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Valorization of plantain peels waste (*Orishele*) in biosorbents for the removal of methylene blue in aqueous solution: Screening and optimization of factors by experimental designs

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ABSTRACT

Today, the aqueous discharge of textile dyes into surface waters is a dramatic source of pollution, disturbance of aquatic life and, therefore, presents a potential danger that can affect humans through the food chain. To remedy this problem, several techniques for treating this polluted water have been developed and others constitute fields of investigation by the scientific community. Among those still under study is removal by biosorption. In this work, it was a question of removal methylene blue by biosorption from the experimental designs. The biosorbent used was prepared from ripe (Pp_{rip}) and unripe (Pp_{unrip}) plantain peels, considered as "agricultural waste" in Côte d'Ivoire. The effect of the variation of the parameters (pH of the solution, the type and the mass of the biosorbent, the granulometry, concentration of the solution, time of agitation and speed of agitation) was studied to establish the optimal conditions of removal of methylene blue in aqueous solution by the biosorbent. A design by Plackett and Burman using the Hadamard matrix established, as a first approach, showed that only three parameters (granulometry, solution concentration and pH) actually have an influence on the response. The results of the second design, the full two-level factorial design, showed that the maximum removal rate of methylene blue in synthetic aqueous solution is reached when a solution of BM of concentration 50 mg/L is stirred at 200 rpm, with a mass of 0.50 g of adsorbent (PBm) with a granulometry of 2 mm for 60 minutes. Under these optimal conditions, the removal rate achieved is around 96.11 %.

KEYWORDS: Pollution, biosorption, Optimisation, Experimental design, methylene blue

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1. INTRODUCTION

Used since decades before Christ in the decoration of caves, the dyes experienced an increasing production in the middle of the 19th century after the synthesis of the first synthetic dye (mauveine) by Willian Henry Perkin in 1856. Today, the dyes have many applications in different fields such as, for example, dyeing and printing on fibers and fabrics of all kinds, coloring foodstuffs, dyes for medicinal and cosmetic uses [1]. For the most part, these dyes are compounds that are difficult to biodegrade, they are known to be toxic or harmful to humans and animals [2].

Environmental protection having become a major concern of our society, the reduction or even the removal of these dyes is therefore necessary given the proven toxicity of some of them [3,4]. Operational treatment methods on a laboratory and industrial scale already exist, they include physico-chemical processes (adsorption, membrane filtration, solid-liquid separation methods: precipitation, coagulation, flocculation and settling) chemicals (resin exchange of ions, oxidation by oxygen, ozone, etc.) and biological (aerobic and anaerobic treatment) [5].

Although having shown their effectiveness, these techniques remain very expensive and also require regeneration, which is a limiting factor [6]. This has therefore encouraged research work by directing it towards treatment processes using less expensive and widely available natural materials [7,8]. This study falls within this perspective. Its objective is to remove methylene blue by biosorption from experimental design. The biosorbents used were prepared from ripe (Pp_{rip}) and unripe (Pp_{unrip}) plantain peels, considered as "agricultural waste" in Côte d'Ivoire. The effect of the variation of the factors (pH of the solution, mass of the biosorbent, the granulometry, concentration of the solution, time of agitation and speed of agitation) was studied to establish the optimal conditions of removal of the blue of methylene in aqueous solution by the biosorbent. A plan of Packett and Burman using the Hadamard matrix, as a first approach, made it possible to detect the significant factors which effectively have an influence on the response. The results of the second plan, the full two-level factorial design, made it possible to establish the optimal conditions for the removal of methylene blue in aqueous solution by the biosorbent.

2. MATERIALS AND METHODS

2-1. Preparation of synthetic solution of methylene blue

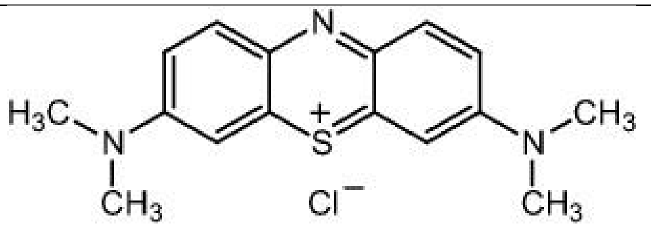
For this study, a stock solution of methylene blue at 100 mg/L was prepared by introducing 100 mg of methylene blue powder with a purity of 99 % into a 1.00 L volumetric flask which was supplemented with distilled water. The methylene blue product comes from the company CHIMITEC based in Abidjan (Ivory Coast). All the solutions of concentrations 1 mg/L, 30 mg/L and

50 mg/L are obtained by dilution of a volume V_i of the 100 mg/L solution. V_i is determined using the conservation of matter according to eq. 1:

$$\tau_i v_i = \tau_f v_f \quad \textbf{(eq.1)}$$

Table 1 indicates the characteristics of the molecule of Methylene Blue.

