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A statistical approach based on the full factorial experiment for optimization of dyes adsorption on biomaterials prepared from mint and tea

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Abstract
The objective of this work is the optimization by statistical approach of adsorption methylene blue on biomaterials based of mint and tea: waste of mint (WM), fresh mint leaf (FML) and waste of tea (WT). In the first part, we studied the effect of the three adsorbent on the yields adsorption by analysis of variance (ANOVA), hence the analysis of experiments conducted by this statistical tests shows that the waste of mint (WM) gives yields better than other biomaterials studied. The second part was devoted to a study of adsorption yields by full factorial design for three biomaterials (WM), (FML) and (WT), therefore a statistical approach realized on this part, is based on the identification and evaluation of influences of each factor independently and dependently on the amount adsorbed of methylene blue on the three biomaterials. These factors selected are: initial concentration of adsorbate (C_0), adsorbent dose (W) and size of the adsorbent grains (d). The results for the three biomaterials of this section prove that the initial adsorbate concentration influences the amount adsorbed of methylene blue, by against the other two parameters have absence influence. Also, the study of parameters interaction between them, it was found that the interaction between the adsorbate concentration and the adsorbent dose is most influential on the amount adsorbed relative to the others interactions.

Keywords: Statistical approach, Adsorption, Methylene blue, Biomaterials, ANOVA, Full factorial design.

Introduction
The field of management of experimental processes has seen its scope extended following a technical revolution by generalization of the use of statistics **[1-2]**. On the other hand, the experimental designs that are part of the statistics are used in industrial studies in research and development **[3]**. They are involved in many industrial fields, these include: chemical industry, petrochemical industry, pharmaceutical industry, ... **[4]** Their use is the purpose of the determination of the key factors in the design of a new product or a new process, and optimization settings of a manufacturing or a meter and for process target prediction by modeling the behavior of a process **[5-7]**. The experimental designs are part of a general approach to improving quality, and then the success of the original approach of experimental conception is the ability of interpretation of experimental results with minimal effort experimentally: minimizing the necessary number of experiments allows a gain in time and financial cost. It should nevertheless understand that the experiences of plans are not a priori a tool for basic research because they never allow an explanation of the physical-chemical phenomenon studied **[8-10]**.
On the other hand, the effluent containing dyes are highly coloration, resulting in major environmental problems. As international environmental standards are becoming more stringent, these coloration wastes need treatment before disposal **[11-12]**. Several methods for the removal of dyes have been developed. Physical methods, mainly adsorption on various supports, are the most frequently used. Biological methods such as

biodegradation have been proposed **[13]**. However, due to the low biodegradability of dyes, conventional biological waste water treatment processes are not very efficient for the treatment of dyeing wastes. **[14]** Chemical treatment processes (ozonation and chlorination) are more effective **[15]**. The photocatalytic degradation and ultrafiltration over supports are interesting recent propositions, but the adsorption is one of the promising methods to remove the dye pollutants from aqueous system completely **[16-17]**.

This work is the optimization of conditions methylene blue adsorption of biomaterials prepared from mint and tea, by the use of statistical studies to improve and develop this process of adsorption by utilization of ANOVA and Full Factorial Design. The aim of this work included the continuation of previous work done by our collaborators.

These studies realized by our team are:

- "A novel bio-adsorbent of mint waste for dyes remediation in aqueous environments: study and modeling of isotherms for removal of methylene blue" **[18]**.
- "Study and modelling of kinetics biosorption of methylene blue on biomass material from waste mint" **[19]**.
- "Optimization of adsorption performance of an industrial dye on waste mint by the design of experiments method - composite centered plan" **[20]**.

2. Materials and methods

2.1. *Biomaterials*

The adsorbents used in this work are three biomaterials based on mint and tea: 1st the waste of mint (WM), 2nd the fresh mint leaf (FML) and 3rd the waste of tea (WT). The three biomaterials selected have been dried at a temperature 60 °C for two days and finally milled and sifted by sieve of the 80 µm.

