
	Methylene blue concentration	0.2	-1		
	Contact time	90	+1		
	pH	2	0		
Beech wood	**Mass of adsorbent**	0.305	0	100	99.17
	Methylene blue concentration	0.2	-1		
	Contact time	90	+1		
	pH	0.2	0		

Conclusion

This study demonstrated the efficiency of sawdust from red wood and beech wood on the adsorption of methylene blue. The influence of the parameters related to the operating conditions such as the contact time, the quantity of the adsorbent, the pH and the initial concentration of the methylene blue was examined. The kinetic study showed that the adsorption process follows a pseudo-second order model. The percentage of adsorption increases with the increase of the initial concentration of the methylene blue and the mass of the adsorbent. The optimization by the experimental plans of the factors influencing the adsorption shows that the percentage of adsorption increases for low concentrations of methylene blue and large masses of wood sawdust.

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