Table 1: Characteristics of Methylene Blue

Characteristics	Methylene Blue
Structure	
Formula	$C_{16}H_{18}N_3SCl$
Molar Mass (g/mol)	319,852 ± 0,022
Solubility ($g.L^{-1}$)	40 à 20 °C
λmax (nm)	664

2-2. Preparation of biosorbents based on ripe (Pp_{rip}) and unripe (Pp_{unrip}) plantain peels

The biosorbents were prepared from the ripe and unripe peels of plantain from the Orishele variety. This variety is highly prized by growers due to its high productivity. These ripe and unripe plantain peels were collected at the plantain market at Abobo station. They have been carefully washed with tap water and then rinsed twice with distilled water to remove sand and coarse elements.

(a) **(b)**

Figure 1: Unripe plantain peels (Pp_{unrip}) (a) and ripe plantain peels (Pp_{rip}) (b)

The preparation of the biosorbents required four (04) physical steps which are: drying, grinding, sieving and washing. The previously washed banana skins were dried for three days (03) at a temperature of 18 °C. After this drying stage, there followed that of the oven where they were maintained at a temperature of 80 °C for 60 hours. This drying method prevents any alteration of their physico-chemical properties. After drying, the plantain peels were ground using a laboratory porcelain mortar to obtain biosorbents of different granulometry. The sizes of the biosorbents (granulometry 0.50 mm and 2 mm) were isolated manually using the sieves. Washing is done first with tap water until the wash water is colorless. In order to whiten them, the samples are then impregnated for 40 minutes in a solution of 250 mL of 8 degree chlorometric bleach and 5 g of soda. After these 40 minutes, the biosorbents were drained and then dried in an oven at a temperature of 60 °C for 24 hours.

2-3. Design of Plackett and Burman using the Hadamard matrix

Hadamard matrices are optimal matrices for design of experiments without interactions. This type of plan makes it possible to have an initial evaluation of the influences of the factors on the experimental response; with very few tests to perform even for a large number of significant factors. It was chosen to do a screening, i.e. to detect the relative “weights” of the factors on the measured response. The choice of a screening design as a first approach is justified by the objective of separating the factors into several classes according to their influence on the removal of methylene blue (MB). This first desgn made it possible to know very quickly which of the various factors considered had the most influence on the response. The factors retained are: the pH of the solution (U_1), the type of biosorbent (U_2), the granulometry (U_3), the concentration of the solution (U_4), the stirring time (U_5) and the stirring speed (U_6). These six (6) factors led to the experimental field shown in Table 2.

Table 2: Experimental field of the Plackett and Burman design

Factors	**Name**	Low levels (-1)	High levels (+1)
U_1	pH solution	2,00	12,00
U_2	Type of adsorbent	PBnm	PBm
U_3	Granulometry (mm)	≤0,50	≤2,00
U_4	Solution concentration (mg/L)	10,00	50,00
U_5	Stirring time (min)	20,00	60,00
U_6	Stirring speed	150,00	300,00

The six (6) factors, at two levels each, make it possible to obtain an experience matrix. This experiment matrix led to the experiment design. The answer which is, within the framework of this study, the MB removal rate (Y) is a linear function (eq.2) of all the coded variables X_1, X_2, X_3, X_4, X_5 and X_6 corresponding respectively to the variables real values U_1, U_2, U_3, U_4, U_5 and U_6.

$$\mathbf{Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_5X_5 + a_6X_6} \quad \textbf{(eq.2)}$$

With a_i the effect of the factor X_i.

The various coefficients are calculated using the NEMROD-W software version 2000 as well as the standard deviations and the calculated responses (Ycalc.). The significance tests for each coefficient were established by considering that a coefficient is statistically significant if its absolute value is greater than 2σ (σ being the standard deviation).

The determination of the influential factors in the field studied led us to set up a second experimental plan. This is the full factorial design (PFC). It makes it possible to calculate the average effect, the main effects of the factors and their interactions 2 to 2, 3 to 3, etc. [9]. The main objective is to find the optimal conditions for the elimination of methylene blue in synthetic aqueous solution.

2-4. Full factoriel design (FD)

The first experimental design (namely the Hadamard design) having highlighted the factors influencing the phenomenon, the full factorial design is used to optimize the removal of the dye. This requires the study of the mean effect, the main effects and the interactions. Three factors were retained in this plan taking into account the result of the Hadamard design. They are: the mass of the biosorbent (U_1), the pH (U_2) and the concentration (U_3). Table 3 presents the established experimental field.

Table 3: Experimental design of Full Factorial Design (FD)

Factors	Name	Low levels (-1)	High levels (+1)
U_1	Mass of biosorbent Pp_{rip} (g)	0,50	0,80
U_2	pH	08,00	12,00
U_3	Solution concentration (mg/L)	30,00	50,00

These three (3) factors, at two levels each, make it possible to obtain the experimental design of the PFC deduced from the factorial matrix. The answer which is also the MB removal rate (Y) is a linear function (eq.3) of all the coded variables X_1, X_2 and X_3 corresponding respectively to the real variables U_1, U_2 and U_3:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 \qquad (eq.3)$$

With a_i the effect of factor X_i and a_{ij} that of the interactions between factors i and j.