2.2. *Adsorbate*

A cationic dye, methylene blue (MB), having molecular formula $C_{16}H_{18}N_3SCl$ was chosen as adsorbate **[21]**. Methylene blue (Figure 1) was purchased from Merck with water solubility as 50 g/L (20°C) and molecular weight as 319.85 g. The methylene blue was chosen in this work because of its known strong adsorption onto biomasses and it often serves as a model compound for removing organic contaminants. The dye stock solution was prepared by dissolving accurately weighted methylene blue in distilled water to the concentration of 100 mg/L. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to required initial concentrations. Methylene blue had been determined using a UV-Visible spectrophotometer at its maximum adsorption λ_{max} = 664 nm.

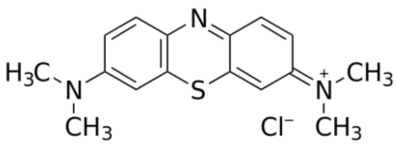

Figure 1: Chemical structure of methylene blue.

2.3. *Adsorption experiments*

The experiments were carried out by introducing a well-defined mass of three biomaterials and with a known grain size, in an aqueous solution using C_0 initial concentration of methylene blue at pH 7.1. The mixture had then been stirred in a room temperature for two hours to ensure a good homogenization of the solution, and a better contact between the adsorbate and adsorbent. After the stirring time, we determine the equilibrium concentration C_{eq}. The adsorption yields are calculated using the following equation (1) **[22]**:

$$Yield\ (\%) = \frac{C_0 - C_{eq}}{C_0} \times 100 \qquad (1)$$

And the amount adsorbed Q_e is defined by the following equation (2) **[23]**:

$$Q_e(mg/g) = \frac{C_0 - C_{eq}}{W} \qquad (2)$$

Where: C_0: Initial concentration (mg /L).

C_{eq} : Equilibrium concentration (mg /L).

W: adsorbent dose (mass per unit volume of solution) (g/L).

2.4. *Protocol of optimization of adsorption*

In the first, the adsorption of MB on the three materials WM, FML, and WT was carried out in 8 repetition for realization of statistical approach by ANOVA.

The experiments relating to the optimization of adsorption conditions by the full factorial design was made with three factors: adsorbate concentration C_0, adsorbent dose W and adsorbent grain size d, were performed according to a matrix given in experiences displayed in the table 1. The experimental matrix consists of two sub-tables: the first defines the tests to be performed and the second the study field.

The first defines the tests to be performed and includes three columns, the first identifies the tests to be performed using the notation (3).

$$Number of\ test = 2^k \qquad (3)$$

Where, superscript k means the number of studied factor and number 2 means that each factor takes two levels -1 and +1. In our study, the number of factors is equal 3, which corresponding to 8 tests.

The second, third and fourth in the first table column indicate the coded units of the factors studied, the second sub-table indicates, in current units, the values for high and low levels of each factor.

Table 1: Matrix of experiences.

Test number	Input Factor C_0	Input Factor W	Input Factor d
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1
Field of study			
Level -	10 mg/L	0.2 g/L	d < 80 µm
Level +	35 mg/L	1.0 g/L	d > 80 µm

2.5. *Statistical software*

The statistical softwares: Nemrodw and SPSS (Trial version), were used for statistical analysis of experimental data to fit the equations developed and also to plot Bar-chart Coefficients.

3. Results and discussion

The results obtained in previous works **[18-20, 24]** on the adsorption of methylene blue on waste biomasses of mint and tea have shown that such wastes can be used as a good adsorbents at room temperature T = 25 °C and pH = 7.1, particularly for the elimination of methylene blue and generally for all colors. However, all these results show the efficacy of these biomasses in the treatment of polluted water contaminated with organic dyes and treatment of polluted water. Also, a new way for environmental applications by recycles waste of mint and waste of tea. The continuation of these works is targeted towards statistical approaches for another optimization of the conditions of methylene blue adsorption on biomasses produced from waste and mint tea by applying analysis of variance (ANOVA) and Full Factorial Design.