2-5. Description of removal tests

The treatment of the colored solutions is done according to the predefined experimental design. A volume of 25 mL of colored water of well-defined concentration is poured into a beaker and the given mass of the biosorbent is added. The mixture is stirred at a precise speed for a given time. It is then centrifuged at a speed of 3000 rpm using an EBA 200 brand centrifuge. Finally, the mixture is filtered and a quantity of the filtrate is measured using a HACH LANGE DR3900 brand spectrophotometer at the length wave of 663 nm.

2-6. Calculation of removal rate

The removal rate (T) of methylene blue is calculated from eq. 4:

$$\mathbf{T}(\%) = \frac{\mathbf{C_i} - \mathbf{C_f}}{\mathbf{C_i}} \mathbf{\,x\,100} \qquad (\mathbf{eq.4})$$

Where C_i is the content of the ion in the raw water and C_f that in the treated water.

3. RESULTS AND DISCUSSION

3-1. Screening of factors with Plackett and Burman results (Hadamard matrix)

3-1-1. Analysis and interpretation

The application of this desgn made it possible to obtain the experimental results recorded in table 4 below. From these experimental results, table 4 and the statistical diagram (fig. 2) extracted from the statistical software NEMROD-W are obtained.

The figure 2 presents the quartile plot of the experimental results for the Hadamard matrix. The statistical results obtained show a strong dispersion of the data in the first quartile. In the second quartile ranging from 88.425 to the median 92.8 the dispersion observed remains weaker. It is also even lower in the third quartile (92.8 to 93.625). Finally, in the last quartile, the distribution is also weaker. These results confirm the relevance of the bounds of the chosen experimental field. Indeed, for all the tests carried out, high removal rates (> 90 %) were observed.

Table 4: Experimental design and experimental responses to Plackett and Bumans design

No Exp	pH	Type of biosorbent	Granulo-metry (mm)	Concentra-tion (mg/L)	Stirring time (min)	Stirring speed (rpm)	Removal Rate of Methylene blue (%)
1	12,00	PBm	2,00	10,00	60,00	150,00	**93,70**
2	2,00	PBm	2,00	50,00	20,00	300,00	***95,80***
3	2,00	PBnm	2,00	50,00	60,00	150,00	**93,30**
4	12,00	PBnm	0,50	50,00	60,00	300,00	**93,60**
5	2,00	PBm	0,50	10,00	60,00	300,00	***82,20***
6	12,00	PBnm	2,00	10,00	20,00	300,00	**90,00**
7	12,00	PBm	0,50	50,00	20,00	150,00	**92,00**
8	2,00	PBnm	0,50	10,00	20,00	150,00	**83,70**

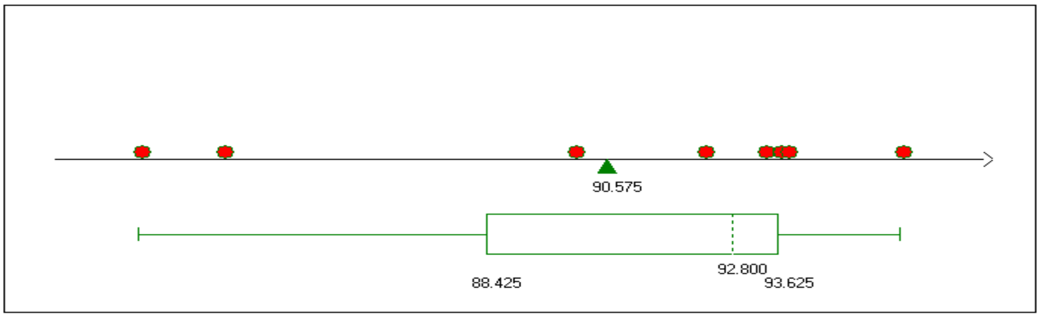


Figure 2: Diagram of the quartiles of the Hadamard design

The results vary from 82.20 to 95.80 % (table 4) with a high methylene blue reduction rate obtained in experiment 2 at a concentration of 10.00 mg/L at pH = 2 in contact with 0.50 g of Pp_{rip}, a granulometry of 2 mm when the stirring time and the stirring speed are 20 min and 300 rpm respectively. We observe an average variability through the results obtained by this Hadamard plan. This variability is noted by the standard deviation on the response which is of the order of 4.977 given by the statistical software NEMROD-W. The same software makes it possible to obtain the estimates and statistics of the response coefficients recorded in table 5.

Table 5: Estimates and statistics of the coefficients of the Hadamard design

Name	b_0	b_1	b_2	b_3	b_4	b_5	b_6
Coefficients	90,537	+1,787	+0,388	**+2,662**	**+3,137**	+0,162	-0,138
Standard Deviation	1,162	1,162	1,162	1,162	1,162	1,162	1,162

The mean removal rate is expressed by b_0 and is equal to 90.537 in this chosen experimental field (table 5). We already note a good rate of removal of the BM in this one. The “+” or “-” signs in front of the coefficients reflect the increase or decrease, respectively, of the removal rate when the factor studied varies from low to high level.

3-1-2. Contribution of factors to Removal rate of MB

The influence of the six factors in the removal of methylene blue in aqueous solution is summarized in the histogram below (figure 3) called Pareto diagram.

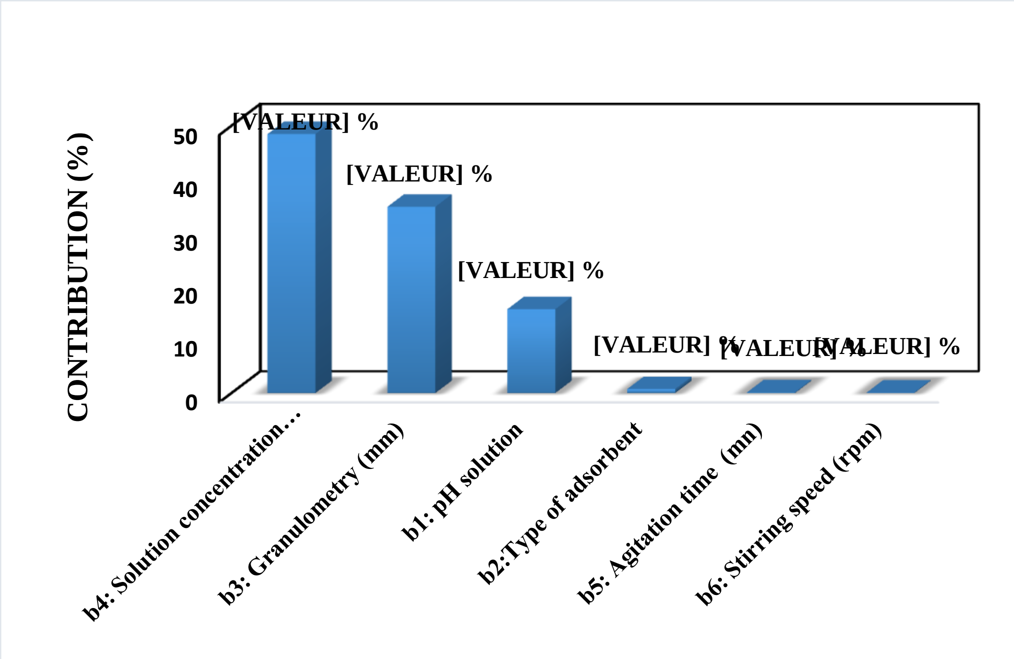


Figure 3: Pareto diagram of the Plackett and Burman design

This diagram confirms that the concentration, particle size and contributing pH respectively indicated 48.44 %, 34.88 % and 15.72 % (figure 3) are the most important factors in the removal of methylene blue. The pH was added as the third important factor because it has a considerable effect according to the Pareto diagram on the removal of BM in the chosen experimental field. The three other factors which are type of adsorbent, stirring speed and stirring time have a globally low contribution as shown in the diagram.

3-1-3. Study of the influence of factors

3-1-3-1. Influence of pH

The coefficient b_1 = +1.787 associated with the factor indicates that the reduction rate of methylene blue undergoes an increase of 1.787 x 2 = 3.574 %, when the pH of the solution increases from 2 to 12. The coefficient b1 is positive so that means that we must move the range of variation towards the highest value which in our case is 12 to have a better reduction rate of methylene blue in synthetic aqueous solution. This is how the rest of the manipulations will be carried out in a basic medium. The good MB reduction rate at pH = 12 was also obtained by [10] who studied the removal of MB in aqueous solution by potato peelings. They explained this by the fact that the surface of the adsorbent is negatively charged in a basic medium, thus resulting in better absorption of BM (cationic dye) by the phenomenon of electrostatic attraction.

3-1-3-2. Influence of the type of biosorbent

The coefficient b_2 = +0.388 associated with the factor indicates that the reduction rate of methylene blue undergoes a slight increase of 0.388 x 2 = 0.776 %, when going from unripe banana peel to ripe banana peel keeping the mass at 0.50 g. The coefficient b_2 is positive so that means that we must move the range of variation towards the highest value which in our case is the peels of ripe plantain, to have a better reduction rate of methylene blue in synthetic aqueous solution . This is how we chose biosorbents from plantain peel ripe for further work. Our results are in line with those of [11] who found that the amount of biosorbent needed to adsorb the maximum dye varies according to the type of biosorbent and for the same mass, the biosorbent from ripe plantain peels has a better rate of absorption removal than the biosorbent from unripe plantain peel. The best results obtained with Pp_{rip} could be explained by a modification of the physico-chemical (pH, titratable acidity) and biochemical (total carbohydrates, reducing sugars, starch) properties of the different functions present on the surface of plantain peels during the process ripening [12]. Indeed, the removal of methylene blue molecules by biosorption being a surface phenomenon, the appearance or distribution of certain functions is likely to alter or increase the adsorption capacity of bioadsorbents.

3-1-3-3. Influence of biosorbent granulometry

The coefficient b_3 = +2.662 associated with the factor indicates that the reduction rate of methylene blue undergoes an increase of 2.662 x 2 = 5.324 %, when the granulometry increases from 0.50 to 2 mm. The coefficient b3 is positive so that means that we must move the range of variation towards the highest value which in our case is 2 mm, to have a better reduction rate of methylene blue in synthetic aqueous solution. The work of [13] **(N'guessan, 2021)** led to similar results. In addition, the experimental error (standard deviation) obtained is 1.162 or b_3 = 2.662 so the grain size is a significant factor.