3.1. *Analysis of variance*

As we described above, we carried out an 8 experiences series of adsorption of MB for each biomaterial. The results of the yields of adsorption obtained in these experiments are shown in Table 2. Also Table 3 gives preliminaries results of statistical study of the three adsorbents by determining the mean, the standard deviation (SD), the standard error of the mean (SEM) and confidence intervals for the mean for the experiments at a 95%, and Table 4 shows the results obtained during the analysis of variance of experience. Several parameters were calculated:

- SS means: the sum of squares due to the source.
- df means: the degrees of freedom in the source.

- MS means: the mean sum of squares due to the source.
- F means: the F-statistic.
- P means: the P-value.

Analysis of the data in table 3 indicates that the biomaterial WM gives an adsorption yield of 88.25% compared to others biomaterials, such 84.5% for the FML and 81.88% for the WT. Subsequently, calculated parameters for ANOVA have shown in Table 4, and analysis of these results of our tests shows that the p-value is less than 0.05, which demonstrates that there is a significant difference between the process adsorption for three biomaterials.

Table 2: Yields adsorption of the performed experiments.

Adsorbent 1 (WM)		Adsorbent 2 (FML)		Adsorbent 3 (WT)	
$Y_{1;1}$	87 %	$Y_{2;1}$	84 %	$Y_{3;1}$	81 %
$Y_{1;2}$	90 %	$Y_{2;2}$	83 %	$Y_{3;2}$	83 %
$Y_{1;3}$	89 %	$Y_{2;3}$	86 %	$Y_{3;3}$	81 %
$Y_{1;4}$	88 %	$Y_{2;4}$	84 %	$Y_{3;4}$	81 %
$Y_{1;5}$	87 %	$Y_{2;5}$	86 %	$Y_{3;5}$	82 %
$Y_{1;6}$	87 %	$Y_{2;6}$	84 %	$Y_{3;6}$	82 %
$Y_{1;7}$	90 %	$Y_{2;7}$	84 %	$Y_{3;7}$	82 %
$Y_{1;8}$	88 %	$Y_{2;8}$	85 %	$Y_{3;8}$	83 %

(*) Y i;j : Yield of adsorption for adsorbent i and experience j.

Table 3: Statistical parameters of adsorption experiments.

Adsorbent	Number of exp.	Mean (%)	SD (%)	SEM (%)	Confidence Interval		Min (%)	Max (%)
					Upper 95% limit	Lower 95% limit		
1: WM	8	88.25	1.28	0.45	87.18	89.32	87	90
2: FML	8	84.50	1.07	0.38	83.61	85.39	83	86
3: WT	8	81.88	0.84	0.30	81.18	82.57	81	83
Total	24	84.88	2.86	0.59	83.67	86.08	81	90

Table 4: Statistical parameters of adsorption experiments by ANOVA.

Source	SS	df	MS	F	F_{obs}	P
Between Groups	164.25	2	82.13	70.75	4.42	0.000
Within Groups	24.37	21	1.16			
Total	188.63	23	-			

3.2. *Full Factorial Design*

The second part of this work is interested to optimize of adsorption methylene blue on three biomaterials by the full factorial design with three factors: adsorbate initial concentration (C_0), adsorbent dose (W) and the adsorbent grain size (d) comprise two numbers of levels (-1) and (+1) (Experiences that are mentioned in Table 1).The study of a full factorial design is associated with the use of 1 degree polynomials. In this case, the polynomial model is written in equation (4).

$$Y' = b_0 + b_1.C_à + b_2.W + b_3.d + b_{12}.C_0.W + b_{13}.C_0.d + b_{23}.W.d \qquad (4)$$