3-1-3-4. Influence of methylene blue concentration

The coefficient b_4 = +3.137 associated with the factor indicates that the reduction rate of methylene blue undergoes an increase of 3.137 x 2 = 6.274 %, when the concentration of the solution increases from 10 to 50 mg/L. The coefficient b_4 is positive, this means that we must move the range of variation towards the highest value which in our case is 50 mg/L, to have a better of removal rate of methylene blue in synthetic aqueous solution. These results could be explained by the fact that the increase in the initial concentration of BM induces the increase in the driving force of the concentration gradient, therefore the increase in the diffusion of the molecules of dyes in solution in the surface of the adsorbent [14,15]. In addition, the experimental error (standard deviation) obtained is 1.162 or b_4 = 3.137 so the concentration is a significant factor.

3-1-3-5. Influence of stirring time

The coefficient b_5 = +0.162 associated with the factor indicates that the reduction rate of methylene blue undergoes a small increase of 0.162 x 2 = 0.324 %, when the stirring time increases from 20 to 60 min. The coefficient b_5 is positive so that means that we must move the range of variation towards the highest value which in our case is 60 minutes, to have a better of removal rate of methylene blue in synthetic aqueous solution. The increase in the removal rate of MB is due to the availability of the high number of vacant adsorption sites on the surface of the biosorbent at the initial stage of adsorption. In addition, BM molecules are medium in size and can be easily diffused into internal pores until saturated, which will reduce mass transfer between liquid phase and solid phase over time. These lead to a decrease in the adsorption rate and a plateau is observed which corresponds to the state of equilibrium after 60 minutes [16].

3-1-3-6. Influence of stirring speed

The coefficient b_6 = -0.138 associated with the factor indicates that the removal rate of methylene blue undergoes a slight decrease of 0.138 x 2 = 0.276 %, when the stirring speed increases from 150 to 350 rev/ min. The coefficient b_6 is negative, so it follows that we must move the range of variation towards the lowest value which in our case is 150 rpm, to have a better removal rate. Our results are in line with those of [13] who found a removal rate that decreases as the speed of agitation increases. This could be explained by the fact that the increase in speed could break the established electrostatic bonds [17].

3-2. Mathematical modeling of the treatment with the full factorial design (FD)

3-2-1. Analysis of results full factorial design (FD)

The results of the implementation of the full three-factor factorial design are presented in table 6 below. These results show a satisfactory removal rate of methylene blue in synthetic aqueous solution. The removal rate of methylene blue varies from 90.36 to 95.48 %. The high rate is obtained with experiment 7, when we took 25 mL of the solution of methylene blue with a concentration of 50 mg/L in contact with 0.50 g of biosorbent at a pH = 12. The experiment was carried out with a biosorbent granulometry of 2 mm, a stirring time of 60 minutes and a stirring speed of 200 rpm. From these experimental results, the tables (Tables 6 and 7) and statistical diagram (fig. 4) below extracted from the statistical software NEMROD-W are obtained.

Table 6: Experimental design and experimental responses to full factorial design (FD)

N°Exp	Mass of biosorbant (g)	pH	Concentration of Solution (mg/L)	Removal rate of Methylene blue (%)
1	0,50	08,00	30,00	95,00
2	0,80	08,00	30,00	**90,36**
3	0,50	12,00	30,00	95,42
4	0,80	12,00	30,00	93,77
5	0,50	08,00	50,00	95,16
6	0,80	08,00	50,00	93,88
7	0,50	12,00	50,00	**95,48**
8	0,80	12,00	50,00	95,06

The dispersion of the experimental results is shown in figure 4 through the quartile Plot. The statistical results obtained show a strong dispersion of the data in the first quartile. In the second quartile ranging from 93.852 to the median 96.030 the dispersion appears weaker. It is also even weaker in the third quartile (95.030 to 95.240). Finally, the distribution is relatively weaker in the last quartile. These results reinforce the relevance of the chosen experimental field where, for all the tests carried out, removal rates greater than 90 % were observed.

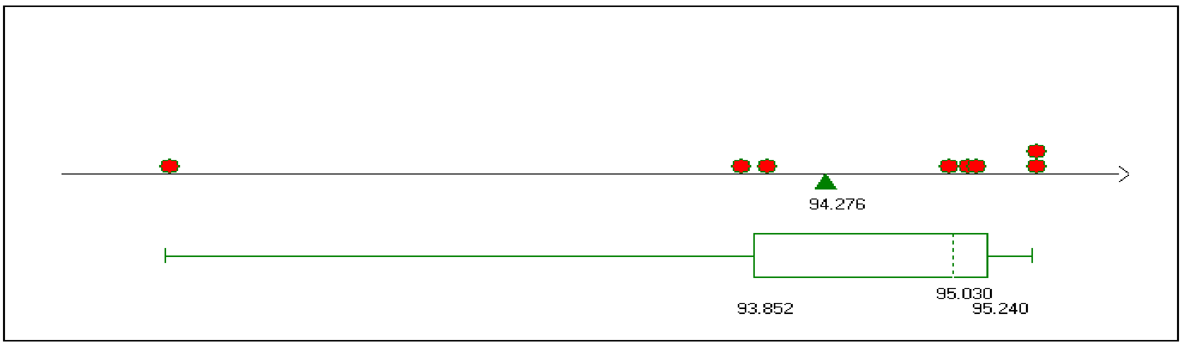


Figure 4: FD Quartile diagram

By applying the FD, the experimental results made it possible to obtain the statistics contained in table 7 below extracted from the statistical software NEMROD-W.

Table 7: Estimates and statistics of the coefficients of the Full Factorial Design (FD)

Name	b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}
Coefficients	94.276	*-1,009*	*+0.676*	*+0.619*	+0.471	+0.584	-0.301
Standard Deviation	0.256	0.256	0.256	0.256	0.256	0.256	0.256

The coefficient 94.276 represents the average of the responses from the 8 tests. This coefficient indicates a mean removal rate of methylene blue of around 94.28 %. This confirms the choice of a better experimental field for this second experimental design of this study. The experimental error (standard deviation) obtained is 0.256. Significant factors are those whose absolute value is greater than twice the standard deviation. Therefore, the three main factors are significant ie the mass of biosorbent of the biosorbent, the pH and the concentration of the solution. This confirms the previous study. As for the effects of interactions, only the interaction between the mass and the concentration of the solution is significant.

3-2-2. Contribution of factors to the MB removal rate

During the treatment, the contribution of the various factors in the removal of methylene blue is represented in the following diagram:

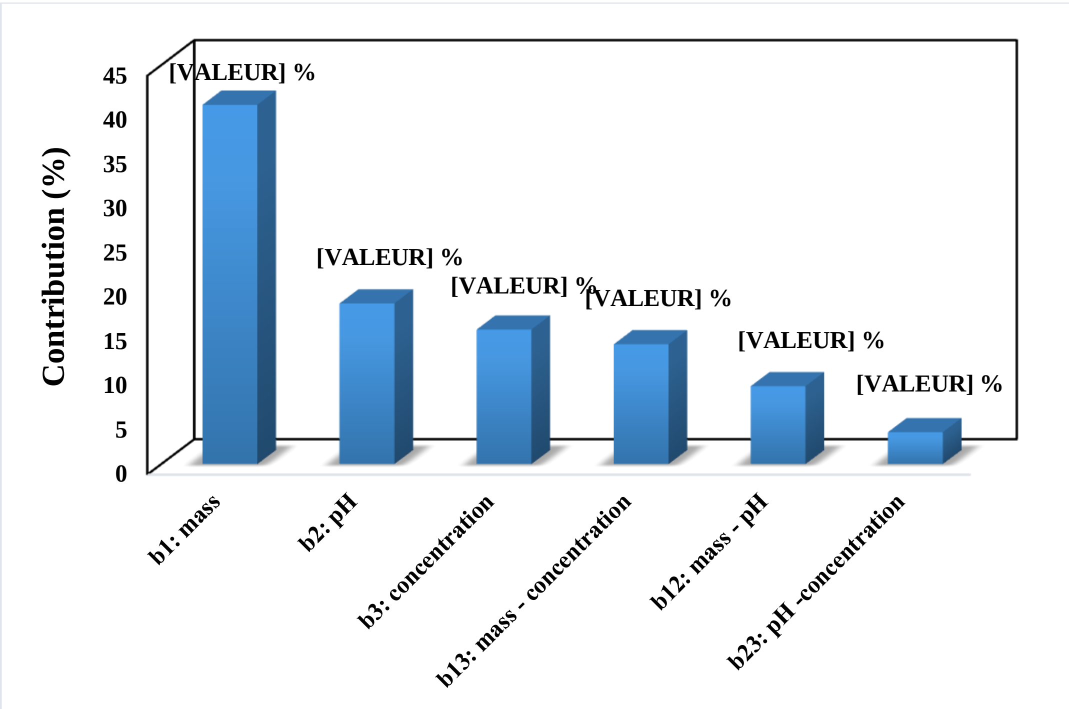


Figure 5: Pareto diagram of the full factorial design

The figure 5 shows that the contributions of the factors that are the mass of the biosorbent, the pH of the mixture and the concentration of the solution on the elimination of methylene blue are respectively 40.53 %, 18.19 % and 15.25 %. The three interaction effects, mass-pH, mass-concentration of the solution and pH-concentration of the solution, contribute 08.83 % respectively; 13.58 % and 3.62 %. It should be noted that the effects of mass-pH and pH-concentration interactions are weak.

3-2-3. Study of the influence of factors of full factorial design

3-2-3-1. Influence of mass of Pp_{rip}

The mass of the biosorbent has a significant influence on the removal of methylene blue. Its increase from 0.50 g to 0.80 g leads to a decrease in the removal rate of methylene blue by 2.02 %. The decrease in the adsorption capacity as a function of the mass of the biosorbent is explained by the formation of agglomerations of the particles of the biosorbent at high doses of biosorbent. There is steric hindrance at the moment, only a few particles at the periphery of the sphere formed actually participate in the adsorption [18].

3-2.3-2. Influence of pH

The pH of the solution has a significant influence on the removal rate of methylene blue. It produces a positive effect on the response. Its increase from 8 to 12 leads to an increase in the removal rate of 1.35 %. At higher pH, the biosorbent can become negatively charged, which enhances the sorption of positively charged coloring cations by electrostatic forces of attraction [19].