Following the experiments required in Table 1, the results of amounts adsorbed of the three biomaterials are displayed in Table 5. On the other hand, the Student test allows individual test effect of each of the terms of each factor. Hence, the estimated values coefficients of the model, standard deviation (SD), experimental value of the Student test (t_{exp}) and significance are given in the table 6. So, It's noticeable from this table that the coefficients b_0, b_1, b_2 and b_{12} are influential on the amount adsorbed for the three biomaterials WM, FML and WT because the value of $t_{0.05}$ at a confidence level of 95% is below the t_{exp} values ($t_{0.05} = 12.7 < t_{exp}$), but the coefficients b_3, b_{13} and b_{23} are not influential on the amount adsorbed for the three types of adsorbents. Finally, substituting the coefficients of equation (1) with the values of table 6 we get equations (5), (6) and (7):

$$Y'_{1:WM} = 56.5 + 30.25C_0 - 36.5W - 0.5d - 18.25C_0.W - 0.25C_0.d \quad (5)$$

$$Y'_{2:FML} = 54.75 + 30.5C_0 - 35W - 1.25d - 18.75C_0.W - W.d \quad (6)$$

$$Y'_{3:WT} = 45.13 + 23.63C_0 - 27.13W - 0.63d - 12.13C_0.W - 0.13C_0.d + 0.13W.d \quad (7)$$

Table 5: Input Factors and responses for amount adsorbed.

Number exp.	Input Factor			Amount Adsorbed (mg/g)		
	C_0 (mg/L)	W (g/L)	d (µm)	WM	FML	WT
1	10	0.2	< 80	45	43	37
2	35	0.2	< 80	142	141	109
3	10	1.0	< 80	8	8	7
4	35	1.0	< 80	33	32	30
5	10	0.2	> 80	44	38	36
6	35	0.2	> 80	141	137	107
7	10	1.0	> 80	8	8	6
8	35	1.0	> 80	31	31	29

Table 6: Analysis of the coefficients by Student test.

Adsorbent	Coefficient	Value	SD	t_{exp}	Significance (%)
1: WM	b_0	56.50	0.25	226	0.70**
	b_1	30.25	0.25	121	0.89**
	b_2	-36.50	0.25	-146	0.82**
	b_3	-0.50	0.25	-2	30.20
	b_{12}	-18.25	0.25	-73	1.14*
	b_{13}	-0.25	0.25	-1	50.00
	b_{23}	0.00	0.25	0	100.00
2: FML	b_0	54.75	0.25	219	0.71**
	b_1	30.50	0.25	122	0.88**
	b_2	-35.00	0.25	-140	0.83**
	b_3	-1.25	0.25	-5	13.20
	b_{12}	-18.75	0.25	-75	1.13**
	b_{13}	0.00	0.25	0	100.00
	b_{23}	1.00	0.25	4	16.40
3: WT	b_0	45.13	0.13	361	0.62**
	b_1	23.63	0.13	189	0.74**
	b_2	-27.13	0.13	-217	0.71**
	b_3	-0.63	0.13	-5	13.20
	b_{12}	-12.13	0.13	-97	0.98**
	b_{13}	-0.13	0.13	-1	50.00
	b_{23}	0.13	0.13	1	50.00

These coefficients were plotted as a bar-chart in figure 2. The analysis of these results shows that: The adsorbate concentration has a very important positive influence on the amount adsorbed (b_1 (adsorbent 1: WM) = 30.25), (b_1 (adsorbent 2: FML) = 30.5) and (b_1 (adsorbent 3: WT) = 23.62). Also, the adsorbent dose has a negative influence on the amount adsorbed since the coefficients are negatives (b_2 (adsorbent 1: WM) = - 36.50), (b_2 (adsorbent 2: FML) = - 35.00) and (b_2 (adsorbent 3: WT) = - 27.12). Thereafter, the bar related to the adsorbent grain size effect remained within the reference line, therefore, this factor doesn't an influence on the amount adsorbed. Also, the most influential interaction is that between the adsorbate concentration and the adsorbent dose.

Finally, all the results obtained in this work shows that: we can use biomaterials made from waste for treatment of water polluted by dyes, either each biomaterial alone, or either combinations between them.