3-2-3-3. Influence of concentration

The concentration of the dye has a significant influence on the removal of methylene blue. Its increase from 30 mg/L to 50 mg/L leads to an increase in the reduction rate of methylene blue by 1.238 %. Indeed, increasing the concentration of the dye increases the number of collisions between the dye ions and the biosorbent, which improves the adsorption process [20].

3-2-4. Analysis of the interaction effect between mass of absorbent and concentration

The effect of the interaction between biosorbent mass and solution concentration on methylene blue removal is shown in figure 6 below.

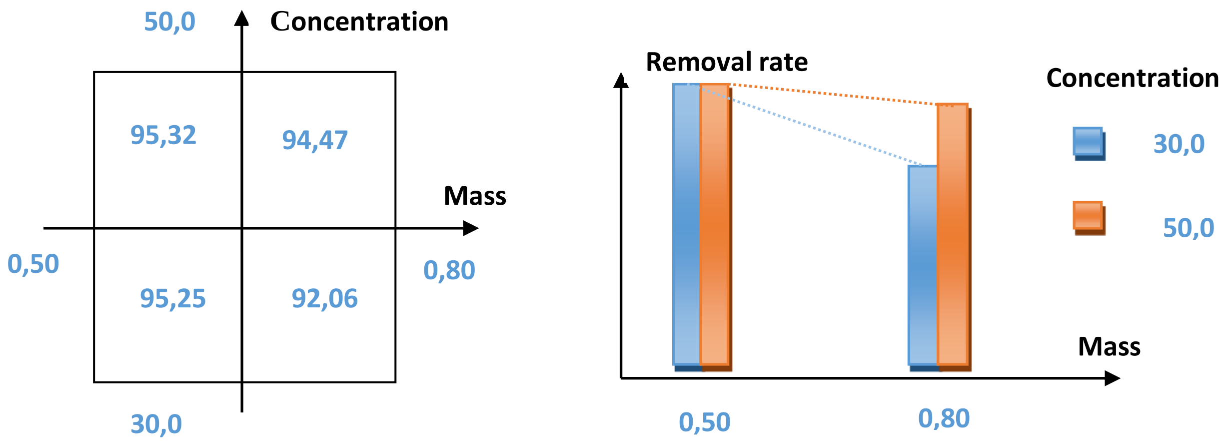


Figure 6 : Biosorbent mass interaction diagram–concentration (b_{23})

Each compartment of the square above represents a combination of the effects related to the levels of the mass of the biosorbent (X_1) and the concentration of the solution (X_3). When the concentration of the solution is at the low level (30. mg/L), the variation of the mass of the biosorbent has a negative influence. The reduction rate goes from 95.25 to 92.06 % when the mass of the biosorbent goes from 0.50 to 0.80 g. When the concentration of the solution is at the high level (50 mg/L), the increase in the mass of the biosorbent also negatively influences the removal rate but it remains slightly higher than that of the low level concentration. Indeed, the rate then goes from 95.32 to 94.47 % when the mass of the biosorbent goes from 0.50 to 0.80 g. In short, the lowest rate of removal is obtained when a solution of concentration 30 mg/L is brought into contact with a mass of 0.80 g of the biosorbent and the highest rate of removal is obtained when brings 0.50 g of the biosorbent into contact with the solution with a concentration of 50 mg/L.

3-2-5. Analysis of the mathematical model from the FD

Table 8 below translates the statistics on the coefficients calculated from the results.

Table 8: Analysis of variance of the PFC

Source of variation	Sum of squares	Standard deviation	Correlation coefficient (R^2)
Regression	20,0907		
Residues	0,5253	0,725	0,975
Total	20,6160		

The analysis of variance shows that the model used is well adjusted since the sum of squares due to the error (0.5253) is very low compared to the total sum of squares (20.6160). This good adjustment is confirmed by the analysis of the value of the linear correlation coefficient (R^2 = 0.975 or 97.50 %) presented in table 8 given by the software. This coefficient tends towards 1, this allows us to affirm that we have a good adjustment because the value of this coefficient indicates that the model describes at 97.50 % the phenomenon of removal of MB in synthetic aqueous solution. The adjustment of the model is also checked with table 9 given by the software presenting the residues of the sorption of BM by FD and the plot (figure 7) Yexp (measured responses) as a function of Ycalc (responses predicted by the model).

Table 9: Analysis of residues from MB biosorption by FD

N°Exp	Yexp.	Ycalc.	Residue
1	**95,000**	**94,744**	0,256
2	**90,360**	**90,616**	-0,256
3	**95,500**	**95,756**	-0,256
4	**93,770**	**93,514**	0,256
5	**95,160**	**95,416**	-0,256
6	**93,880**	**93,624**	0,256
7	**95,480**	**95,224**	0,256
8	**95,060**	**95,316**	-0,256

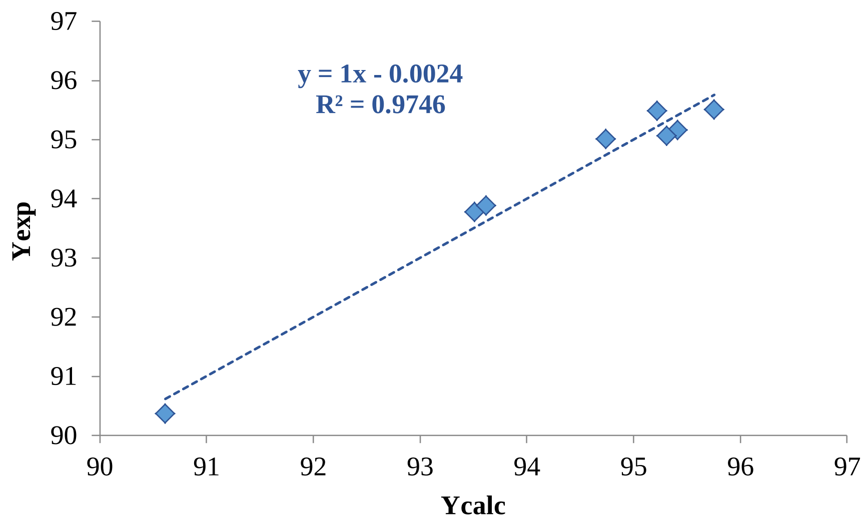


Figure 7: Variation of experimental removal rates as a function of those of the calculated response

The analysis of the residuals (table 9) also shows a quality adjustment of the model studied. Indeed, the correlation coefficient obtained previously by the software has the same value as that obtained by the plot (figure 7) Yexp (measured responses) as a function of Ycalc (responses predicted by the model) presented in table 9 (given by the software). Moreover, the comparison between the Yexp and Ycalc columns (table 9) confirms the conclusion obtained above. Indeed, the difference of all the residuals does not exceed 5 % [9]. All these findings validate the linear model of the phenomenon studied. The multiple linear regression made it possible to calculate the coefficients and to define the mathematical equation below which describes the phenomenon studied:

$$\mathbf{Y = 94{,}276 - 1{,}009X_1 + 0{,}676X_2 + 0{,}619X_3 + 0{,}584X_1X_3 \qquad (4)}$$

3-3. Optimization of the factors acting on the removal rate of methylene blue

3-3-1. Determination of optimal conditions

In this part, we will call optimal output response: Y = 97.164, which amounts to eliminating 97.164 % of the effluent after its treatment with the biosorbent (Pp_{rip}). Thus, finding the conditions to satisfy this answer is equivalent to solving equation (5):

$$97.164 = 94.276 - 1.009X_1 + 0.676X_2 + 0.619X_3 + 0.584X_1X_3 \qquad (5)$$

Using the Excel Solver utility, we get the following results:

$$Y = 97.164 \text{ for } X_1 = -1 \text{ ; } X_2 = +1 \text{ et } X_3 = +1$$

Thus, with a pH= 12, a mass of biosorbent (Pp_{rip}) of 0.50 g with a granulometry of 2 mm, a concentration of 50 mg/L with a stirring time of 60 min and a stirring speed of 200 rpm, the maximum value predicted by the model of the theoretical reduction rate of methylene blue in a synthetic aqueous solution is 97.164 %.

3-3-2. Verification of optimal conditions

The tests under the optimal conditions were carried out three times. The results obtained are summarized in table 10.

Table 10: Removal rate of experiments carried out under optimal conditions

N°Exp	Removal rate (%)	Residue (%)
1	96,000	+ 1,164
2	96,320	+ 0,844
3	96,020	+ 1,144

In fact, the average rate of removal of methylene blue in the synthetic solution obtained is (96.11 ± 1.05) %. The error is less than 5 % [9]. Based on this fact, the comparison with the predicted value gives residuals between 0.004 and 2.104, thus indicating an almost perfect agreement between the experimental values and the predicted values. The removal rate of MB obtained in this study (96.11 %) is better than that obtained in the work of Kifline et al., in 2018 [18]. Indeed, in their studies, they removed MB up to 80 % with biosorbents from agricultural waste. .

4. CONCLUSION

At the end of this study, it appears that the biosorbent prepared from ripe plantain peel (Pp_{rip}) is effective for the removal of methylene blue in aqueous solution. This process is interesting because of the accessible cost of realization. The statistical analysis of the experimental designs used (Hadamard matrix and full factorial design) shows that the mathematical model used to describe these results is correct. Moreover, the exploitation of the data resulting from these two plans of experiments also showed that the granulometry, the concentration and the pH are the factors which influence considerably the removal of BM in synthetic aqueous solution as well as the interaction between the mass of the biosorbent and the concentration of the solution. Under the conditions of the study, an increase in the mass of the biosorbent leads to a decrease in the removal rate of methylene blue while the increase in the concentration of the solution and the pH of the mixture produces the opposite effect. Stirring time and stirring speed have very insignificant effects. The optimization of the process showed that the mean removal rate of 96.11 % is obtained for a mass of 0.50 g of the biosorbent (Pp_{rip}) of particle size 2 mm, a concentration of the solution of 50 mg/L at pH = 12, a stirring speed of 200 rpm and a stirring time of 60 min.

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