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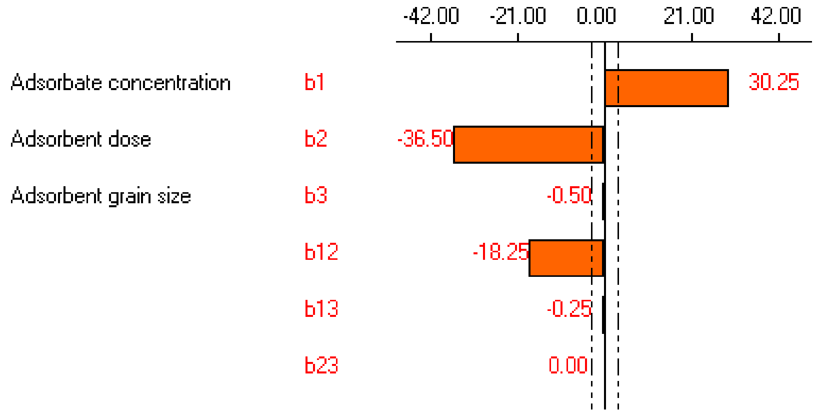
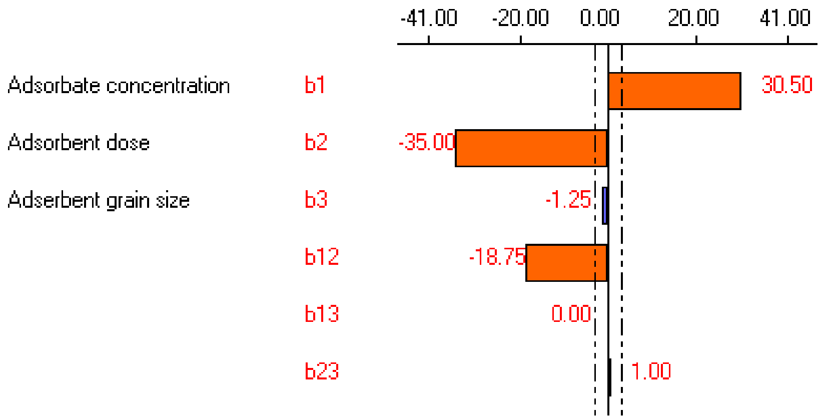
Adsorbent 1: WM



Adsorbent 2: FML



Adsorbent 3: WT

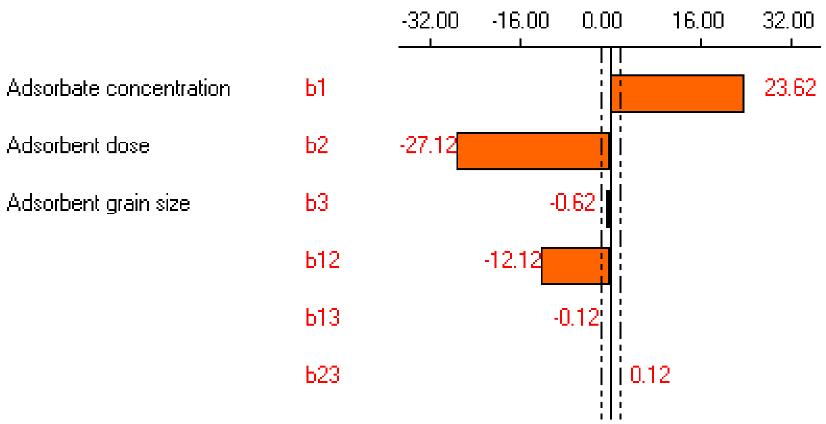


Figure 2: Bar-chart Coefficients for the three biomaterials WM, FML and WT.

Conclusion

Statistical approach of optimization the methylene blue adsorption by biomaterials prepared from mint and tea (WM, FML and WT) was carried using ANOVA and full factorial design. From optimization results of this study, we can conclude:

- The adsorbent 1 prepared from waste mint (WM) gives better yields adsorption against the others adsorbent 2 Fresh mint leaf (FML) and adsorbent 3 obtained from waste tea (WT).
- The amount adsorbed of methylene blue on the three biomaterials WM, FML and WT is better for a high adsorbate concentration and a low adsorbent dose.
- The adsorbent grain size does not influence on the amount adsorbed for all biomaterials.
- The biomaterials used are efficacious for adsorption with a single use or with a combination.

References

1. Wohlin C., Runeson P., Höst M., Ohlsson M. C., Regnell B., Wesslén A., "Experimentation in software engineering". ISBN : 978-3-642-29044-2. *Springer Science & Business Media* (2012) 3.
2. Hubka V., Eder W. E., "Design science: introduction to the needs, scope and organization of engineering design knowledge". *Springer Science & Business Media* (2012) 1.
3. Unterkalmsteiner M., Gorschek T., Cheng C. K., Permadi R. B., Feldt R., *Soft. Eng. IEEE Trans.*, 38 (2012) 398.
4. Woodley J. M., Breuer M., Mink D., *Chem. Eng. Res. Des.*, 91 (2013) 2029.
5. Chaabane A., Ramudhin A., Paquet M., *Inter. J. Prod. Eco.*, 135 (2012) 37.
6. ElMaraghy W., ElMaraghy H., Tomiyama T., Monostori L., *CIRP Ann. Manuf. Tech.*, 61 (2012) 793.
7. Shi J., Zhang G., Sha J., Resources, *Cons. and Recy.*, 55 (2011) 639
8. Crump M. J., McDonnell J. V., Gureckis T. M., *PloS one*, 8 (2013) e57410.
9. Besseris G. J., *Chemo. and Intell. Labo. Syst.*, 116 (2012) 47.
10. Aurigemma J., Chandrasekharan S., Nersessian N. J., Newstetter W., *J. Eng. Educ.*, 102 (2013) 117.
11. Kaur H., Kaur R., *J. Mater. Environ. Sci., 5* (2014) 1830.
12. Sakr F., Sennaoui A., Elouardi M., Tamimi M., Assabbane A., *J. Mater. Environ. Sci.*, 6 (2015) 397.
13. Nahli A., Sakhraoui N., Hebabaze S., Hmimidi C., Brand C. Chlaida M., *J. Mater. Environ. Sci.*, 7 (2016) 30.
14. Aarfane A., Salhi A., El Krati M., Tahiri S., Monkade M., Lhadi E.K., Bensitel M., *J. Mater. Environ. Sci., 5* (2014) 1927.
15. Jeddi S., Ouassini A., Elouahhaby M., Mghafri H., *J. Mater. Environ. Sci.*, 7 (2016) 488.
16. Aarfane A., Tahiri S., Salhi A., Elkadiri B.G., Siniti M., Bensitel M., Sabour B., El Krati M., *J. Mater. Environ. Sci.*, 6 (2015) 2944.
17. Elharrak N., Elazhar F., Belhamidi S., Elazhar M., Touir J., Elmidaoui A., *J. Mater. Environ. Sci.*, 6 (2015) 383.
18. Ainane T., Khammour F., Talbi M., *Orie. J. Chem.*, 30 (2014) 1183-1189.
19. Ainane T., Khammour F., Belghazi O., Kabbaj M., Yousfi S., Talbi M., Elkouali M., *BioTech. Ind. J.*, 11 (2015) 281.
20. Khammour F., Laasri L., Kenz A., Ainane T., Yousfi S., Talbi M., *Inter. J., Scie. Res*, 4 (2015) 1171.
21. Ainane T., Abourriche A., Kabbaj M., Elkouali M., Bennamara A., Charrouf M., Talbi M., *J. Chem. Pharm. Res.*, 6 (2014) 599.
22. Amegrissi F., Talbi M., El Kouali M., Dahbi L., Ainane T., Maghri I., *J. Mater. Environ. Sci.*, 3 (2012) 744.
23. Ainane T., Abourriche A., Kabbaj M., Elkouali M., Bennamara A., Charrouf M., Talbi M., *J. Mater. Environ. Sci.*, 5 (2014) 975.
24. GokceY., and Aktas Z., *Appl. Sur. Sci.*, 313 (2014) 352-359.

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